UNIVERSITÀ DELLA CALABRIA

SOCIETÀ CHIMICA ITALIANA

XXV Congresso Nazionale della Società Chimica Italiana

Arcavacata di Rende
07-12 Settembre 2014

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XXV Congresso Nazionale
della Società Chimica Italiana

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Programma Comune

Nobel Lecture

Nobel Lecture

The use of recent advances in electron microscopy to study ribosome structures

V. Ramakrishnan

MRC Laboratory of Molecular Biology, Cambridge, UK

For the last hundred years, the main technique to determine the atomic structures of molecules has been x-ray crystallography.

Recently, advances in both detectors and algorithms for data analysis has made it possible to reach ~3 Å resolution using single-particle electron microscopy.

This has for the first time made it possible to obtain atomic models of large macromolecules without the use of crystals and with very small amounts and heterogeneous samples.

I will discuss how my laboratory has used these advances to determine an atomic model for the large mitochondrial ribosomal subunit de novo.

Programma Comune

Plenary

PL1

Catalysis provide Innovations for the Chemical Industry and Sustainable Energy Technologies

Matthias Beller

Leibniz-Institut für Katalyse an der Universität Rostock, Albert-Einstein-Str. 29a, 18059 Rostock, Germany

matthias.beller@catalysis.de

Despite numerous important methodological advancements in all areas of chemistry, still most organic synthesis as well as the industrial production of chemicals can be improved. Currently, more than 80% of all products of the chemical industry are made via catalysis. In this regard, the development of new and more efficient catalysts constitutes a key factor for achieving a sustainable production of all kinds of chemicals today and in the future. Here, several major challenges will be presented in the talk; e.g. the selective reduction of amides to bio-relevant amines. Furthermore, it will be shown that recently developed molecular-defined as well as nano-structured cobalt and iron catalysts enable us to perform catalytic hydrogenation processes of esters and nitro derivatives with high yields and unprecedented selectivity. Specific examples which demonstrate the potential of catalytic processes with bio-relevant metal complexes compared to more traditional catalytic reactions will include apart from hydrogenations also dehydrogenations for the synthesis of heterocycles. In the future, also for industrial processes improved economics based on the presented novel catalysts might be expected.

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[4] S. Fleischer, S. Zhou, K. Junge, M. Beller, Angew. Chem. Int. Ed. 2013, 52, 5120-5124.
[5] A. Boddien, D. Mellmann, F. Gärtner, R. Jackstell, H. Junge, P. J. Dyson, G. Laurenczy, R. Ludwig, M. Beller, Science 2011, 333, 1733-1736.

PL2

Imaging Mass Spectrometry: Molecular Microscopy for Discovery in Biological and Clinical Research

Richard M. Caprioli

Departments of Biochemistry, Chemistry, Pharmacology and Medicine, and the Mass Spectrometry Research Center, Vanderbilt University School of Medicine, Nashville, TN, U.S.A.

R.Caprioli@Vanderbilt.edu

MALDI Imaging Mass Spectrometry (IMS) produces molecular maps of peptides, proteins, lipids and metabolites present in intact tissue sections. It employs desorption of molecules by direct laser irradiation to map the location of specific molecules from fresh frozen and formalin fixed tissue sections without the need of target specific reagents such as antibodies. Molecular images of this nature are produced in specific m/z (mass-to-charge) values, or ranges of values. Thus, each specimen gives rise to many hundreds of specific molecular images from a single raster of the tissue. In a complementary approach where only discrete areas within the tissue are of interest, we have developed a histology-directed approach that integrates mass spectrometry and microscopy. Thus, mass spectra are collected from only selected areas of cells within the tissue following laser ablation and analysis.

We have employed IMS in studies of a variety of biologically and medically relevant research projects. One area of interest is the molecular mapping of molecular changes occurring in diabetes in both a mouse model and in the human disease. Major molecular alterations have been recorded in advanced diabetic nephropathy involving both proteins and lipids. Other applications include developmental studies of embryo implantation is mouse, assessment of margins in renal cancers as well as that in other organs, and neurodegenerative disease. Molecular signatures have been identified that are differentially expressed in diseased tissue compared to normal tissue and also in differentiating different stages of disease. These signatures typically consist of 10-20 or more different proteins and peptides, each identified using classical proteomics methods. One such application described is that concerning the differentiation of benign skin lesions from melanomas. In addition, Imaging MS has been applied to drug targeting and metabolic studies both in specific organs and also in intact whole animal sections following drug administration.

This presentation will also describe recent technological advances both in sample preparation and instrumental performance to achieve images at high spatial resolution (1-10 microns) and at high speeds so that a typical sample tissue once prepared can be imaged in just a few minutes. Finally, new biocomputational approaches will be discussed that deals with the high data dimensionality of Imaging MS and our implementation of ‘image fusion’ in terms of predictive integration of MS images with microscopy and other imaging modalities.

PL3

Nutraceuticals: results, reasons, solution

Stephen L. De Felice M.D.

In 1965 I brought carnitine into the United States and conducted the first clinical trial with it in patients with hyperthyroidism. In collaboration with my good friend and the late proprietor of Sigma Tau Farmaceutici, Dr. Claudio Cavazza, we developed carnitine as a drug in the United States, Italy and internationally.

Shortly after, we began our drug development effort in the United States, it surprisingly became available as a dietary supplement freely available for anyone to purchase for unsubstantiated claims. This led to my involvement in the nutrition field. What was striking is that almost all of the health claims were not supported by clinical studies so I a) coined the term “nutraceutical” and b) designed the NREA, The Nutraceutical Research and Education Act for Congress to enact which would encourage both basic and clinical nutraceutical research. A nutraceutical is a food or part of a food that has a demonstrated proof of efficacy in clinical studies. This includes plant products. By an intensive educational effort, our Foundation (fimdefelice.org) succeeded in encouraging both the government and health industry to conduct clinical studies.

The results? A truly profound disappointment. Clinical studies, though not the best, have been almost consistently negative from herbal remedies to vegetables and to fruit, fiber, fats, multivitamins and many other natural substances.

The reasons? They are multiple, the principal one being an unimaginative, traditional global approach to nutritional research.

The solution? A new, revolutionary nutraceutical research approach. The rationale of such an approach will be presented.

PL4

Crystal Engineering: From Molecule to Crystal

Gautam R. Desiraju

Solid State and Structural Chemistry Unit, Indian Institute of Science,

Bangalore 560 012, India

desiraju@sscu.iisc.ernet.in

How do molecules aggregate in solution, and how do these aggregates consolidate themselves in crystals? What is the relationship between the structure of a molecule and the structure of the crystal it forms? Why do some molecules give more than one crystal structure? Why do some crystal structures contain solvent? How does one design a crystal structure with a specified topology of molecules, or a specified coordination of molecules and/or ions, or even with a specified property? What are the relationships between crystal structures and properties, for molecular crystals? These are some of the questions that are being addressed today by the crystal engineering community, which is drawn from the larger communities of organic, inorganic and physical chemists, and, of crystallographers and solid state scientists. This talk will give a brief historical introduction to crystal engineering itself, and an assessment of the importance and utility of the supramolecular synthon which is one of the most important concepts in the practical use and application of the subject. It is also hoped to provide a look to the future, and indicate some directions in which the subject of crystal engineering might be moving.

[1] G. R. Desiraju, *Angew. Chem. Int. Ed.*, *2007*, **46**, 8342-8356.
[2] G. R. Desiraju, *J. Am. Chem. Soc.*, *2013,* **135**, 9952-9967.

PL5

The Periodic System as the paradigm for modern chemistry

Eric Scerri

Department of Chemistry & Biochemistry, UCLA, Los Angeles, CA 90095

The periodic table of the elements provides an excellent unifying principle for bringing together many themes in chemistry including the relationship between macroscopic and microscopic properties, the history of modern chemistry and physics and the question of the reduction of chemistry to quantum mechanics.

The lecture will examine some key fundamental issues in chemistry against the backdrop of the developing periodic table beginning with the work of Dalton, Cannizzaro and the pioneers of the periodic system, continuing through the discovery of the noble gases, the work of Moseley. I will consider the extent to which quantum physics explains the periodic system from first principles starting with Bohr's old quantum theory and then quantum mechanics. Finally I will turn to some contemporary issues including the disputed positions of some elements in the table and whether relativistic effects present a challenge to the validity of chemical periodicity at high atomic numbers.

E.R. Scerri, *The Periodic Table, Its Story and Its Significance*, Oxford University Press, New York, 2007.

E.R. Scerri, *A Tale of Seven Elements*, Oxford University Press, New York, 2013.

PL6

Technology transfer from scientific community to industry. The importance of close cooperation

Amilcare Collina
MAPEI R&D

I think the theme of collaboration between Companies and Scientific Community is of vital importance: if we are unable in Italy to make it active and effective I cannot look forward with optimism at the future of the Italian Entrepreneurial System and then of our Country. There are certainly Italian Companies that cooperate effectively with the Scientific Community, but they are too few. In order to have a functional chain of innovation the three conceptual stages of research – i.e. basic research, applied research and industrial research – must be present and viable. Looking at the Companies in the chemical sector operating in Italy, most of them have a profile characterized by small or micro size, by the lack of dedicated resources to research, as well as by cultural limitations. Besides these genetic traits that do not allow them to carry out applied research, these Companies have, however, proven capabilities of industrial research, by creatively combining technology and know-how to give life to an "architectural" innovation which puts them in a position to meet with extraordinary celerity the needs of their customers. In synthesis the interaction with the Scientific Community is problematic for the most Italian chemical Companies and the synergy is very weak.

The innovation chain is polarized at the extremes (basic research and industrial research), it loses its functionality and cannot guarantee the systematic supply of innovative technologies to the industrial system in order to get a “structural” innovation.

These Companies are ready to address the business risks associated with innovation but do not have the resources to deal with the technical and economic risks of applied research. Therapy to get out of this situation is to restore the functionality of the innovation chain with the identification of a New Actor with the specific mission of applied research, actor different from the Industry which cannot do that with the exception of a small minority. Investments related to such a mission, and their nature - in particular the distinctive characteristics of high-risk investments and returns deferred in time - address the choice within the Public System of research. The National Research Council (CNR) is in my opinion the institution best suited to play this role; it was in fact born with this mission that they lost over the years. Of course it is not sufficient to identify the New Actor of applied research and entrust him with the specific mission; we must also provide it with the means to accomplish it. In particular, the CNR has to be supported by public investment to face the risks and anticipate the costs of applied research. These investments will be allocated only in presence of a binding commitment of the Companies to the industrialization of the results and to the payment of royalties for the rights to the industrial exploitation. There is no future for Italian Industry and then for the entire Country whether we will not be able to restore the functionality of the innovation chain, as I am convinced that if it is true that innovation does not arise without the basic research, it is also true that it does not grow without the applied research and it does not become economic value with a weak industrial research.

PL7

Accademia e Industria.

Una collaborazione strategica per il comparto chimico italiano.

Walter Cabri

Fresenius-Kabi Innovation & Development, Piazza Maestri del Lavoro 7, 20063 Cernusco sul Naviglio-Milano-Italy

walter.cabri@fresenius-kabi.com

L'interazione e la collaborazione fra Accademia (Università e CNR) e Industria è l'unico modo per sviluppare tecnologie innovative nel comparto chimico farmaceutico ed essere competitivi nel mondo globalizzato.

La riforma della pubblica amministrazione di cui l'Università e il CNR fanno parte, l'ottimizzazione delle risorse dell'Università, la focalizzazione su formazione e ricerca, sono passaggi fondamentali per il nostro paese.

Con qualche eccezione l'industria italiana si caratterizza purtroppo per progetti di ricerca a breve termine. Questo è determinato dalla struttura del comparto legata alle piccole e medie aziende.

In questo contesto l'interazione è estremamente difficile, farraginosa ed inefficiente.

Probabilmente sono necessari nuovi strumenti per combinare ricerca di base ed applicata. Sempre che queste definizioni siano ancora attuali. Di fatto rispetto ad altre discipline scientifiche la chimica ha rallentato e dimostra una mancanza di "brillantezza".

I finanziamenti statali debbono andare alla ricerca ed alla formazione, limitando all'essenziale la parte amministrativa e burocratica. Al contrario in questo momento i finanziamenti alla ricerca sono insufficienti e talvolta frammentati.

Strumenti come gli Uffici del Trasferimento Tecnologico debbono probabilmente essere rivisti. Lo scopo di questi uffici dovrebbe essere quello di attrarre finanziamenti, favorire ed ottimizzare le interazione con l'Industria e non semplicemente quello di trarre maggior profitto.

In questa comunicazione di discuteranno alcune proposte per la soluzione di questi problemi.

PL8

Towards Modeling Structure and Reactivity of Supported Catalysts

Francesc Illas
Departament de Química Física & Institut de Química Teòrica i Computacional (IQTCUB), Universitat de Barcelona, Barcelona, Spain

Francesc.illas@ub,edu

Heterogeneous catalysts most often consists of metal nanoparticles supported on oxides or sulfides. The interplay between particles size, nature of the support and metal-support interface results in a very rich but also very complex chemistry. To optimize the performance of these systems, it is highly desirable to disentangle the contribution of each effect to the final catalytic activity and selectivity. This is, however, not a simple task and the use of model systems, from both experiment and theory, becomes crucial. To illustrate the subtle interplay between particle size and support effects, two examples will be discussed, namely the water gas shift reaction (WGSR) catalyzed by Pt/CeO_2 and CO_2 hydrogenation to methanol catalyzed by a new class of catalysts consisting of Cu or Au nanoparticles supported on TiC and other transition metal carbides. In all cases, theoretical models are supplemented with careful experiments carried out under controlled conditions. In the case of the WGS we will provide evidence that small Pt nanoparticles are the most active and the activity is accompanied by reduction of the underlying ceria support. This strong metal-support interaction is precisely the key for the high activity of this system.[1] In the case of the Cu/TiC and Au/TiC catalysts we will show that the polarization of the electronic density induced by the underlying carbide is the reason for their high catalytic activity. The experiments show that the major product over these model catalysts is CO which is produced by the reverse water-gas shift reaction (RWGS, $CO_2 + H_2 \rightarrow CO + H_2O$) whereas the secondary product is methanol ($CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$). Density functional theory based calculations show that these systems strongly activate CO_2 and point to HOCO as a key intermediate for the generation of CO through the RWGS, with the production of methanol probably involving the hydrogenation of a HCOO intermediate or the CO generated by the RWGS.[2]

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PL9

Understanding paintings at molecular level

Maria Perla Colombini

Istituto di Conservazione e Valorizzazione dei Beni Culturali del CNR
via Madonna del Piano 10, Sesto Fiorentino

direttore@icvbc.cnr.it

The desire to understand the painting masterpieces and tell the story behind them has driven the science to develop more and more sophisticated analytical chemical procedures and instrumental techniques. As a result, successful multidisciplinary collaborations have flourished among researchers in museums, conservation institutions, universities and scientific laboratories.

Over the past two decades, particular attention has been focused on the characterization of organic materials occurring as binders, organic dyes and varnishes in paintings: the mixture of many materials and the chemical changes induced by ageing, long term chemical reactions with pigments, and environmental pollution make the study difficult and challenging. Therefore, the employment of advanced analytical technologies and techniques to understand the material behavior and to develop methods for material stabilization, strengthening, monitoring, and repair is fundamental.

Paintings, composed of multiple layers of various materials (binders, pigments, fillers and dryers, preparation and support) undergo modifications leading to change of the physical stability and appearance: up to now, they have been investigated to identify the original composition of the materials but only seldom to understand the degradation processes which occur over time and which may have significant effects on their properties. For instance, many modern materials composing works of art are inherently unstable and there is the need to early recognize the deterioration reactions in order to apply a method to prevent or delay the decay.

Investigation relies heavily on structural information at molecular level, and thus the application of mass spectrometry plays a prominent role. Coupling mass spectrometry with chromatographic techniques (Py-GC, GC and HPLC), makes it the most powerful tool to investigate the complex and aged mixtures of organic molecule that are currently encountered as constituents of paints.

The lecture focuses on the advancement obtained by MS based techniques in the characterization of organic materials in paintings and highlights how these techniques may increase the knowledge of art history. The chemical characterisation of painted fragments from Buddhas of the Bamiyan valley, Scott-Jacobean easel painting Collection, Munch' paintings is discussed.

PL10

Conoscenza, conservazione e musealizzazione dei legni di Murecine

Massimo Osanna

Soprintendenza Speciale per i Beni Archeologici di Pompei, Ercolano e Stabia (SAPES)
Via Villa dei Misteri 2, 80045 Pompei (NA), Italia

massimo.osanna@beniculturali.it

La Soprintendenza Speciale per i Beni Archeologici di Pompei, Ercolano e Stabia ha avviato da molti anni ricerche interdisciplinari che riguardano l'uso dei diversi materiali, fra i quali quelli di origine biologica quale il legno. Parallelamente ha intrapreso una campagna di studi finalizzati alla conservazione dei manufatti lignei, che si presentano con due diverse tipologie: reperti con aspetto carbonizzato e legni imbibiti.

Un caso particolare è rappresentato dal ritrovamento effettuato in località Murecine, dove la diversa genesi litologica ha fatto sì che il fabbricato riportato alla luce venisse a trovarsi al di sotto del livello di falda in una situazione di totale sommersione in acqua. Si tratta di una condizione molto favorevole alla conservazione del legno e degli altri materiali biologici che subiscono un degrado molto lento ad opera di agenti batterici. I ritrovamenti effettuati in questo ambiente costituiscono quindi quasi un *unicum* per l'area di riferimento e probabilmente per tutta l'archeologia romana. Si tratta di manufatti lignei di varia natura che comprendono sia elementi strutturali sia elementi di arredo e serramenti, in alcuni casi recanti le originarie decorazioni policrome.

I reperti sono stati sottoposti ad una prima campagna di studio, mirante anche alla predisposizione di un piano di stoccaggio a lungo termine, e sono oggi oggetto di un piano di conservazione che dovrà portare al trattamento conservativo ed alla loro musealizzazione. In questo progetto grande importanza assume la caratterizzazione del materiale che verrà eseguita mediante analisi microscopiche e chimiche miranti a stabilire il degrado raggiunto dai manufatti fra loro diversi per specie, dimensione e funzione.

Si tratta di un approccio metodologico innovativo, applicato a Pompei prima che in altri siti in Italia, che mira a scegliere le tipologie di trattamento e le pratiche di manutenzione dei manufatti partendo dall'esame del livello di degrado raggiunto dal legno, cercando di agire secondo il principio del minimo intervento, in modo meno invasivo possibile per la struttura del materiale e nel rispetto della reversibilità dei trattamenti.

PL11

Arte e Scienza, Arte è Scienza

Salvatore Lorusso

Dipartimento di Beni Culturali, Alma Mater Studiorum Università di Bologna (sede di Ravenna)

L'arte e la scienza sono due modi diversi di "leggere la realtà". Questo concetto di "lettura della realtà" è molto importante nello studio dei beni culturali. Infatti "lettura" è sinonimo di conoscenza, interpretazione, valutazione delle opere d'arte. Tale sequenza di stadi è alla base della valutazione soggettiva di carattere storico, estetico, stilistico, iconografico effettuata dagli storici e della valutazione oggettiva di carattere tecnico-diagnostico-materico-conservativo effettuata dai tecnici.

Di qui il bisogno di completamento e integrazione di competenze diverse e, quindi, di interdisciplinarità in riferimento al valore olistico del bene culturale, e, ad un tempo, il porsi dei limiti nell'ambito degli interventi di valutazione nel tempo di una istanza superiore "etica" nell'esprime il conseguente giudizio.

D'altra parte è pur vero che, quale legame che sancisce l'incontro fra arte e scienza, è opportuno far presente che:

«Tutte le opere artistiche sono manufatti, ma non tutti i manufatti sono opere d'arte. Ciò che riconosce il valore artistico è il giudizio. Esso tuttavia viene formulato in base a dati parametri, non è neppure l'espressione del piacere estetico dell'emozione che l'opera suscita nello spettatore. La legittimità del giudizio dipende dal processo mentale, attraverso il quale viene raggiunto il giudizio».

A tal riguardo vengono presentati alcuni casi di studio particolarmente emblematici, relativi ai manufatti di interesse storico artistico, che sottolineano l'importanza della suddetta integrazione, fornendo in tal maniera una risultanza ed un giudizio più prossimi alla "verità scientifica".

Programma Comune

Medaglie

M1

Medaglia “Emanuele Paternò”

A journey through materials, structures and processes

Giuseppe Bellussi

Eni SpA, Development, Operation and Technology, R&D, Via Maritano 26, 20097

San Donato Milanese, Italy.

giuseppe.bellussi@eni.com

In the coming decades, humanity will be facing some major challenges related to the availability of energy and resources and to the environmental impact of anthropogenic activity. It will be necessary to act on several fronts, including the efficiency of the conversion processes and the production of energy vectors, over most of the processes of refining and chemical conversion, natural gas upgrading and biomass processing.

The research will be addressed to the improvement of existing processes or the development of new processes through the definition of new engineering solutions and the development of new catalysts, more active, selective and stable, thus able to reduce the formation of by-products and the energy consumption. These achievement are often the results of an improvement of active sites composition or of the mass transfer limitations determined by the catalyst structure.

To face the complexity of the reference systems the holistic integration of skills in the fields of engineering, chemistry and physics, with a large contribution from materials science is required. Above all it is important to find new catalysts and therefore new materials with ordered structures. Crystalline or amorphous pseudo-ordered oxides with different porosities and surface areas, dispersions of metallic nano-clusters, transition metal sulfides are among the categories of materials that in the past years have been the most frequently studied in academic and industrial research laboratories.

In this presentation, the author will seek to represent the correlation between the structure of materials and their application in industrial processes through examples taken from the direct experience gained in various sectors of industrial conversion processes for the production of chemicals and energy carriers.

M2

Medaglia “Enzo Tiezzi”

L’Energia dai Principi della Termodinamica a Horizon 2020

Riccardo Basosi

Dipartimento di Biotecnologie, Chimica e Farmacia, Via A. Moro 2, 53100, Siena,

riccardo.basosi@unisi.it

L’energia pulita non esiste. L’unica energia pulita è quella risparmiata, cioè quella che non c’è bisogno di usare. Le scelte sulle fonti energetiche dovrebbero quindi essere fatte in termini di analisi costi/benefici e orientate alla minimizzazione dell’impatto ambientale. I fondamenti della termodinamica ed in particolare il II Principio sono la base di tali affermazioni. Infatti lo scorrere unidirezionale del tempo, implicito nelle leggi termodinamiche, permette di collegare tra loro mondi apparentemente distanti come quello dell’ordine, della probabilità e dell’informazione. Il contenuto di informazione delle fonti energetiche è specifico e non illimitato in natura, con la sola eccezione delle risorse rinnovabili. Ciò suggerisce l’uso razionale ed efficiente dell’energia (il cosiddetto risparmio energetico) come la prima gamba della sostenibilità ambientale. La seconda ugualmente necessaria è la sostituzione dei fossili con l’utilizzo, compatibile con le loro caratteristiche, delle fonti energetiche rinnovabili, tutte direttamente o indirettamente connesse all’attività solare. Esempi concreti di risparmio termodinamico di I e II ordine presi dalla esperienza di ogni giorno e una panoramica sugli sviluppi recenti delle rinnovabili suggeriscono una varietà di buone pratiche in accordo coi principi della Termodinamica per uno sviluppo sostenibile. L’efficienza energetica, le fonti a basso tenore di carbonio e le azioni per la diminuzione dei climalteranti nella prospettiva del pacchetto clima/energia, rappresentano anche gli elementi chiave del Work Program “Clean, secure and efficient Energy” di Horizon 2020.

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M3

Medaglia “Amedeo Avogadro”

Exploring routes to enhance sensitivity and specificity of MRI agents

Silvio Aime

Department of Molecular Biotechnologies and Health Sciences, Università di Torino, Via Nizza 52, 10126, Torino, Italy

silvio.aime@unito.it

The possibility of exploiting the superb anatomical resolution of MRI continues to make this modality highly desirable for Molecular Imaging applications in spite of the low sensitivity of the currently available contrast agents. Whereas chemists have tackled this issue by designing novel structures endowed with enhanced sensitivity, important achievements have also been reached by using nanocarriers (e.g. apoferritin, LDL or liposomes, etc.) able to deliver a large number of paramagnetic agents to the targeting sites. This approach is bringing relevant insights also to the emerging field of imaging-guided drug delivery (“theranostics”)[1]. Besides paramagnetic relaxation systems (e.g. Gd(III) or Mn(II) complexes), two new classes of frequency-encoding probes, namely the CEST agents (CEST= Chemical Exchange Saturation Transfer) and the class of hyperpolarized molecules, have been considered as powerful tools for Molecular Imaging applications. The use of frequency-encoding agents has opened the interesting perspective of detecting more than one agent in the same anatomical region[2]. Moreover, hyperpolarized molecules have the potential for being a real breakthrough as diagnostic agents reporting on cellular metabolism and transport across cellular membranes[3].
All together, the development in the design and testing of new probes has significantly improved the potential of MRI in respect to competing imaging modalities.

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M4

Medaglia “Domenico Marotta”

La dualità nella chimica nella produzione di armi chimiche

Ferruccio Trifirò

Dipartimento Chimica Industriale Viale Risorgimento 4 Bologna

ferruccio.trifiro@unibo.it

In questa conferenza racconterò perché l’OPCW , l’Organizzazione per la distruzione delle armi chimiche, ha preso nel 2013 il premio Nobel per la chimica, spiegherò cosa è l’OPCW e quali sono i suoi compiti e parlerò della distruzione delle armi chimiche e della situazione siriana. L’utilizzo di armi chimiche in Siria aveva fatto decidere gli Stati Uniti di intervenire in Siria. L’esistenza di una organizzazione mondiale come l’OPCW che poteva garantire il controllo e la distruzione delle armi chimiche presenti in Siria ha evitato un intervento armato. Il primo obiettivo della convenzione è stato di disattivare gli impianti che producevano armi chimiche e distruggere le armi chimiche immagazzinate, erano stati individuati 70 siti in 13 paesi diversi che producevano armi chimiche e sono stati tutti disattivati, erano stati individuati 35 siti in 7 paesi diversi dove erano armi chimiche immagazzinate e 80% è stato distrutto. Un’ arma chimica è qualsiasi sostanza chimica che attraverso la sua azione chimica sui processi vitali può causare morte, invalidità permanente o temporanea sugli uomini e sugli animali e deve essere una sostanza mortale, stabile, facile da disperdere e da produrre. Un secondo obbiettivo della convenzione é quello di tenere sotto controllo anche i siti dove ci sono produzioni chimiche a scopi pacifici, ma che potrebbero essere utilizzate per produrre armi chimiche: ne sono stati dichiarati 5426 in tutto il mondo e sono state fatte 5286 ispezioni. L’obbligo della dichiarazione della presenza di queste attività da parte dei paesi firmatari ed il successivo controllo da parte dall’ OPCW con diverse ispezioni, indirettamente ha una forte ricaduta sulla sicurezza di questi impianti o laboratori di ricerca, in quanto spinge ad un maggiore controllo delle emissioni di materie prime , sottoprodotti, intermedi, prodotti e coprodotti che presentano tossicità acuta. Un terzo obiettivo della Convenzione é controllare le possibili scoperte di nuove armi chimiche (o nuove sostanze a tossicità acuta) e questo obiettivo è uno dei compiti principali del comitato scientifico dell’OPCW. Diverse sono le attività che i membri del SAB devono seguire che possono portare alla creazione di nuove armi chimiche alcune di queste sono : convergenza fra chimica e biologia, la nanotecnologia, lo sviluppo accelerato di nuove sostanze chimiche con tecniche combinatorie e l’uso di micro reattori Per distruggere le armi chimiche ed i suoi precursori le tecnologie più utilizzate sono l’incenerimento seguito dall’ idrolisi a bassa temperatura. Recentemente si è proposto l’utilizzo dei sistemi portatili perché diminuisce i rischi del trasporto di armi chimiche che contengono esplosivi e permette di trattarli in zone sicure e lontane dai centri abitati. La tecnologia dell’esplosione ha il vantaggio di poter essere utilizzata facendo esplodere armi che contengono sostanze tossiche, senza effettuare previe estrazioni delle sostanze chimiche. L’esplosione avviene all’interno di un’autoclave di acciaio portando l’arma insieme ad un esplosivo a circa 550°C, con produzione di un gas e formazione di residui solidi che rimangono all’interno dell’autoclave. Le armi chimiche della Siria saranno distrutte su un nave americana che contiene due reattori di idrolisi ed i rifiuti tossici saranno distrutti in diverse nazioni.

M5

Medaglia “Giulio Natta”

Novel functional materials designed to solve old problems

Maurizio Prato
Center of Excellence for Nanostructured Materials, Dipartimento di Scienze Chimiche e Farmaceutiche, Università degli Studi di Trieste, Piazzale Europa 1, 34127 Trieste, Italy

prato@units.it

Many problems of our times have not been solved yet, mostly due to the complexity of the problems and their difficult solutions. New approaches and new materials are therefore needed, to produce breakthroughs and generate new hopes. Among the wide range of novel materials available today, carbon nanotubes (CNTs) stand as unique materials for fundamental research and potential applications. During this talk, we will report on the most recent advances in our group, which have led to several interesting applications in many fields. For instance, functionalized carbon nanotubes stimulate neuronal communication or can serve as carriers for innovative drug delivery systems. On the other hand, carbon nanotubes are ideal supports for catalysis in water splitting devices, for the production of hydrogen as a clean source of energy.

M6

Medaglia "Stanislao Cannizzaro"

From magnetochemistry to molecular magnetism. A lifelong attraction

Dante Gatteschi

Department of Chemistry, University of Florence, Lastruccia 3, 50019 Sesto Fiorentino Italy

dante.gatteschi@unifi.it

The development of my scientific activity has been characterized by a substantial staticity. In a sense I never changed type of interest: at the beginning I studied the magnetic properties of coordination compounds with the goal of obtaining structural information. At the end I study molecular magnets which in many cases are coordination compounds. What has drastically changed is the sophistication of the investigation techniques. And the area is no longer only chemistry, it has intensive overlap with physics, materials, and biology.

My achievements ? At the beginning low symmetry magnetic properties of coordination compounds. Which rapidly became the attempt to synthesize bulk magnets using molecular materials. I started to use paramagnetic nitronyl nitroxides as ligands obtaining new classes of magnets. Including classes of compounds which could not be obtained with magnetic metals and oxides. The breakthrough came by chance. A molecule containing twelve manganese ions was found to behave as a ferrimagnet at low T. the most exciting feature was that the molecules showed hysteresis opening the opportunity of storing information in one molecule. Single molecule magnet it was called, and the next step was the observation of quantum tunneling of the magnetization. The number of new systems which have been produced is rapidly increasing and more are under development and the original paper has ca. 2000 quotations. The present exciting themes under development correspond to molecular spintronics and quantum computing, which show that chemistry in the last 45 years has moved in a long winding road which started from magnetochemistry and currently is in the land of molecular magnetism. And more places will be visited.

The list of people to thank is long. Let me stop at 3, the perfect number. My maestro Luigi Sacconi, my elder brother Ivano Bertini, and above all Roberta Sessoli. Most merit for molecular magnets must be given to her.

M7

Medaglia “Ivano Bertini”

Selective catalysis & spectroscopies: an essential pair at the frontier between fundamental and industrial chemistry

Elena Groppo

Dipartimento di Chimica, Università di Torino, Via Quarello 15, 10125 Torino, Italia

elena.groppo@unito.it

Selective catalysis is at the base of a large number of industrial processes and still represents a challenge for both modern catalysis industry and academic researchers. Selectivity is closely related to the catalyst’s structure and composition. The possibility to tune the properties of the catalyst in order to influence the selectivity of the process has been largely explored in the patent literature, but up to now has been driven mainly by a trial-and-error approach. However, it is becoming increasingly evident that only by getting over the trial-and-error approach, and by moving to a rational methodology based on the fundamental mechanistic understanding of structure-property relationships, there would be some room for new developments in many fields of catalysis science.

The establishment of a structure-activity-selectivity relationship is particularly demanding for heterogeneous catalysts, compared to the homogeneous analogs. The plurality and low concentration of the surface sites, which can be active sites or simply spectators, combined with difficulties in investigating the catalysts under reaction conditions, are just a few examples of the challenges that need to be faced in order to properly understand the catalytic sites. Whatever the characterization techniques used for the investigation of the active sites, they should be very sensitive, able to discriminate between active and spectator species and versatile enough to work under conditions as close as possible to the reaction ones. The aim of this contribution is to show that, although not easy, this goal is at least feasible. The proposed strategy involves the combination of several, highly sensitive, spectroscopic techniques.

Two case studies will be discussed to illustrate the potential of this multi-technique approach in the investigation of the catalytic active sites at a molecular level: i) heterogeneous catalysts for olefin oligomerization and polymerization; and ii) supported metal nanoparticles for hydrogenation reactions. These two examples evidence that fundamental studies conducted in strict connection with industrial realities are essential for the future development of catalysts relevant in important chemical processes.

Programma Comune

Premi

R1

Premio Levi 2012

Tackling Big Challenges Using Tiny Nanocrystals

Matteo Cargnello

Department of Chemistry, University of Pennsylvania, 231 South 34th Street, Philadelphia, PA 19104 (USA)

mcargn@sas.upenn.edu

Precisely formed nanocrystals can be viewed as analogues of atoms. They can show quantized energy states that depend on their size and shape (quantum-size effects). Furthermore, because of their uniformity (nanocrystals can be prepared with precision of more or less one atomic layer), they can self-assemble into superlattices to give supracrystals as atoms in a crystal do. These characteristics prompted some to call these new building blocks “artificial atoms” or “atom equivalents”. One can also view these precisely formed nanocrystals as building blocks similar to toy construction bricks. Just as toy construction bricks can have different sizes/lengths, shapes, colors, nanocrystals can be prepared in different sizes, shapes and compositions. Similarly to how complex structures can be built by connecting the various toy construction bricks, nanocrystals can be manipulated by exploiting chemical interactions (from weaker van der Waals forces to stronger covalent or ionic bonds) to precisely place components onto surfaces in a desired fashion. By functionalizing the protective organic monolayer, doors are opened for further manipulation of these tiny building blocks. Self-assembly can also be exploited to organize the pieces into ordered superstructures. In this way, large structures prepared from individual building blocks can show properties that cannot be found in the individual components alone due to the special interactions between the parts.

I will show some recent results in the preparation of tailored structures and architectures based on nanocrystals to extract fundamental insights in catalytic reactions and to prepare more active, stable and/or selective catalysts and photocatalysts. Additionally, I will present the preparation of ordered nanocrystal superlattices of uniform building blocks by self-assembly to study energy transfer processes for potential photocatalytic applications. These works highlight how the successful implementation of well controlled synthesis and self-assembly can lead to nanostructured systems with unprecedented properties that can help answer fundamental questions related to the fields of catalysis and energy.

R2

Menzione Speciale Premio Levi 2012

Strategy to tune extend and narrow the dynamic range of switching DNA-based biosensors

Porchetta A.[a], *Plaxco K.*[b], *Palleschi G.*[a], *Ricci F.*[a]

a Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata,
Via della Ricerca Scientifica, 00133, Roma, Italia
b Department of chemistry, University of California, 93106, Santa Barbara, USA

alessandro.porchetta@uniroma2.it

The high specificity and affinity binding of proteins and nucleic acids have inspired decades of research aimed at employing biomolecular recognition in novel diagnostic tools. Despite this enthusiasm, however, biological recognition elements often exhibit a potentially significant limitation: the single-site binding characteristic of the majority of such receptors produces a hyperbolic dose-response curve with a fixed dynamic range. This can limit the utility of biomolecular receptors in applications which require the measurement of large changes in target concentration or that require a strong sensitivity response. Here we demonstrate multiple, complementary approaches by which we can tune, extend and narrow the dynamic range of a model aptamer-based cocaine sensor (1). Specifically, using a mutational approach we have generated sets of cocaine aptamers varying in their affinity for the target. Using various combinations of these receptors we were able to both narrow and broaden the dynamic range of biochemical receptors. In a second approach we have used a model cocaine aptamer and have changed its affinity using allosteric effectors. Compared to the mutational approach, this method provides a more rational, more efficient, and more cost-effective approach by which we can tune the affinity of an oligonucleotide-based receptor. Moreover, we demonstrated that using different combinations of allosteric effectors we can extend the dynamic range of the aptamer up to 4 orders of magnitude.

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R3

Menzione Speciale Premio Levi 2012

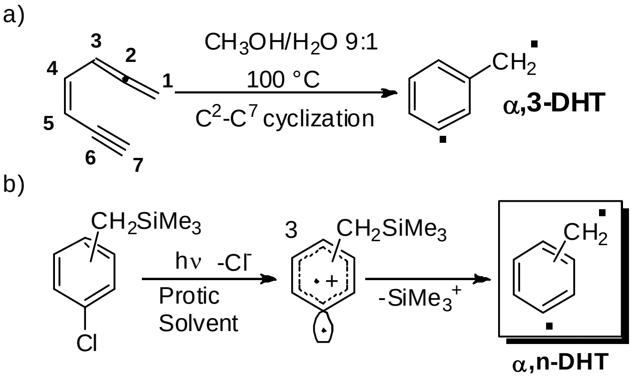
α,n-Didehydrotoluenes by Photoactivation of (Chlorobenzyl)trimethylsilanes: An Alternative to Enyne-Allenes Cyclization

Stefano Protti, Davide Ravelli, Maurizio Fagnoni, Angelo Albini

PhotoGreen Lab, Dept. Chemistry, University of Pavia, Via Taramelli 12, 27100 Pavia

davide.ravelli@unipv.it

The activation of a chemotherapeutic prodrug requires that an aggressive intermediate is generated in situ by a mild mechanism. This in turn should be able to abstract hydrogen atom(s) from DNA, finally inducing DNA cleavage. Among the few chemical classes that come close to this paradigm are highly unsaturated hydrocarbons, such as enyne-allenes present in some natural compounds known as antibiotics (e.g. Neocarzinostatin). These moieties cyclize through the Myers-Saito reaction to a α,3-didehydrotoluene (α,3-DHT), the only isomer accessible by this approach (Scheme, part a). [1]



We report herein an alternative route to the generation of all of the α,n-DHT isomers starting from (chlorobenzyl)trimethyl-silanes. This involves the photochemical generation of a triplet phenyl cation via heterolytic cleavage of the Aryl-Chlorine bond followed by loss the trimethylsilyl cation (see Scheme, part b). The photochemistry of the examined precursors and the structure of the involved intermediates has been investigated by means of a combined experimental/computational approach. [2,3]

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Programma Comune

Riflessioni sulle Armi Chimiche

Riflessioni sulle Armi Chimiche

Il Disarmo Chimico: l'Evoluzione della Convenzione di Parigi

Carlo Cesare Bonini

Autorità Nazionale per l'Attuazione della Convenzione per la Proibizione delle Armi Chimiche
Ministero degli Affari Esteri

carlo.bonini@esteri.it

Nell'ambito di una serie di incontri programmati presso le Università sulla tematica delle Armi Chimiche, verranno esaminate le principali linee di attuazione e di evoluzione della convenzione di Parigi del 1993. In particolare verranno illustrati i seguenti punti:

-Tematiche della Convenzione di Parigi sulla distruzione delle Armi Chimiche e sugli aspetti generali della non-proliferazione

.Le armi chimiche nella classificazione iniziale: esempi di evoluzione della Convenzione

-Ruolo e funzioni dell'OPAC (Organizzazione per la Proibizione delle Armi Chimiche)

-Compiti dell'Autorità Nazionale in Italia nel settore industriale ed economico

-"Scientists awareness" ed educazione alla non proliferazione, etica della ricerca: il ruolo e la responsabilità degli scienziati verso i giovani.

Chimica dell’Ambiente e dei Beni Culturali

Keynote

ABC-K1

Fluidi nanostrutturati confinati in gel chimici ad alta ritenzione per la pulitura di opere d'arte

Rodorico Giorgi [a], *Nicole Bonelli* [a], *David Chelazzi* [a], *Piero Baglioni* [a]

[a] *CSGI - Dipartimento di Chimica, Università di Firenze, Via della Lastruccia 3, 50019, Sesto Fiorentino, Italia*

rodorico.giorgi@unifi.it

La rimozione di materiali indesiderati da superfici dipinte e particolarmente sensibili all'azione di solventi polari, come ad esempio la carta, la pergamena o le tele, costituisce una problematica assai complessa nel restauro. L'impiego di fluidi nanostrutturati come soluzioni micellari e microemulsioni ha recentemente consentito di ottenere risultati eccellenti sia in termini di efficacia e completezza, nonché di selettività [1]. Tali sistemi però presentano come fase continua disperdente l'acqua, che è mal tollerata dai substrati sopra menzionati.

Lo sviluppo di idrogeli chimici semi-interpenetrati ad alta ritenzione, formati attraverso reazioni di polimerizzazione, ha consentito il confinamento delle soluzioni detergenti a base acquosa e la loro applicazione su simili superfici. Tali sistemi si sono dimostrati efficaci per la rimozione di numerose classi di sostanze, sia naturali, ad esempio la vernice dammar, sia sintetici, come i polimeri acrilici e vinilici [2,3].

Questo approccio ha prodotto risultati rilevanti in numerosi casi-studio, nei quali è stato possibile rimuovere materiali idrofobici da superfici sensibili all'acqua, utilizzando sistemi detergenti a base acquosa.

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ABC-K2

Un approccio multidisciplinare per la caratterizzazione dei materiali lapidei

Gino Mirocle Crisci

Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria

I materiali lapidei costituiscono la più ampia classe di materiali utilizzata nell'ambito dell'edilizia storica ed architettonica del nostro patrimonio culturale. La comprensione della natura del materiale lapideo e conoscerne le forme di degrado costituiscono un punto fondamentale per condurre un corretto intervento di restauro, nonché per fornire informazioni in campo puramente archeometrico.

Un approccio multidisciplinare, che unisce competenze chimiche, chimico-fisiche, geologiche, petrografiche e biologiche costituisce il miglior metodo per raggiungere tali scopi.

Un appropriato intervento di restauro di un materiale lapideo, non può prescindere da una diagnostica ad ampio spettro, atta a descrivere le cause e le dinamiche di degrado. Ad esempio metodologie chimiche e biologiche si riesce a distinguere una crosta nera da un attacco biologico. Predire o descrivere la dinamica con la quale la cristallizzazione di un sale indurrà un determinato degrado è possibile solo grazie alla combinazione di competenze chimiche, fisiche e minero-petrografiche.

La compatibilità di un prodotto consolidante o protettivo, sia esso organico che inorganico, può essere valutata solo attraverso metodologie che comprendono competenze sia di tipo chimico che petrografico.

In campo archeometrico, gli approcci multianalitici sono applicati con successo nella risoluzione di problemi quali la provenienza dei lapidei, la determinazione delle tecniche di confezionamento (nel caso di lapidei artificiali), nonché la datazione di malte, laterizi e ceramiche.

Lo studio della provenienza dei lapidei ha conosciuto negli ultimi anni un sostanziale progresso, grazie all'uso di tecniche di analisi elementare, quali ICP-MS e LA-ICP-MS, che unite a conoscenze geologiche e petrografiche hanno permesso di raggiungere un alto livello di conoscenza della composizione, della struttura dei materiali, nonché del territorio, rendendo così possibile la determinazione dei siti di origine dei materiali.

ABC-K3

From Chemical Structure to Environmental Hazard: exploiting QSAR for screening, prioritization and safer alternative design

P.Gramatica, S.Cassani, S.Kovarich, N.Chirico, A.Sangion, E.Papa

Dipartimento di Scienze Teoriche e Applicate, Università dell'Insubria, Via Dunant 3, 21100, Varese, Italia

paola.gramatica@uninsubria.it

309.000 of the over 29 million of commercially produced substances, listed by the Chemical Abstracts Services Registry, are regulated as priority chemicals. However, a higher number of compounds could be potential environmental pollutants. The new European regulation REACH (Registration Evaluation Authorization and restriction of Chemicals) will help in identifying hazardous chemicals, because a risk-based evaluation is required to evaluate the impacts of chemical uses or releases, for regulatory action, and to set priorities for pollution prevention. The time and resources, however, are not reasonably available to test all of these chemicals for their potential health and environmental effects. Therefore, modeling tools to prioritize and focus limited resources on selected chemicals for rigorous evaluation will yield the greatest environmental and socio-economic benefits. Computational models, based on the chemical structure, such as Quantitative Structure-Activity Relationships (QSARs), are highly useful in the screening of chemicals in order to identify those of higher concern, even not yet synthesized. Some examples of screening and priority setting for the assessment of some hazardous properties/activities will be presented, in particular for Substances of Very High Concern (SVHC), such as Endocrine Disruptors (EDs) or PBTs (Persistent Bioaccumulative Toxics). The inherent tendency of a compound to be PBT can be identified by the PBT Index model [1], included in our software QSARINS [2]. These screening tools can be also usefully applied *a priori*, in the benign by design approach, before the chemical synthesis of safer alternatives to dangerous compounds.

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Chimica dell’Ambiente e dei Beni Culturali

Oral

ABC-O1

Towards a diagnostic and cleaning tool for paper artworks

L. Micheli[a], C. Mazzuca[a], E. Bartolini[a], S. Iannuccelli[b], S. Sotgiu[b], D. Moscone, A. Palleschi[a], G. Palleschi[a]

[a]Dipartimento di Scienze e Tecnologie Chimiche, Università degli studi di Roma "Tor Vergata", Via della ricerca Scientifica snc – 00133 Rome, Italy

[b]Laboratorio di Restauro ICRCPAL, Ministero per i Beni e le Attività Culturali, Via Milano 76 - 00184 Rome, Italy

laura.micheli@uniroma2.it

The design and application in the Cultural heritage field of new tools for diagnostic and cleaning use, based on biocompatible hydrogels and electrochemical sensors, are reported in this work. The use of hydrogels is intriguing because they do not require liquid treatment that could induce damages on artworks; moreover, electrochemical biosensors are not only easy to prepare, but also selective for a specific compounds, thus suitable to monitor the cleaning process.

In the field of conservation of paper artworks, more efforts are still necessary in order to know how to perform a restoration wet treatment in an optimal way. The gels used demonstrated to be highly efficient in removing pollutants and degradation products, and electrochemical biosensors, widely employed in other scientific areas, may be used to verify the effectiveness of cleaning treatment performed with gel. In fact, by choosing the appropriate enzymes to be immobilized, specific biosensors, selective for the substances that have removed from the gel have been obtained. In this way, it is possible to stop the cleaning process when it is completed, avoiding lengthy and sometimes unnecessary gel applications.

ABC-O2

Utilizzo di DES (Deep Eutectic Solvents) per la pulitura enzimatica di superfici pittoriche

Silvia Prati[a], *Giorgia Sciutto*[a], *Gialuca Chiapponi*[a], *Francesca Volpi*[a], *Rocco Mazzeo*[a], *Chiara Samorì* [b], *Paola Galletti* [b], *Emilio Tagliavini* [b]

a Microchemistry and Microscopy Art Diagnostic Laboratory, Dipartimento di Chimica G. Ciamician, Università di Bologna, Via Guaccimanni 42, Ravenna, Italy.
b Centro di Ricerca Interdipartimentale Energia e Ambiente, Università di Bologna, Via Sant'Alberto 163, 48123, Ravenna, Italy

s.prati@unibo.it

A partire dagli ultimi quarant'anni, sull'onda dello sviluppo delle biotecnologie, si sono diffusi nel campo del restauro metodi di pulitura basati sull'impiego di enzimi e batteri. Tali procedimenti sono stati sviluppati con lo scopo di impiegare substrati che da un lato favorissero la selettiva rimozione di materiali (che a causa dell'invecchiamento presentano una ridotta solubilità) e dall'altro consentissero di evitare l'impiego di solventi tossici per gli operatori. Una limitazione relativa all'impiego dei metodi di bio-pulitura riguarda le condizioni ottimali di applicazione dei prodotti. Infatti, l'uso di enzimi richiede l'impiego di soluzione caratterizzate da un elevato pH (circa 9) ed una temperatura di applicazione che solitamente si aggira sui 38°C [1]. Inoltre, il solvente acquoso può adsorbirsi nelle porosità degli strati pittorici e preparatori e creare problemi di rigonfiamento. Il presente lavoro si prefigge lo scopo di valutare la possibilità di impiegare i DES (Deep Eutectic Solvents) in alternativa ai tamponi basici tradizionalmente impiegati, come solventi per eseguire puliture enzimatiche a temperatura ambiente. I DES sono solventi ionici di nuova generazione , molto promettenti nel campo delle tecnologie "green" grazie alla loro ridotta tossicità ed elevata economicità rispetto ai liquidi ionici tradizionali [2]. Nello specifico, i DES sono costituiti da miscele di colina e vari donatori di legami idrogeno (es etilen glicole, urea, glicerolo) e sono altamente compatibili con l'attività enzimatica.Nel presente lavoro DES di diversa composizione sono stati testati come solventi per promuovere reazioni di transesterificazione catalizzate da lipasi con lo scopo di mettere a punto un protocollo "green", efficace ed alternativo a quelli attualmente in uso. Prove batch su substrati modello (acidi carbossilici, esteri semplici e trigliceridi) e su provini contenenti strati di olio di lino puro e vernici olio-resinose hanno confermato l'efficacia dell'azione enzimatica anche a temperatura ambiente.

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ABC-O3

Restoration of the *Codex K.13.4 – K.13.5*, from Angelica's Library, in Rome

F. Valentini[a], *C Coletti*[b], *A. Boaretto*[a,c], *A. Rubechini*[b,d]

[a] *Dipartimento di Scienze e Tecnologie Chimica, Università Tor Vergata, Via della Ricerca Scientifica 1, 00133, Rome, Italy*
[b] *Dipartimento di Studi Umanistici & Antichità Classiche, Università Tor Vergata, Via Columbia, 00133, Rome, Italy*
[c] *CAPES Fundation, Ministry of Education of Brazil, Brasilia – DF 70040-020, Brazil*
[d] *Archivio di Stato del Vaticano, Rome (Italy)*

federica.valentini@uniroma2.it

The oxidation and the hydrolytic degradation represent the serious problems of the ancient manuscript damages that are preserved in libraries and archives. The possibility to minimize the hydrolytic degradation in the chain of cells by an elimination of the free acids could be an interesting approach. Several de-acidification strategies have been proposed in literature[1] but in order to select non-invasive restoration procedures, a specific diagnosis should be required. For this purpose, highly resolution spectroscopic and microscopic techniques are employed, as: μ-Raman spectroscopy, X-Ray Fluorescence (XRF), Fourier Transform-Infrared spectroscopy (FT-IR) and Field Emission-Scanning Electron Microscopy/Energy Dispersive X-Ray Analysis (FE-SEM/EDX). In the present work, the *Codex K.13.4 – K.13.5* (*dated 1600-1601*), *located in Angelica's library in Rome*, has been investigated and then, restored. This particular art work has been selected because it describes the works & actions of *St. Athanasius* (who lived between the third and fourth centuries), Patriarch of Alexandria and Father of the Church. The *Codex* still shows the original green parchment cover. The diagnosis demonstrates a serious oxidation damages and evident corrosion effects, this latter due to the metal gall inks. For its restoration, a reference treatment[1] has been applied using the calcium propionate combined with the borane tert-butylamine complexes[1]. The standard restoration treatment has been also compared with that performed using new eco-friendly/biocompaible nano-graphene based derivatives.

1. Ministero per i Beni e le Attività Culturali-Istituto Centrale per il Restauro&la Conservazione del Patrimonio Archivistico e Librario: Capitolato Speciale Tecnico Tipo, anno **2005,** a cura di: L. R. De Bella et al.;.

ABC-O4

La terra cruda a *pisé*: dal manufatto storico al modello di laboratorio

Giulia Ricci[a], *Laura Falchi*[a], *Laura Pirolandi*[a], *Fabio Fratini*[b], *Francesca C. Izzo*[a], *Eleonora Balliana*[a], *Elisabetta Zendri*[a]

a DAIS, Università Ca' Foscari di Venezia, Via Torino 155 b , 30170, Venezia, Italia
b ICVBC-CNR, Via Madonna Del Piano 10, Sesto Fiorentino, 50019 Firenze, Italia

giulia.ricci@stud.unive.it

Nell'ambito della riscoperta di materiali e tecnologie storico-tradizionali [1] assume particolare rilievo l'utilizzo di terre crude grazie alla loro compatibilità con i materiali storici e sostenibilità ambientale. Questo lavoro parte dallo studio di campioni storici in terra cruda stabilizzata con calce e lavorata a *pisé* provenienti da una raffineria di zucchero del XVI sec. vicino Marrakech [2]. La composizione mineralogica ha mostrato la presenza di attapulgite, in grado di ritenere alti contenuti di umidità, e di prodotti di idratazione dovuti a reazione di tipo pozzolanico tra la calce e l'argilla. La presenza di attapulgite potrebbe aver favorito l'idratazione garantendo il giusto grado di umidità del sistema nel clima secco di Marakech. In un ottica di "reverse engineering", sono stati realizzati modelli in terra cruda con e senza attapulgite. Grazie ad analisi XRD, TG-DSC, FT-IR, SEM-EDX su campioni a diversi tempi di maturazione si è osservata la reattività del sistema [3]. I modelli preparati sono stati caratterizzati attraverso prove di imbibizione d'acqua, analisi porosimetriche e meccaniche, che hanno evidenziato una connessione tra proprietà meccaniche e idratazione/ carbonatazione del sistema. I modelli sono stati utilizzati per valutare gli effetti del consolidamento con TEOS [4], mostrando dei buoni risultati in relazione al grado di penetrazione del consolidante.

[1] M. Karoglou, A. Bakolas, N. Kouloumbi and A. Moropoulou, *Prog.Org.Coat.*, 2011, **72, 1–2**, 202-209
[2] L. Rovero, F. Fratini, *Constr.Build.Mater*, 2013, **47**, October 2013, 465-479.
[3] L. Falchi, U. Müller, P. Fontana, F. C. Izzo and E. Zendri, *Constr.Build.Mater.*, 2013, **49**, 272-280
[4] E. Zendri, G. Biscontin, S. Riato, *Constr.Build.Mater.*2007, **21**, 1098-1106

ABC-O5

Leather: an important art work to restore

F. Valentini[a], *I. Camerino*[b], *A. Boaretto*[a,c], *G. Pace*[d]

[a] *Dipartimento di Chimica, Università di Roma Tor Vergata, Via della Ricerca Scientifica 1, 00133, Rome, Italy*
[b] *Dipartimento di Studi Umanistici & Antichità Classiche, Università di Roma Tor Vergata, Via Columbia, 00133, Rome, Italy*
[c] *CAPES Fundation, Ministry of Education of Brazil, Brasilia – DF 70040-020, Brazil*
[d] *Laboratorio di Restauro dell'Istituto Nazionale per la Grafica, Roma, Italy*

federica.valentini@uniroma2.it

In this work, the ***"Drawings of various authors' vol. 157 G2,*** belonging to the Corsini's collection, stored in the National Institute for Graphics (in Rome), has been investigated and restored. We selected this art work because it contains 481 drawings of various authors, dating back to the second half of 1500 and the end of 1700, as: *Pietro da Cortona*, *Lazzaro Baldi*, *G.B. Leinardi*. Among them, 477 are currently present in ***volume 157 G2*** and they need to be restored. Before to select non-invasive restoration&conservation strategies, a diagnosis of the specific damages, exhibited by the leather cover and the paper drawings, has been also performed. For this purpose, several techniques are used. Mainly, the X-Ray Fluorescence, Raman spectroscopy and Scanning Electron Microscopy are employed. The leather surface of the cover essentially shows abrasions, releasing particulate powdery. The paper drawings exhibit serious damages, firstly due to the oxidation of the metal gallic-inks. According to the diagnostic results, different non-destructive restoration treatments have been applied, according to the standard procedures, widely described in literature[1]. In this study, a comparative investigation has been also carried out, applying: **1**-nano-graphene for the restoration of the oxidized paper drawings and, **2**-nano-collagen for the conservation of the leather cover. We select these two nanomaterials because they result eco-friendly, compatible with the art work substrata and mainly, they are highly biocompatible for the end-users, as restorers.

Abrasion of the Leather cover. Oxidation of the drawing for the inks.

[1] *Ministero per i Beni e le Attività Culturali-Istituto Centrale per il Restauro&la Conservazione del Patrimonio Archivistico e Librario: Capitolato Speciale Tecnico Tipo, anno 2005, a cura di: L. R. De Bella et al.*

ABC-O6

Innovative method for the extraction of soluble salts from frescoes paints

Giulia Torrielli[a,b]*, Maurizio Ferretti*[b]*, Laura Gaggero*[a]*, Silvia Vicini*[b]

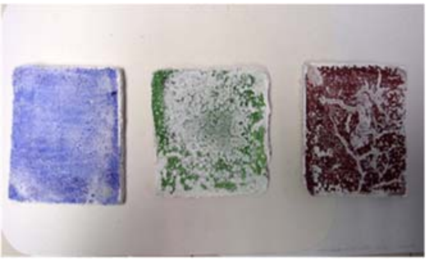
[a] *Department of Earth Sciences, Environment and Life, University of Genoa,*
Corso Europa 26, 16132, Genoa, Italy
[b] *Department of Chemistry and Industrial Chemistry, University of Genoa,*
Via Dodecaneso 31, 16146, Genoa, Italy.

giulia.torrielli@libero.it

An innovative method for desalination treatment has been systematically investigated on frescos samples expressely prepared with controlled composition and stratigraphy and contaminated with saline solutions. The effectiveness of the new method was compared with results obtained with absorbent materials i.e. cellulose and clays, used in the cleaning of artworks.

Results proved that the experimental method for the extraction of soluble salts is effective, and in particular provides an implemented alternative to the traditional wraps, mostly when combined with them.

The experiments using only absorbent materials showed that the cleaning is partial and focussed on the surface down to some mm, leaving unaltered the amount of salts in the deeper layers. Soon after the traditional restoration, the effects obtained with the wrap applications would be obscured by further emerging efflorescence, following the migration of salts inside outwards on the surface. Few applications of the innovative method considerably enhance the rise of salts to the surface. In this way they can then be easily removed with cycles of wraps, as shown in figure. A significant benefit of the innovative method is the dramatic decrease of time length in processing times.



ABC-O7

Effetto della Zona a Traffico Limitato di Milano sulla composizione chimica del PM

C. Rizzi, L. Ferrero, M.G. Perrone, G.Sangiorgi, V. Rozzoni,
E. Bolzacchini
Dipartimento di Scienze dell'Ambiente e del Territorio e di Scienze della Terra, Università degli Studi di Milano-Bicocca, Piazza della Scienza 1, 20126, Milano, Italia

ezio.bolzacchini@unimib.it

Il traffico veicolare è considerato la principale fonte di inquinamento atmosferico nelle aree urbane, tanto da indurre le autorità competenti a disporre blocchi del traffico o identificare zone a traffico limitato per ridurne il fenomeno. La città di Milano, a partire da gennaio 2012, ha istituito AREA C, un sistema di accesso a pagamento alla zona centrale della città.

Scopo di questo studio è valutare quale effetto ha avuto l'introduzione della zona a traffico limitato (ZTL) su Idrocarburi Policiclici Aromatici (IPA), Elemental Carbon (EC) e alcani lineari presenti nel PTS di Milano in Area C e fuori AREA C. Il particolato totale sospeso (PTS) utilizzato per questa ricerca è stato campionato in due siti rappresentativi dell'atmosfera urbana milanese, uno interno ad area C (via San Vittore, SV) e uno esterno ad essa (Torre Breda, TB)

L'EC è emesso da sorgenti di combustione. Nel particolato si utilizza come marker primario della sorgente traffico. I risultati ottenuti mostrano una netta riduzione dell'EC in ZTL del 36%.

Le concentrazioni di IPA nel periodo autunnale sono in media 2,56 ng/m^3. I risultati mostrano che esiste una buona correlazione (R^2= 0,86) per quanto riguarda la concentrazione degli IPA nei due siti TB e SV, con una diminuzione passando dal sito esterno alla ZTL a quello interno (riduzione media del 25%). Nei due siti, il modello di distribuzione degli IPA è lo stesso. Sono stati monitorati anche gli ossi-IPA, in particolare l'1,9-benz-10-antrone ed il Benzo(a)antracene-7,12-dione. Anche in questo caso si nota una diminuzione delle concentrazioni nel sito SV, all'interno della ZTL, del 19%.

Gli alcani lineari sono presenti in concentrazioni che vanno da un minimo di 20 ng/m^3 ad un massimo di 70 ng/m^3 (somma da C20 a C32). I più abbondanti risultano gli alcani dispari, in particolare il C29, con un'abbondanza pari al 15% rispetto al totale degli alcani analizzati, seguito dal C27 (11%), dal C31 (11%) e dal C25 (9%); anche in questo caso si nota una riduzione all'interno della ZTL del 14. In conclusione le concentrazioni di PTS, non variano significativamente tra i due siti selezionati, al contrario cambia la qualità del PTS, provvedimenti come le ZTL possono essere utili strumenti per ridurre le concentrazioni del componenti del PM che più provocano effetti sulla salute.

ABC-O8

Emission characterization of a pellet stove in non-steady state conditions

Ivano Vassura[a,b], *Elisa Venturini*[b], *Cristian Zanetti*[a], *Andrea Pizzi*[c], *Giuseppe Toscano*[c], *Elena Bernardi*[a], *Fabrizio Passarini*[a,b]

a Department of Industrial Chemistry "Toso Montanari", University of Bologna, Viale Risorgimento 4, I-40146, Bologna, Italy
b Interdepartmental Centre for Industry Research "Energy and Environment", University of Bologna ,Via Angherà 22, 47900, Rimini, Italy
c Department of Agricultural, Food and Enviromental Sciences, Polytechnic University of Marche, Via Brecce Bianche 10, 60131, Ancona, Italy

ivano.vassura@unibo.it

In last years, the use of pellet devices as heating system in Europe-28 has strongly increased [1]. Besides advantages of renewability and greenhouse gas emission mitigation (CO_2), emission from residential wood combustion has been considered as a major contributor to ambient air pollution [2]. Emission factors for residential pellet heating systems are obtained from measurements primarily during standard operation, quite far from a realistic utilization. The emission characteristics of transient operations (start-up, increases in power and stop phase) of the residential pellet devices are rare [2,3,4], while nobody has never considered another transient operation: the increases in power.

In this work, the emission factors of a pellet stove were measured for the different phases associated to pollutant emission: ignition, partial load, power increase and full load. The flue gases composition was on-line analysed along the standard stack connected to the device. The particulate emissions were collected in a dilution tunnel, to take into account the condensable fraction. The PM characterization includes: As, Ni, Cd and Pb, inorganic ions, PAHs and TC.

Results show that the emission factors are higher during ignition phase for almost all the determined contaminants. Particularly, PAHs show markedly higher emission factors and different relative distribution during start-up.

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[3] C. Schmidl, et al., *Atmos.Environ.*, 2011, **45**, 7443-54.
[4] G. Toscano D. Duca, A. Amato and A. Pizzi, *Energy*, 2014, **68**, 644-50.

ABC-O9

Characterization of metal content in PM10 collected in Piedmont Region

Mery Malandrino[a], *Ornella Abollino*[a], *Agnese Giacomino*[b], *Antonella Pannocchia*[c], *Milena Sacco*[c], *Mauro Grosa*[c], *Francesco Lollobrigida*[c]

a Dipartimento di Chimica, Università di Torino, Via P. Giuria 5, 10125, Torino, Italia
b Dipartimento di Scienze e Tecnologia del Farmaco, Università di Torino, Via P. Giuria 9, 10125, Torino, Italia
c Dipartimento di Torino, ARPA Piemonte, Via Pio VII 9, 10135, Torino, Italia

mery.malandrino@unito.it

Atmospheric pollution resulting from airborne particulate matter, especially PM10, continues to be a major problem since epidemiological studies have established a linkage between the concentration of the PM10 and its elemental concentration with adverse respiratory health effects [1, 2].

In this study the concentrations of 23 elements, namely As, Ba, Br, Ca, Cd, Ce, Co, Cr, Cu, Fe, K, La, Mg, Mn, Mo, Ni, Pb, Sb, Sr, Ti, V, Zr and Zn, in PM10 samples collected by A.R.P.A. in three urban and two rural sites of Piedmont Region were determined. More precisely the PM10 samples collected in four different months of 2011, namely February, May, August and November, were considered.

A clear seasonal pattern with higher concentrations of the most likely anthropogenic elements (Cu, Zn, Mo, Co, Ni, As, Pb and W) in the cold periods was observed. This trend was more evident in the site most exposed to pollution sources, namely the urban area localized in the northern outskirts of Turin city. Conversely, some elements, namely Ni, V and As, were characterized by a different trend in the atmospheric particulate matter (PM10) collected in rural site of Saliceto (Province of Cuneo). Indeed, these elements were present in higher concentrations in the warm periods, particularly in August. A possible explanation for this behaviour can be found in their different origin: Ni and V likely arise from heavy fuel oil combustion emissions, linked to shipping in the near Ligurian Sea, while As should be related to local resuspension of soil dust, rich in arsenopyrite, by the action of the drier summer wind.

Finally, the application of multivariate chemometric techniques to the experimental results allowed us to identify correlations among the investigated elements and to reveal similarities and differences between sampling sites.

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[2] N. Englert, *Toxicol. Lett.*, 2004, **149**, 235–242.

ABC-O10

Spatial and seasonal variations of carbonaceous particulate matter in the Veneto Region, Italy

Md. Badiuzzaman Khan[a], *Mauro Masiol*[a,b],*Gianni Formenton*[c], *Alessia Di Gioli*[d], *Gianluigi De Gennaro*[d], *Claudio Agostinelli*[a], *Bruno Pavoni*[a] …

a Dipartimento di Scienze Ambientali, Informatica e Statistica, Università Cà Foscari Venezia., Dorsoduro 2157, 30123 Venice, Italy
b Division of Environmental Health & Risk Management, School of Geography, Earth & Environmental Sciences, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom
c Dipartimento Provinciale di Padova, Agenzia Regionale per la Prevenzione e Protezione Ambientale del Veneto (ARPAV), Via Ospedale 22, 35121 Padova, Italy
d Dipartimento di Chimica, Università degli Studi di Bari, via Orabona 4, 70126 Bari, Italy

brown@unive.it

This study observed the spatial and temporal variations in organic (OC) and elemental carbon (EC) and their contribution to total carbon. A total of 360 $PM_{2.5}$ samples were collected in every alternate month from six provinces from April 2012 to February 2013 in the Veneto region. During summer, OC concentrations ranged from 0.98 µg m^{-3} to 5.03 µg m^{-3}, while the mean value was 2.66 µg m^{-3}, contributing almost 77% of the total carbon. EC concentrations fluctuated from 0.19 to 2.09 µg m^{-3} with a mean value of 0.77 µg m^{-3}, contributing for 23% of the total carbon. Differently, in winter, OC carbon concentrations varied from 1.06 to 22.34 µg m^{-3} with a mean value of 8.92 µg m^{-3}, contributing 80% of the total carbon, while the EC concentrations ranged between 0.30 to 11.90 µg m^{-3} with a mean value of 1.98 µg m^{-3}, accounting for 20% to the total carbon. In both the seasons, the highest average OC and EC concentrations were observed in Padova and Rovigo, respectively. The mean OC/EC ratios during summer and winter were 3.80 and 5.45, respectively, while the annual mean value was 4.54. This is higher than the values observed in most of the other European cities. A low correlation between elemental and organic carbon exists in both the seasons (r=0.49: summer, r=0.41: winter). The secondary organic carbon (SOC) was calculated from the EC tracer method and the SOC contribution to TOC was higher during winter as compared to summer.

ABC-O11

Influenza di sorgenti antropiche e naturali sui livelli di Black Carbon (BC) e sulla distribuzione dimensionale delle particelle

Andrea Piazzalunga[a], *Ugo Cosentino*[b], *Demetrio Pitea*[b], *Naim Malaj*[a], *Irene De Franco*[a], *Francesca Sprovieri*[c], *Alessandro Servidio*[c], *Annalisa Rosselli*[c], *Franco Cofone*[c], *Massimiliano Vardè*[c]

[a] *Dipartimento di Scienze dell'Ambiente e del Territorio e di Scienze delle Terra, Università di Milano Bicocca (Sede di Rende),Via Pietro Bucci, 87036, Rende(Cs), Italia*
[b]*Dipartimento di Scienze dell'Ambiente e del Territorio e di Scienze delle Terra, Università di Milano Bicocca, Piazza della Scienza 1, 20156, Milano, Italia*
[c]*Istituto sull'Inquinamento Atmosferico, CNR, c/o UNICAL Polifunzionale - 87036 Rende(Cs), Italia*

andrea.piazzalunga@unimib.it

Nell'ambito del progetto SNIFF-Sensor Network Infrastructure For Factors (PON01_02422) è stata effettuata una campagna di misura per la valutazione della Qualità dell'Aria a Lamezia Terme (CZ) in prossimità dell'aeroporto e a poca distanza dall'autostrada A3. Nella campagna di misura, in aggiunta ai parametri PM_{10}, O_3, CO, NO, NO_2, NOx, SO_2 regolamentati dal D.lgs. 155/2010, sono state monitorate ad elevata risoluzione temporale sia le concentrazioni di BC che la distribuzione dimensionale delle particelle. Il BC è stato determinato utilizzando il PAX (Photoacoustic Extinctiometer, Droplet), strumento per la prima volta impiegato in Italia, che permette di misurare il coefficiente di assorbimento delle particelle mediante la tecnica fotoacustica. La distribuzione granulometrica delle particelle è stata effettuata con un impattore multistadio (ELPI+, Dekati) che conta e campionale particelle segregandole in 14 classi dimensionali (0.006-10µm). L'elevata risoluzione temporale delle misure, integrata ai principali parametri meteo, ha permesso una valutazione preliminare del contributo di eventi di origine naturale (sabbie sahariane) e delle due principali sorgenti antropiche (traffico autoveicolare ed aeroportuale) sulla qualità dell'aria. Lo studio integrato della distribuzione dimensionale delle particelle, BC, PM_{10} e di inquinanti in fase gassosa è una strategia adeguata per la caratterizzazione di un sito di monitoraggio e relativa valutazione della qualità dell'aria.

ABC-O12

Confronto metodologico per la determinazione della composizione ionica del PM

G. de Gennaro[a,b], *A. Di Gilio*[b], *P.R. Dambruoso*[b], *P. Fermo*[c], *A. Piazzalunga*[c], *R. Vecchi*[d.]

[a]*Dipartimento di Chimica, Università degli Studi di Bari, Via Orabona 4 , 70126, Bari, Italia*
[b]*ARPA Puglia, Corso Trieste 27, 70126 Bari, Italia*
[c]*Dipartimento di Chimica, Università di Milano Bicocca, Piazza della Scienza, 3, 20126 Milano, Italia*
[d]*Dipartimento di Inorganica, Metallorganica e Chimica Analitica, Università di Milano, via Celoria,18, 20133 Milano, Italia*

gianluigi.degennaro@uniba.it

In questo lavoro sono state valutate le potenzialità del campionatore automatico di nuova generazione Ambient Ion Monitor (AIM 9000D-URG), che direttamente in campo e con risoluzione temporale oraria, determina la concentrazione di anioni e cationi adsorbiti sul particolato fine e dei precursori ionici gassosi in atmosfera. Tale strumento è stato sperimentato sul campo nell'ambito di tre campagne di monitoraggio condotte nel Campus Universitario di Bari e di Milano. L'analisi dei dati raccolti ha permesso di osservare eventi emissivi e di trasporto transfrontaliero anche limitati nel tempo e di seguire l'evoluzione temporale di sorgenti di particolato atmosferico occasionali. Inoltre le informazioni simultanee ed ad alta risoluzione temporale circa le concentrazioni di gas inorganici e degli ioni, hanno permesso di studiare i processi chimico fisici di ripartizione gas-particella dei componenti inorganici e di valutare i fattori meteo-climatici che influiscono su tali processi; mettendo in luce le differenze tra Sud e Nord Italia. Infine nell'ambito di apposite campagne di campionamento del PM è stato possibile approfondire gli artefatti inorganici di campionamento confrontando le performance del sistema automatico AIM9000D sia con il metodo tradizionale di campionamento ed analisi della componente ionica del PM sia con il metodo più rigoroso suggerito dall'USEPA (USEPA IO 4.2).

ABC-O13

On the source apportionment of PM2.5 in the port city of Brindisi (IT)

A. Genga[a], *P. Ielpo*[b,c], *M. Siciliano*[a], *D. Contini*[b], *D. Cesari*[b], *R. Buccolieri*[a], *S. Di Sabatino*[a]

a Dipartimento di Scienze e Tecnologie Biologiche e Ambientali, Università del Salento, Lecce, Apulia, 73100, Italy

b Istituto di Scienze dell'Atmosfera e del Clima, ISAC-CNR, Lecce, Apulia, 73100, Italy

c Istituto di Ricerca sulle Acque, IRSA-CNR, Bari, Apulia, 70132, Italy

alessandra.genga@unisalento.it

Air emissions from maritime transport currently represent a significant portion of total emissions, whose impact on air quality, climate change and human health still remain to be quantified in several port cities. The research project CESAPO (Contribution of Emission Sources on the Air quality of the POrt-cities in Greece and Italy-2012-2014), funded within Interreg Italy-Greece 2007/2013 framework, is a contribution towards such a quantification. Specifically, the focus was on the two cities of Brindisi (IT) and Patras (GR) with emphasis on the maritime transport and the activities within the port areas, in search for common/integrated actions to support a sustainable urban development in the Mediterranean Region. Here, we present an analysis of the chemical characterization of PM2.5. Data were collected during an experimental campaign in port of Brindisi during June to October 2012, during which 148 PM2.5 samples were collected. Soluble ionic species (water soluble organic and inorganic carbon; major ions: SO_4^{2-}, NO_3^-, NH_4^+, Cl^-, $C_2O_4^{2-}$, Na^+, K^+, Mg^{2+}, Ca^{2+}), 12 elements (Ni, Cu, V, Mn, As, Pb, Cr, Sb, Fe, Al, Zn and Ti) and OC/EC contents are analyzed. Results of source apportionment based on PM2.5 composition, using the Positive Matrix Factorization (EPA PMF3.0), Absolute Principal Component Scores model (APCS) are discussed in details. PM2.5 concentrations are calculated using the dispersion model ADMS-urban and consequences on local air quality are critically analyzed. This work was supported by the Interreg Greece-Italy 2007-2013 program under grant.

ABC-O14

Potenziale ossidativo del particolato atmosferico in funzione delle sorgenti e della composizione chimica

Perrone M.G.[a], *Ferrero L.*[a], *Sangiorgi G.*[a], *Bolzacchini E.*[a]

[a] *Dipartimento di Scienze dell' Ambiente e del Territorio e Scienze della Terra, Università di Milano-Bicocca, Piazza della Scienza 1 , 20126, Milano, Italia*

grazia.perrone@unimib.it

Diverse evidenze sperimentali e studi epidemiologici hanno dimostrato che l'esposizione all'inquinamento da particolato atmosferico (PM) è causa di effetti nocivi sulla salute umana. Una delle principali ipotesi è che tali effetti derivano dallo stress ossidativo, avviato dalla formazione di specie reattive dell'ossigeno (ROS). Per questo la misura del potenziale ossidativo del PM è stato proposto come un parametro importante per la valutazione delle risposte biologiche all'esposizione da PM.

Il particolato atmosferico è un insieme di particelle di dimensione e composizione chimica differente, e in studi precedenti è stata investigata la relazione tra la composizione chimica e gli effetti biologici (*in vitro*) osservati per campioni stagionali di PM in diversi siti del Nord Italia (Perrone et al., 2013; Perrone et al., 2010).

In questo lavoro è stato sperimentato un metodo chimico (ditiotreitolo, *DTT assay*) per determinare il potenziale ossidativo di campioni di PM prelevati nell'area urbana di Milano. Nel DTT assay, il potenziale ossidativo di campioni estratti di PM è ricavato dal consumo di DTT, usato come agente riducente, misurando il DTT residuo per via spettrofotometrica (Cho et al. 2005). Il *DTT assay* si è rilevato un metodo sensibile per la misura del potenziale ossidativo di campioni giornalieri di PM (24 ore di campionamento, massa PM analizzata 1-2 mg).

I più alti valori di potenziale ossidativo sono stati misurati per il PM campionato durante la stagione estiva, con valori circa 3-5 volte maggiori rispetto all' inverno (Milano. Estate: 2.8-5 μM DTT min^{-1} mgPM^{-1}; inverno: 0.5-2 μM DTT min^{-1} mgPM^{-1}). Il potenziale ossidativo del PM varia in funzione della diversa composizione chimica delle particelle: inquinanti primari derivanti da sorgente traffico (es. IPA ed EC) non hanno mostrato un effetto sul potenziale ossidativo misurato, che invece aumenta significativamente in presenza di aerosol secondario (es. ossiIPA).

[1] A. Cho, et al., *Environmental Research*, **2005**, 99, 40-47
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ABC-O15

Degradation of the emerging contaminant ibuprofen in water by cavitation

Pasquale Iovino[a], *Mauro Capocelli*[b], *Marina Prisciandaro*[b], *Amedeo Lancia*[c], *Stefano Salvestrini*[a], *Sante Capasso*[a], *Dino Musmarra*[d]

a Department of Environmental, Biological and Pharmaceutical Sciences and Technologies, Second University of Naples, Via Vivaldi, 43, 81100 Caserta, Italy
b Department of Chemistry, Chemical Engineering and Materials, University of L'Aquila, Zona Industriale di Pile, 67100 L'Aquila, Italy
c Department of Chemical Engineering, University Federico II of Naples, Piazzale V. Tecchio, 80, 80125 Napoli, Italy
d Department of Civil Engineering, Second University of Naples, Via Roma, 29, 81031 Aversa (CE), Italy

pasquale.iovino@unina2.it

In this study the degradation of the Non-Steroidal Anti-Inflammatory Drug, ibuprofen (IBP), by hydrodynamic cavitation (HC) was evaluated. Many studies show that some emerging contaminants originating from human therapies are not totally eliminate in the municipal sewage treatment plants and are, thus, discharged as contaminants into the receiving waters [1, 2]. For such reason, in the last years some Advanced Oxidation Processes have been developed as new technologies for water purification. HC is the phenomenon of nucleation, growth and implosion of vapor - or gas - filled cavities. This results in extreme collapse conditions and dissociation of water molecules into OH and H radicals. OH radicals diffuse into the liquid and react with IBP molecules resulting into a very effective oxidation [3]. This paper deals with the HC degradation of ibuprofen. The effects of various operating parameters such as inlet pressure and pH were studied with the aim of maximizing the extent of degradation. The main byproducts observed consisted mostly of the decarboxylated and the hydroxylated ibuprofen. The degradation of IBP was found to be dependent on the solution pH and the highest degradation was achieved in the acidic medium.

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[2] R. Andreozzi, R. Marotta, N. Paxéus *Chemosphere* 2003, **50**, 1319-1330.
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ABC-O16

Hydrodechlorination of Aroclor 1260 with a biogenerated Pd catalyst

Oreste Piccolo[a], *Franco Baldi*[b], *Michele Gallo*[b], *Stefano Paganelli*[b], *Riccardo Tassini*[b], *Rossano Piazza*[c], *Stefano Zambon*[c], *Lidia Armelao*[d], *Marta Maria Natile*[d]

a SCSOP, Via Bornò 5, 23896 Sirtori (Italy). b Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari Venezia, Calle Larga S. Marta 2137, 30123 Venezia (Italy). c Dipartimento di Scienze Ambientali, Informatica e Statistica, Università Ca' Foscari Venezia, Calle Larga S. Marta 2137, 30123 Venezia (Italy). d IENI – CNR and INSTM, Dipartimento di Scienze Chimiche Università di Padova, Via F. Marzolo 1, 35131 Padova (Italy).

contact@scsop.it

A strain of Klebsiella oxytoca, BAS-10, which is able to produce a specific exopolysaccaride (EPS), was grown anaerobically on sodium citrate as sole energy and carbon sources. The cultures were amended with 50 mg of $Pd(NO_3)_2$ to generate Pd-EPS catalytic species that were recovered by a cold 70% ethanol solution and well characterized using different analytical techniques. Up to 70% of the metal was present as Pd(0) in the form of aggregated nano-clusters. Polychlorinated biphenyls (PCBs) are a class of 209 organic pollutants that, due to their hydrophobic nature and high stability, are strongly persistent in the environment, with significant values of contamination of the water. In combination with their toxicity this stimulates researches for reducing their concentration in the ecosystem by improved and/or innovative technologies. In a preliminary study on 1,2,4-trichlorobenzene chosen as model substrate, Pd-EPS showed a high activity producing not only the three dichlorobenzene derivatives but also chlorobenzene and benzene with a total dechlorination yield of 76%. After this new catalyst was tested in water on a methanolic solution of Aroclor 1260 PCBs mixture, at 3 MPa H_2 and 60°C for 20 h. Under these conditions a significant removal (67%) of the more toxic highly chlorinated PCBs was achieved. So the bio-generated Pd-EPS catalyst seems potentially promising for applications aimed at pulling down PCBs content in aqueous environment and is surely more efficient and rapid in comparison with alive microbial communities.

ABC-O17

Heterogeneous catalysts for the production of glycols from glycerol derivates

R. Cucciniello[a], C. Pironti[a],C. Capacchione[a], M. Di Serio[b], A. Proto[a]

*a Dipartimento di Chimica e Biologia, Università di Salerno, Via Giovanni Paolo II 132 ,
84084, Fisciano (SA),Italia*
*b Dipartimento di Scienze Chimiche, Università di Napoli, Via Cintia-Complesso Monte S.
Angelo 21 ,80133, Napoli, Italia*

rcucciniello@unisa.it

Glycerol is the major by-product of biodiesel production and for every gallon of biodiesel produced, one pound of glycerol is produced. The increasing production of biodiesel is closely related with glycerol conversion and uses[1].

One of the most important and studied processes involves glycerol conversion to acrolein, a versatile intermediate employed by the chemical industry for the production of acrylic acid esters, detergents and polymers. Acrolein preparation route involves the byproduct 2-monochlorohydrin formation that can be treated with basis to form glycidol[2].

Glycidol represents an important feedstock for glycols productions, such as 1,2-propandiol and 1,3-propandiol (PDO). PDO is actually produced with good performances only through fermentation of sugars, but this procedure in not economically advantageous[3].

In this work we report the glycidol conversion to glycols by hydrogenation using several catalysts based on transition metals (Rh, Pd, Pt, Cr, Ni) exploring the effect of the reaction conditions on selectivity to PDO. Reactions were conducted in a closed steel reactor under mild conditions of temperature and hydrogen pressure. Moreover, an active metal catalyst support were synthesized and employed in glycidol conversion, showing a significant effect on selectivity to PDO, compared to commercial available catalyst supports.

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ABC-O18

Removal of alkyl benzyl dimethyl ammonium surfactant C12 from aqueous solutions by sorption onto natural zeolites

Vincenzo Leone[a]

a Dipartimento di Scienze e Tecnologie Ambientali, Biologiche e Farmaceutiche, Seconda Università degli Studi di Napoli, Via Vivaldi 43, 81100, Caserta, Italia

vincenzo.leone@unina2.it

This communication report recent results on the sorption of cationic alkyl benzyl dimethyl ammonium surfactant with alkyl chains 12 C atoms onto natural zeolite. A commercial sample of phillipsite/chabazite-rich tuff (PCT) with grain size ranging between of 0.5 and 1.0 mm, coming from an outcrop of the Campanian Ignimbrite formation located in Comiziano (Napoli, Italy), was used in the present investigation. This material has been initially enriched in calcium or natrium ions. Equilibrium and kinetics of benzalkonium chloride (BKC) adsorption onto PCT enriched in Na^+ or Ca^{2+} cations (Na-PCT or Ca-PCT) have been studied in batch system. Benzalkonium chloride is the active ingredient of many pharmaceutical formulations, cosmetics, commercial disinfectants, industrial sanitizers and food preservatives [1]. The adsorption was investigated in an sample concentration range from 10 mM to 100 mM. It has been demonstrated that the adsorption of BKC onto Na-PCT or onto Ca-PCT depend of the temperature, the ionic strength but not of the pH. The kinetic studies revealed that the adsorption of BKC was rapid and complied with pseudo second-order kinetic (R2= 0.99). Alkyl benzyl dimethyl ammonium sorption analysis has been demonstrated that the natural zeolite had good adsorbing properties. Moreover, the zeolitic tuff enriched in natrium cation showed a higher sorption propriety compared with zeolitic tuff enriched in calcium cation. These results point to prospective application of the natural zeolite as a low-cost and environmentally friendly sorbent for water purification from BKC and possibly other new emerging organic contaminants

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ABC-O19

Surface enhanced vibrational techniques for the detection of dyes in thin layer chromatography

<u>G. Sciutto</u>[a], S. Prati[a], I. Bonacini[a], L. Litti[b], M. Meneghetti[b], R. Mazzeo[a]

a Microchemistry and Microscopy Art Diagnostic Laboratory, University of Bologna, Via Guaccimanni 42, 48121 Ravenna, Italy
b Department of Chemical Sciences, University of Padova, Via Marzolo, 1, 35131 Padova

giorgia.sciutto2@unibo.it

The present research is focused on the development of an advanced analytical system based on the combination of an improved thin layer chromatography (TLC) plate coupled with infrared (FTIR) and Raman microscopies for the detection of synthetic dyes. Indeed, the characterization of organic colorants, which are commonly present in mixtures with other components and in a very limited amount, still represents a challenging task in scientific analyses of cultural heritage materials. The approach provides selective spectral fingerprints for each compound, foreseeing the complementary information obtained by micro ATR-FTIR and SERS-Raman analyses, which can be performed on the same separated spot. In particular, silver iodide (AgI) applied on a gold coated slide is proposed as an efficient stationary phase for the discrimination of complex analyte mixtures, such as dyes present in sample of art-historical interest. The gold-AgI-TLC plate shows high performances related both to the chromatographic separation of analytes and to the spectroscopic detection of components. The use of a mid-IR transparent inorganic salt as the stationary phase avoids interferences of the background absorption in FTIR investigations. Moreover, by ATR microscopy measurements performed on the gold-AgI surface, a considerable enhancement in the intensity of spectra is observed. Complementary information can be obtained by Raman analyses, foreseeing a SERS activity of the AgI substrate. The method has been tested for the characterization of a mixture of three synthetic organic colorants (basic green 1, rodhamine B, and basic blue 9), widely used in dyeing processes.

The work is part of two master theses in Science for conservation-restoration of cultural heritage and in Advanced spectroscopy in chemistry carried out by Lara Cassone e Silvia Frizzera

ABC-O20

Corrosione atmosferica del Cor-Ten in ambiente urbano costiero

Simona Raffo [a]*, *Ivano Vassura* [a], *Cristina Chiavari* [b], *Carla Martini* [c], *Maria Chiara Bignozzi* [d], *Elena Bernardi* [a#]

a) Dipartimento di Chimica Industriale, Università di Bologna, Viale del Risorgimento 4, 40136, Bologna, Italia
b) C.I.R.I. Meccanica Avanzata e Materiali, Università di Bologna, Viale del Risorgimento 2, 40136, Bologna, Italia
c) Dipartimento di Ingegneria Industriale, Università di Bologna, Viale del Risorgimento 4, 40136, Bologna, Italia
d) Dipartimento di Ingegneria Civile, Chimica, Ambientale e dei Materiali, Università di Bologna, Via Terracini 28, 40131, Bologna, Italia

**simona.raffo2@unibo.it*, *#elena.bernardi@unibo.it*

Il Cor-Ten (weathering steel) è un acciaio basso-legato, largamente sfruttato in campo artistico e architettonico, che mostra una elevata resistenza alla corrosione atmosferica grazie alla presenza in lega di basse percentuali di alliganti che favoriscono la formazione di una patina superficiale aderente e compatta. La struttura e la capacità protettiva di questa patina dipendono tuttavia dalle caratteristiche dell'ambiente di esposizione: l'azione di agenti atmosferici e la presenza di inquinanti gassosi possono, infatti, accelerare i processi di corrosione e dilavamento e, di conseguenza, provocare il rilascio dei metalli di lega in ambiente. Alla luce di ciò, obiettivo di questo lavoro è stato quello di studiare l'evoluzione della corrosione del Cor-Ten A in tre diverse finiture (grezzo, pre-patinato e pre-patinato cerato) durante i primi anni di esposizione (necessari per la formazione ed eventuale stabilizzazione della patina) in ambiente urbano-costiero (Rimini, Italia). la scelta del sito di esposizione ha permesso di valutare l'influenza di una condizione ambientale piuttosto critica per il materiale, dovuta alla presenza di inquinamenti urbani e di alte concentrazioni di cloruri. Con cadenza mensile sono state determinate le variazioni di massa di ciascun provino ed il rilascio di metalli di lega (Fe, Cr, Cu, Mn, Ni) in ambiente in seguito a dilavamento; sono state costantemente monitorate le principali variabili metereologiche, gli inquinanti gassosi e la deposizione dei principali ioni. L'evoluzione della patina superficiale è stata periodicamente analizzata tramite SEM-EDS e Spettroscopia Raman. Per analizzare e interpretare correttamente l'elevata quantità di variabili e di dati raccolti durante i primi tre anni di esposizione atmosferica è stato adottato un approccio multivariato. In particolare l'applicazione di tecniche chemiometriche di esplorazione dei dati, quali la Two-Way e la Three-Way Principal Component Analysis, ha permesso di esaminare i trend di corrosione di ciascun campione ed evidenziare l'influenza delle diverse finiture superficiali sul comportamento corrosivo.

ABC-O21

FTIR and Raman database of inks on Italian postage stamps

E. Imperio[a], *G. Giancane*[b], *L. Valli*[c],

a Dipartimento di Ingegneria dell'Innovazione, Università del Salento, Via per Monteroni, 73100, Lecce, Italia
b Dipartimento di Beni Culturali, Università del Salento, Via D. Birago, 64, 73100, Lecce, Italia
c Dipartimento di Scienze e Tecnologie Biologiche e Ambientali, Università del Salento, Via per Monteroni, 73100, Lecce, Italia

eleonora.imperio@unisalento.it

Crossing 150 years of Italian issues from 1862, it has been possible to discover the different types of printing inks employed on the stamps. Two complementary techniques FTIR and Raman spectroscopy have become an useful tool, making possible the identification of material composition of the painted surface of these little piece of paper. The analysis made also allow determining the period of production of the samples, which is a powerful tool in the detecting of counterfeits samples. Indeed, throughout the analyses Chrome Orange, a chromate compound ($PbCrO_4PbO$) pigment which has been detected in the first orange Italian stamp, the 10c of the 1863, by its signal at about 849 cm^{-1}, due to CrO_4^{2-} stretching vibrations. Characterizing year by year every sample has been important to determine the precise period in which a different pigment has been introduced. Although some studies in this direction have been made [1][2], the spectra obtained for these stamps provide the first attempt to build a complete database of the entire italian production. This study is an additional demonstration of the importance of making use of scientific approaches to the world of Cultural Heritage. Technological data supply information to historical and classical notions.

[1] T.D.Chaplin, A.J.Lòpez, R.J.H.Clark, D.R.Beech, *J Raman Spectrosc*, 2004, **35**, 600-60.

ABC-O22

Studio archeometrico dei dipinti murali di Spyros Papaloukas nel Duomo di Amfissa in Grecia

Antonella Casoli [a] *, Clelia Isca* [a] *, Ernesto Borrelli* [b]*, Georgios Tavlaridis* [c]

[a] *Dipartimento di Chimica, Università degli Studi di Parma, Parco Area delle Scienze 17/a, 43124 Parma*
[b] *Conservation Scientist, Heritage Independent Consultant, Via Fonteiana 68 00152 Roma*
[c] *Chemist – Conservation Scientist, Piazza dei Campani 13, 00185 Roma*

antonella.casoli@unipr.it

Il Duomo della città di Amfissa (Grecia) è stato costruito nel periodo 1859 – 1869. L'interno del Duomo è stato dipinto interamente dal pittore greco Spyros Papaloukas (1927 – 1932). Lo stato di conservazione della superficie dipinta attualmente versa in condizioni molto precarie ed in vista di un profondo intervento di risanamento e restauro e stata intrapresa una approfondita indagine diagnostica delle superfici dipinte. Allo scopo sono stati avviate una serie di controlli analitici e tecnologici. Nel caso degli intonaci dipinti, particolare attenzione è stata dedicata agli strati pittorici, alla composizione degli strati preparatori, alla caratterizzazione delle malte e ai problemi di deterioramento ad esse connesse. Frammenti di materiale pittorico sono stati analizzati mediante gascromatografia/spettrometria di massa per la ricerca dei leganti organici. E' stato osservato materiale organico in tutti i campioni, in particolare olio di lino invecchiato e uovo. Dai dati analitici e dalle osservazioni in situ si ritiene che la particolarità dell'opera sia che l'intera superficie (1.500 m^2 di superficie) sia stata dipinta con la tecnica pittorica murale "a secco", adoperando esclusivamente dei leganti organici. Il quadro generale dei risultati delle indagini sui materiali inorganici insieme allo studio dei leganti organici ha rappresentato la base di riferimento per una mirata progettazione dell' intervento conservativo necessario.

Il presente lavoro fa parte del "International Multidisciplinary Conservation Project of the Holy Mary Annunciation Metropolitan Church of Amfissa (Greece)".

ABC-O23

Metodi innovativi per un restauro sostenibile dei materiali cellulosici

Luigi Campanella, Ruggero Caminiti, Susanne Heidi Plattner, Eleonora Scarpellini

Dipartimento di Chimica, Università di Roma Sapienza, Piazzale A.Moro 5, 00185, Roma, Italia

luigi.campanella@uniroma1.it

In alcune recenti statistiche sulle malattie professionali e la sicurezza in ambiente di lavoro è emerso come i restauratori, ufficialmente qualche migliaia in realtà qualche decina di migliaia, siano figure professionali molto esposte sia rispetto ai metodi che ai materiali di impiego. In effetti, la maggior parte di questi operatori lavora sulla base di esperienze acquisite in tempi in cui le informazioni sugli effetti nocivi sulla salute, da parte di alcuni composti, erano molto più approssimative di oggi; da qui la scarsa attenzione verso accorgimenti a protezione del restauratore. Oggi la rinnovata e potenziata sensibilità rispetto a questi temi induce a ricercare materiali e metodi più sicuri. In questa direzione si propongono due approcci innovativi al restauro dei materiali cellulosici nei beni culturali, in particolare la carta. Il primo approccio (1) si basa su una forma particolare di biorestauro affidato ad un estratto algale. Il secondo (2) invece impiega i liquidi ionici non tossici come mezzi capaci di recuperare la struttura compromessa della cellulosa da processi ossidativi e idrolitici.

(1) Polisaccaridi contenuti in o prodotti da alghe riscuotono un sempre maggiore interesse, non solo per studi ambientali o farmaceutici, ma anche nel campo del restauro, per le loro particolari proprietà. L'affinità chimica con la cellulosa rende questi polisaccaridi candidati interessanti per studi sul consolidamento. Il presente studio indaga l'effetto di un estratto dell'alga spirulina.

(2) I liquidi ionici di nuova generazione sono materiali ecosostenibili perché biocompatibili, biodegradabili e prodotti a partire da fonti rinnovabili. Questa svolta ha permesso di riconsiderare il ventaglio delle possibili applicazioni di questi composti con caratteristiche uniche. Qui si propone uno studio su formulati a base di Colina ed Amminoacidi per il restauro della carta.

ABC-O24

On the traces of the pioneer of crystallization pressure: investigation on Correns' experiment

Francesco Caruso, *Robert J. Flatt*

Physical Chemistry of Building Materials, Institut für Baustoffe, ETH Zürich, HIF B60.2,
Stefano-Franscini-Platz 3, 8093 Zurich, Switzerland

fcaruso@ethz.ch

Water-soluble salts represent one of the (if not the) main causes of weathering of stone cultural heritage. Although extensive research has been carried out on many applicative and fundamental aspects of crystallization pressure (e.g [1]), the pioneering experiment by C.W. Correns and W. Steinborn [2–4] still remains puzzling.

This consisted in the measurement of the vertical growth – by an ingenious optical system (Fig. 1) – of a potassium alum ($KAl(SO_4)_2 \cdot 12\ H_2O$) monocrystal when placed in its supersaturated solution and under load. Surprisingly, Correns and Steinborn obtained excellent agreement between their experimental data and an incomplete equation.

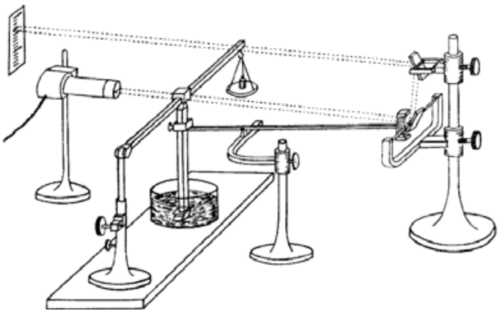

Figure 1 – Scheme of the force balance (*Druckwaage*) that Correns and Steinborn employed in their experiment. Source: [3].

In this paper, we report the experimental and theoretical advances in our modern reproduction of the experiment.

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ABC-O25

Un caso di studio: caratterizzazione dei coloranti organici negli arazzi di Raffaello

Ilaria Serafini[a], *Ulderico Santamaria*[b], *Marcella Guiso*[a],
Armandodoriano Bianco[a],

[a] *Dipartimento di Chimica, Università di Roma "Sapienza",*
Piazzale Aldo Moro 5 , 00185, Roma, Italy
[b] *Musei Vaticani - Laboratorio di Ricerche Scientifiche, Città del Vaticano, Italy*

ilaria.serafini@uniroma1.it

Per la tintura dei filati impiegati nella realizzazione di arazzi, una delle matrici più adoperate fino al XIX secolo è stata la radice di robbia (*Rubia tinctorum L.*). Su alcuni arazzi realizzati su disegno di Raffaello Sanzio e oggi conservati presso i Musei Vaticani è stato osservato un diffuso stato di degrado a carico dei filati tinti in rosso. Tale fenomeno può essere dovuto a molteplici fattori, tra i quali la degradazione totale o parziale delle molecole del colorante per via fotochimica è uno dei più frequenti. La radice di robbia contiene un numero elevato di composti a struttura antrachinonica, che conferiscono al filato una caratteristica tonalità rossa [1]. Durante il processo di tintura, tuttavia, anche altre tipologie di molecole (non necessariamente di natura antrachinonica), presenti nella matrice, si fissano sul filato. Tali sostanze potrebbero essere coinvolte nei processi di invecchiamento e la loro partecipazione o funzione nei processi di degrado è al momento oggetto di studio. Sperimentalmente si è infatti osservato che alcuni composti presentano un degrado marcatamente più avanzato di altri. Al fine di progettare un opportuno intervento di restauro, è perciò necessario identificare tutti i composti coinvolti, così da poter chiarire al meglio tutti i meccanismi di degrado a carico delle fibre. Nell'ambito del presente lavoro sono state effettuate estrazioni di coloranti dalle fibre tessili di alcuni arazzi provenienti dai Musei Vaticani; gli estratti sono stati esaminati mediante HPTLC, NMR e ESI-MS.
I composti così isolati sono stati quindi confrontati con quelli caratterizzati in seguito a estrazione sia dalla radice di robbia tal quale, sia da campioni di filati tinti secondo le ricette antiche [2] e sottoposti a invecchiamento artificiale [3-4].

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[2] Cardon D., *Natural Dyes: Sources, Tradition, Technology and Science*, 2007, Archetype Publications Ltd, London.
[3] Nilsson J., Vilaplana F., Karlsson F. S., Bjurman J., Iversen T., *Studies in conservation*, 2010, **55**, 55-65.
[4] Valianou L., Karapanagiotis I., Chryssoulakis Y., *Anal. Bioanal. Chem.*, 2009, **395**, 2175–2189.

ABC-O26

Tecniche strumentali avanzate per l'identificazione dei composti organici nelle opere policrome: il micro-campionamento associato ad analisi SERS, ESI-MS e NMR

Livia Lombardi[a] , Marcella Guiso[a], Ulderico Santamaria[b], Armandodoriano Bianco[a]

[a] Dipartimento di Chimica, Università di Roma "Sapienza", Piazzale A. Moro5, 00185, Roma, Italia
b Musei Vaticani - Laboratorio di Ricerche Scientifiche, Città del Vaticano, Italy

livia.lombardi@uniroma1.it

Nel presente lavoro, vengono illustrati i risultati ottenuti attraverso il micro-campionamento con matrice Ag-Agar associato ad analisi SERS (Surface Enhanced Raman Spectroscopy), per la prima volta applicato allo studio di coloranti organici in opere policrome. La SERS è una tecnica spettroscopica che associa alla spettroscopia laser le particolari proprietà ottiche delle nanostrutture metalliche, che producono l'amplificazione del segnale Raman e la riduzione del background di fluorescenza, in seguito all'interazione di risonanza fra le molecole del colorante e le nanostrutture d'Ag. Questo consente di superare i limiti che comunemente si incontrano nello studio dei coloranti organici tramite spettroscopia Raman "classica".

Si tratta di una metodologia di recentissima introduzione, basata sull'utilizzo di una matrice costituita da Agar e Ag colloidale, che costituisce sia il supporto per il micro-campionamento che il substrato SERS attivo, per l'esecuzione delle analisi in laboratorio con µ-Raman da banco. Sulla base dell'esperienza maturata e delle criticità riscontrate, è stato ideato un KIT, contenete tutto il necessario per l'esecuzione della procedura, che consente di effettuare il micro-campionamento in maniera semplice, rapida e riproducibile. Utilizzando i dispositivi contenuti nel KIT, è possibile effettuare il prelievo di un campione inferiore al millimetro, dimensione invece comunemente prelevata per le indagini cromatografiche attualmente impiegate. La micro-invasività e la possibilità di eseguire il micro-campionamento *in situ* rendono questa metodologia particolarmente adatta allo studio delle opere di elevata rilevanza storico-artistica, che non possono essere campionate con le comuni metodologie né movimentate. Il colorante prelevato può essere analizzato anche con altre tecniche analitiche, complementari alla SERS, quali ESI-MS, NMR ecc., semplicemente estraendo la sostanza campionata dalla matrice Ag-Agar, sfruttando l'insolubilità di quest'ultima nei comuni solventi organici.

[1] Cristiana Lofrumento, Marilena Ricci, Elena Platania, Maurizio Becuccia, Emilio Castellucci *J. Raman Spectroscopy* **2013**,44, 47–54.

ABC-O27

Data assimilation for atmospheric particulate matter predictions

Angelo Riccio, *Valentina Agresti*

Dipartimento di Scienze e Tecnologie, Università di Napoli Parthenope, Centro Direzionale, Isola C4, 80143, Napoli

angelo.riccio@uniparthenope.it

Numerous epidemiological studies have shown strong associations between particulate air pollution and adverse health effects on the respiratory and cardiovascular systems. Unfortunately, one of the limits of epidemiological studies is the lack of available information: concentrations measured at monitoring stations are not always representative of the spatio-temporal variability on a regional scale, while an air quality model provides information with a global and uniform spatial coverage but tends to underestimate the concentration of particulate matter (PM). An additional source of information can be provided by surface concentrations and Aerosol Optical Depth (AOD) observations, detected by several sensors, e.g. the Multiangle Imaging Spectro-radiometer (MISR) and the Moderate Resolution Imaging Spectro-radiometer (MODIS).

By means of the CHIMERE model [1], the surface concentrations from the AirBase air quality database (*http://www.eea.europa.eu/data-and-maps/data/airbase-the-european-air-quality-database-7*) and AOD values from MODIS and MISR, we greatly improved the estimation of PM surface concentration, on a European domain and on a nested domain centred on the Po Valley, a critical area known for the high concentration of PM values. A data assimilation bias-aware technique described by [2] was used.

The root mean square error of PM concentrations after the assimilation process was significantly reduced on both domains, and this demonstrated that the inclusion of satellite and surface concentration data is critical for the correct evaluation of population exposure to atmospheric PM surface concentration.

[1] L. Menut et al., CHIMERE 2013: A model for regional atmospheric composition modelling, Geoscientific Model Development, 6, 981-1028, 2013.

[2] D.P. Dee and A.M. Da Silva. Data assimilation in the presence of forecast bias. Quarterly Journal of the Royal Meteorological Society, 124(545):269–295, 1998.

ABC-O28

Life Cycle Assessment of building nanomaterials: indoor and outdoor issues

Martina Pini[a] *, Roland Hischier*[b]*, Paolo Neri*[a]*, Bernd Nowack*[b]*,*
Anna Maria Ferrari[a]

a Department of Sciences and Engineering Methods, University of Modena and Reggio Emilia, Via Amendola, 2, 42100 Reggio Emilia, Italy

b Swiss Federal Laboratories for Materials Science and Technology (Empa), Lerchenfeldstrasse 5, CH-9014 St. Gallen, Switzerland.

annamaria.ferrari@unimore.it

Nanomaterials are currently being considered for using in modern technology, with a vast range of applications, such as in medicine, electronics, building materials, commercial products and energy production. On the other hand, there is a serious lack of information concerning the toxicity and environmental impact of nanomaterials. Nanotitania is widely used in building sector since it is well known its photocatalytic properties, which decomposes air pollutants as nitrogen oxides (NOx) and volatile organic compounds (VOCs). LCA is an established method to assess potential impacts to the natural environment and on human health, along the whole life cycle [1]. Moreover, LCA has been recognized as a key tool for assessing the environmental performance of nanoproducts [2]. Four LCA case studies on building materials functionalized with nanoTiO_2 (resin, glass, glaze and tile) have been conducted in order to identify the life cycle steps where the nanoparticle release mainly occurs. Outdoor installations have been considered for all building materials excluding resin case study, where indoor application has been assessed. A preliminary evaluation of the potential damage on human health and environment caused by released nanoTiO_2, during the life cycle stages, has been calculated. The outcomes showed that the phases mainly affected by nanoTiO_2 releases are: nanocoating application, maintenance operations and end of life steps. In collaboration with Empa, Swiss Federal Laboratories for Materials Science and Technology, a framework to evaluate the characterization factor for human indoor exposure using USEtox modelling has been developed [3].

[1] R. Hischier et al., *Scie Total Environ*, 2012, **425**, 271–282.
[2] W. Klöpffer et al., Nanotechnolgy and life cycle assessment a systems approach to nanotechnolgy and the environment, 2007, Washinton DC, 34.
[3] R.K. Rosenbaum et al., *Environment International*, 2007, **33** (5), 624-634.

ABC-O29

Applicazione della metodologia LCA a processi chimici: un approccio globale per valutarne la sostenibilità

E. Neri, F. Cavani, D. Cespi, L. Morselli, F. Passarini, I. Vassura

Dipartimento di Chimica Industriale "Toso Montanari", Università di Bologna, Viale del Risorgimento 4, 40136, Bologna, Italia

esmeralda.neri@unibo.it, fabrizio.passarini@unibo.it

La crescente consapevolezza delle problematiche ambientali che affliggono la società moderna sta portando alla ricerca di nuove tecnologie di produzione più sostenibili, volte allo sviluppo di nuovi prodotti, processi e servizi o al miglioramento di quelli già esistenti. È in questo contesto che si inserisce l'applicazione della metodologia LCA (Life Cycle Assessment) al settore dei processi chimici, al fine di valutarne la sostenibilità in termini ambientali. A tal proposito, questo approccio è stato applicato a due casi studio di rilevanza industriale: la produzione di acrilonitrile e la sintesi di acroleina, confrontando in entrambi i casi vie di sintesi alternative in una prospettiva di ciclo di vita. Il primo approccio è stato applicato alla reazione di ammonossidazione, ponendo a confronto la sintesi tradizionale da propilene (SOHIO) con le possibili alternative da propano. Nel secondo caso la produzione industriale di acroleina è stata investigata paragonando la consolidata via da propilene con quella alternativa da glicerolo, ottenuto come sottoprodotto dei processi di trans-esterificazione e idrolisi di trigliceridi, al fine di verificare la sostenibilità di un suo potenziale riutilizzo come materia prima per la produzione di chemicals. I risultati dell'analisi di ciclo di vita sono stati espressi, in entrambi i casi, in termini di consumo di risorse, danno alla salute umana ed alla qualità dell'ecosistema validando il modello tramite un'analisi di incertezza condotta attraverso il metodo statistico Monte Carlo. Dai risultati ottenuti nei due casi studio considerati, si può evincere che non sempre l'osservanza di alcuni dei principi della Green Chemistry comporti una maggiore sostenibilità complessiva di un processo; mediante uno studio globale si può avere una visione più approfondita delle problematiche esistenti.

ABC-O30

QSARINS: new software for development and validation of MLR models; QSARINS-Chem: datasets and QSAR models for environmental pollutants

S.Cassani, N.Chirico, E. Papa, S. Kovarich, A.Sangion, P.Gramatica
DiSTA, Università dell'Insubria, Via J.H.Dunant 3, Varese, Italia

stefano.cassani@uninsubria.it

The use of *in-silico* methods is required by the REACH legislation and QSAR models are suggested to reduce experimental costs and tests. In fact, when correctly developed and rigorously validated, QSARs are useful for screening and prioritizing chemicals without experimental data or even before their synthesis in the safe chemical design approach. QSARINS (QSAR-INSUBRIA), [1] is a new software for the development of Multiple Linear Regression models, by Ordinary Least Squares and Genetic Algorithm for variable selection. This program is mainly focused on the model development according to the "OECD principles for the validation of QSAR models for their application in regulation", in particular on the rigorous check of the internal and external predictivity of the models (by various statistical parameters). Additional features include tools for explorative analysis of the datasets by Principal Component Analysis (PCA), Applicability Domain (AD) analysis, consensus modelling, selection of the best model by MultiCriteria Decision Making (MCDM) and various plots. QSARINS-Chem, a module of QSARINS, includes several datasets of environmental pollutants with the chemical structures and the corresponding end-points (physico-chemical properties and biological activities). The chemicals with the related data can be accessed in different ways and visualized in 3D. Additionally, several QSAR models, based on molecular descriptors calculated by the open source software PaDEL-Descriptor, are implemented. These models can be easily applied for future predictions on chemicals without experimental data, verifying the AD. QSARINS-Chem can be also used as a tool for ranking and prioritizing chemicals, using MCDM and PCA approaches, as well as a management tool of personal datasets and models.

[1] P. Gramatica, N. Chirico, E. Papa, S. Cassani, S. Kovarich. *J. Comput. Chem. (Software News and Updates)*, 2013, **34**, 2121-2132.

ABC-O31

SUN project: an integrated approach towards sustainable nanoinnovation

Antonio Marcomini, Danail Hristozov, Elena Semenzin,

Dipartimento di Scienze Ambientali, Informatica e Statistica, Università Ca' Foscari di Venezia, Calle Larga S. Marta 2137, 30123, Venezia, Italia

marcom@unive.it

Our understanding of the environmental and health risks from nanotechnologies is still limited, which may result in stagnation of nanoinnovation. This emphasizes the need for an integrative assessment and adaptive management of the long-term risks from manufactured nanomaterials (MN) along the entire supply chains of nano-enabled products towards developing more sustainable nanotechnologies.

Sustainable nanotechnology is being touted as a holistic and pragmatic concept that can guide incremental nanotechnology development amidst significant data gaps and uncertainty. The new European SUN (Sustainable Nanotechnologies) project, worth 14.5 million euro, is based on this concept, embracing the hypothesis that the current knowledge on environmental and health risks from MN, whilst limited, can nevertheless guide more sustainable nanomanufacturing.

SUN applies an integrated approach that estimates risks along the complete lifecycles of nano-enabled products. The project aims to give clear answers to questions from regulatory authorities, and open new possibilities for innovators to design greener nanotechnologies. This will be achieved through development and application of new methods and tools for prediction of long-term exposure, effects and risks for humans and ecosystems (services) and implementable practices for risk prevention and management, including development of guidance for safe disposal and recycling. This approach aims to protect innovation by providing industries with data and prospective tools to streamline effective decision making about safer products and processes.

In order to achieve this, SUN will combine Risk Assessment and Lifecycle Assessment to develop a user-friendly software-based Decision Support System (DSS) for practical use by industries and regulators. The industrial partners in the SUN consortium will evaluate and “reality-check” the DSS against real industrial case studies in terms of cost/benefit and insurance risk. This validation will culminate in guidelines for safe nanoscale product and process design.

ABC-O32

Environmental risk assessment of engineered nanomaterials (ENMs): the n-TiO_2 case study

Elena Semenzin[a], *Elisa Lanzellotto*[a], *Danail Hristozov*[a], *Andrea Critto*[a], *Elisa Giubilato*[a], *Antonio Marcomini*[a]

a Dipartimento di Scienze Ambientali, Informatica e Statistica, Università Ca' Foscari di Venezia, Calle Larga S. Marta 2137, 30123, Venezia, Italia

semenzin@unive.it

Titanium dioxide is the naturally occurring oxide of titanium, which can be present in three mineral forms: rutile, anatase and brookite. When produced at the nano-scale (n-TiO_2) it presents some peculiar physicochemical properties (e.g. very high refractive index, photocatalytic under UV light), which make it suitable for a wide variety of applications (e.g. cosmetics, paint). Its high volume/tonnage production is expected to reach 2 400 000 million tons in 2026 only in the US, including pristine as well as variously coated and functionalized nanoparticles. There is an increasing concern about its potential environmental and health risks which asks for appropriate risk assessment and management approaches. Due to significant epistemic uncertainties and methodological limitations the quantitative Environmental Risk Assessment (ERA) of n-TiO_2 is still beyond the state of the art [1]. Therefore we propose a complementary approach for screening-level ERA that provides a quantitative estimation of ecosystem effects from exposure to ENMs [2]. The methodology further develops the Species Sensitivity Weighted Distribution (SSWD) approach to address nano-specific needs, and was tested with a database on pristine n-TiO_2 including 189 ecotoxicological endpoints (e.g. NOEC, ECx) for species representative of the freshwater, seawater and soil compartments. The application of the model resulted in estimation of environmental quality criteria (i.e. HC_5, Hazard Concentration affecting 5% of the species) and risk (i.e. PAF, Potentially Affected Fraction of species). These results were then compared to similar results from applying the conventional SSD methodology to the same dataset.

[1] D. Hristozov, S. Gottardo, A. Critto and A. Marcomini *Nanotoxicology*, 2012, 1-19.
[2] E. Semenzin, E. Lanzellotto, D. Hristozov, A. Critto, E. Giubilato and A. Marcomini *Environ. Toxicol. Chem.* under submission.

ABC-O33

Caratterizzazione di impatti odorigeni: esperienze e sviluppo di procedure a Trieste

Pierluigi Barbieri[a,b], *Sergio Cozzutto*[b], *Gianpiero Barbieri*[b], *Anna Fabbris*[b],

Gianluigi de Gennaro[c], *Roberto Gaita*[d], *Sabina Licen*[a], *Arianna Tolloi*[a]

a Dipartimento di Scienze Chimiche e Farmaceutiche, Università degli Studi di Trieste, Via L. Giorgieri 1, 34127, Trieste, Italia
b ARCo SolutionS Srl Spin off dell'Università di Trieste, Via Giorgieri 1, 34127, Trieste, Italia
c Dipartimento di Chimica, Università degli Studi di Bari, Via E. Orabona,4 - 70125 Bari, Italia
d SRA Instruments Spa, Viale Assunta, 101, 20063 Cernusco sul Naviglio (Mi), Italia

barbierp@units.it

Processi industriali che trattano materie prime con componenti volatili possono generare emissioni in atmosfera di composti anche odorigeni. Il territorio della provincia di Trieste è caratterizzato da stretta prossimità tra abitato civile ed impianti che generano emissioni osmogene e ne risultano frequenti segnalazioni alle pubbliche amministrazioni ed agli enti di controllo. In attesa di disposizioni normative dedicate alla regolamentazione e gestione su basi tecnico-scientifiche di queste molestie, che segnalano flussi incontrollati di composti da sorgenti a bersagli civili, si è formato un gruppo di lavoro che accanto alla caratterizzazione analitica dell'aria ambiente con campionamenti ed analisi GC-MS e con sensori per composti organici volatili, ha iniziato lo sviluppo di strumentazione e procedure per la caratterizzazione dell'intensità percepita di odore secondo la norma tecnica EN13725 che definisce l'olfattometria dinamica. Accanto alla progettazione, realizzazione e valutazione di strumenti da laboratorio, anche trasportabili, [1] si sono testati olfattometri personali commerciali. Per una corretta caratterizzazione dell'aria odorigena, in considerazione della transitorietà dei fenomeni considerati, risulta imprescindibile un campionamento tempestivo e puntuale, basato su segnalazioni e pronte risposte.
Si riportano esempi tratti da caratterizzazioni in un abitato civile in prossimità di un sito siderurgico, in cui molestie si verificano anche in assenza di alterazioni significative di parametri normati come il benzene.

[1] http://www.arcosolutions.eu/a29_olfattometria.html

ABC-O34

Aerosol deliquescence and crystallization determination: applications to energy saving and cultural heritage.

Ferrero L.[a], *D'Angelo L.*[a], *Rovelli G.*[a], *Casati M.*[a], *Perrone M.G.*[a], *Sangiorgi G.*[a], *Bolzacchini E.*[a]

[a]*Department of Earth and Environmental Sciences, University of Milano-Bicocca, Piazza della Scienza 1, 20126, Milano, Italy*

luca.ferrero@unimib.it

Aerosol chemical composition determines the relative humidity at which the aerosol phase-transition (deliquescence or crystallization) occurs [1]. The aerosol hydration can affect both the corrosion capability on electronic circuitry in Data Centers (which account for 2% of worldwide energy consumption) [2] and the stone decay, due to the time of wetness (TOW) and number of dissolution and crystallization cycles (N_c) induced by deposited aerosol. Thus, in this work, the aerosol mutual deliquescence and crystallization relative humidity (MDRH and MCRH), on aerosol samples collected in the Po Valley (2006-2013), were determined in a new developed aerosol exposure chamber (AEC) measuring both aerosol conductivity and aerosol mass changes while varying the RH at constant temperature. The method was validated through the analysis of pure aerosol types (i.e. pure NH_4NO_3) generated for this purpose in the chamber. Ambient aerosol samples were also chemically analysed by ion chromatography (IC) to relate the MDRH and MCRH to the aerosol chemistry.

Seasonal variability of MDRH and MCRH was identified. MDRH in winter was lower (60.1±1.1%) than in summer (71.8±0.9%); the same happened for MCRH: 39.4±1.7% in winter and at 51.8±1.5% in summer. IC analysis showed that NH_4NO_3 dominate in winter while $(NH_4)_2SO_4$ in summer allowing to explain the seasonal behaviour of MDRH and MCRH which caused a TOW higher during winter (84±8%) than in summer (17±6%). The aforementioned results were applied first to industry (Eni Green Data Center) to avoid aerosol hydration (thus corrosion) while saving a large amount of energy (79%; 215 GWh; 78 kt of equivalent CO_2 not emitted per year) in cooling the electronic circuitry using outdoor air (instead of air-conditioning). A second application allowed to study different damaging impact for cultural heritage developing new stone decay-indicators from the knowledge of the seasonal-predominant decay mechanisms.

[1] Martin S.T. (2000), Chem. Rev. 100:3403–3454.
[2] Ferrero L. et al., (2013), Environ. Sci. Technol. 47:3856-64.

ABC-O35

L’esperienza Vinavil nella sostituzione di sostanze very high concern

Fabio Abbà[a], *Marco Cerra*[b], *Fabio Chiozza*[b], *Francesco Pignataro*[c]

[a] *Vinavil S.pA. , Regulatory Office, Via Toce 7 , 28844, Villadossola (VB), Italia*
[b] *Vinavil S.p.A. , R&S, Via Toce 7 , 28844, Villadossola (VB), Italia*
[c] *Mapei S.p.A. , R&S, Via Valtellina , 63 , 20159, Milano (MI), Italia*

f.abba@vinavil.it

La sostenibilità è un valore che negli ultimi anni è andato radicandosi ed affermandosi. La realizzazione di uno sviluppo sostenibile si ottiene essenzialmente lavorando in 3 ambiti : protezione dell’ambiente, sviluppo economico e compatibilità sociale.

Per facilitare e garantire lo sviluppo di una società sostenibile, non si può però prescindere dall’innovazione. In tal senso anche la legislazione recente si muove in questa direzione: il regolamento REACh è il fulcro di una transizione verso la capacità di innovazione e la competitività attraverso il principio di sostituzione per garantire che le sostanze chimiche più pericolose siano sostituite da alternative più adatte. E’ importante quindi che il sistema pubblico di ricerca, l’accademia e l’industria governino questa transizione.

In quest’ottica, Vinavil ha da sempre perseguito gli obiettivi di innovazione e più in generale di protezione dell’ambiente tra cui una sistematica riduzione delle sostanze organiche (VOC) nei prodotti forniti al mercato, un attento utilizzo delle risorse idriche, una riduzione degli scarti etc.. Grazie a mirati progetti di ricerca, Vinavil ha ottimizzato formule e processi nelle sue attività più rilevanti, con sostanze alternative sostituendo quelle potenzialmente pericolose, tra cui alchilfenoli-etossilati (tensioattivi), ftalati (plastificanti), metalli pesanti (catalizzatori) e derivati del boro (reticolanti), o con lo sviluppo di nuovi polimeri aventi prestazioni analoghe o superiori ai precedenti, perseguendo allo stesso tempo il miglioramento della salute dei lavoratori e la riduzione degli oneri dell’impresa.

La relazione descrive, a grandi linee, l’evoluzione del quadro normativo e l’attività di ricerca di Vinavil per rispettare e possibilmente anticipare scadenze e futuri trends.

ABC-O36

First measurements of Total Mercury (THg) in wet deposition at high altitude site in Southern Italy (1379m a.s.l.)

Massimiliano Vardè[a], Alessandro Servidio[a], Franco Cofone[a], Annalisa Rosselli[a], Francesca Sprovieri[a]

a Istituto sull'Inquinamento Atmosferico, CNR, U.O.S. di Rende, c/o Polifunzionale UNICAL, 87036, Rende, Italia

m.varde@iia.cnr.it

Mercury (Hg) is one of the trace metals of greatest environmental concern due to its propensity to be transported in air for long distances from emission sources, and its complex biogeochemical transformations in the environment. Atmospheric deposition is the dominant pathway for Hg to enter terrestrial and aquatic ecosystems. Once deposited, Hg can be converted to the neurotoxic organic form, monomethylmercury, which bioaccumulates in marine and freshwater fauna and can threaten human and environmental health. Therefore, establishing the rate of Hg deposition is a key element in understanding the environmental cycling of Hg and its impact on ecosystems. As part of the Global Mercury Observation System (GMOS) project, a global-scale network of ground-based monitoring sites is being developed with the objective of expanding the global coverage of atmospheric Hg measurements, and improving our understanding of global atmospheric Hg processes. In this study we present the first reported measurements of total Hg (THg) in precipitation performed from 2012 to early 2014 at Longobucco GMOS monitoring station located at high-altitude (1379 m. a.s.l.), in the Sila massif (Calabria, Italy). The variation of THg concentration, wet deposition Hg fluxes and rainfall depths calculated, will be discussed in this work. The high quality of analytical data is corroborated by the participation in a global inter-laboratory comparison study for THg in water. THg concentrations in wet deposition measured at Longobucco as well as the Hg measurements in deposition collected at the other GMOS stations will help to further our understanding of atmospheric Hg transfer processes to surface environments, the transport of atmospheric Hg on the global scale, and will importantly contribute to future international policy development and implementation.

ABC-O37

Substitution of arsenic trioxide in the production of Murano artistic glass

Elena Semenzin[a], *Valentina Faggian*[a], *Elisa Giubilato*[a], *Lisa Pizzol*[a], *Petra Scanferla*[b], *Andrea Critto*[a], *Antonio Marcomini*[a]

a Dipartimento di Scienze Ambientali, Informatica e Statistica, Università Ca' Foscari di Venezia, Calle Larga S. Marta 2137, 30123, Venezia, Italia

a Consorzio Venezia Ricerche, Via della Libertà 12, 30175, Venezia, Italia

semenzin@unive.it

Arsenic trioxide is included in the Candidate List of Substances of Very High Concern (SVHC) and soon it could be subject to authorization under the REACH regulation, because of its properties of carcinogenicity, mutagenicity and toxicity for reproduction (CMR substance). In the district of Murano artistic glass (Venice, Italy), arsenic trioxide has being used since centuries as additive for refining and bleaching melting glass. It is estimated that about 8 tons per year of arsenic trioxide are currently used in Murano glassworks. Small particles of arsenic powder can be easily inhaled by workers; furthermore, when melting the glass mixture at high temperatures, arsenic toxic fumes are released. To reduce the occupational health risks of glass production, the use of suitable substitutes for replacing arsenic trioxide is being explored and cerium oxide and blast furnace slag are among the most promising candidates. A comparative study has been performed with the aim of evaluating the occupational health risks of substitute substances in comparison with arsenic trioxide [1]. The applied risk assessment procedure proved to be effective in demonstrating that the use of cerium oxide and blast furnace slag would reduce the health risks associated to occupational exposure [1]. Cerium oxide and blast furnace slag are therefore confirmed as interesting candidates to replace arsenic trioxide in artistic glass production.

[1] V. Faggian, E. Giubilato, L. Pizzol, P. Scanferla, A. Critto, E. Semenzin and A. Marcomini *Journal of Hazardous Material*, under submission.

Chimica dell’Ambiente e dei Beni Culturali

Poster

ABC-P1

The technology of production of glazed bricks from Tol-e Ajori (Fars, Iran)

Maria Letizia Amadori [a], *Sara Barcelli* [a], *Pierfrancesco Callieri* [b], *Alireza Askari Chaverdi* [c], *Paola Fermo* [d], *Emad Matin* [b], *Gianluca Poldi* [e]

[a] *Department of Basic Sciences and Fundamentals, University of Urbino*

[b]*Department of Cultural Heritage University of Bologna*

[c] *University of Shiraz (Iran)*

[d] *Department of Chemistry, University of Milano*

[e] *Visual Art Centre, University of Bergamo*

maria.amadori@uniurb.it

Archaeological excavations between 2011 and 2013 at Tol-e Ajori, near the centre of Persepolis (Fars, Iran), brought to light the first sections of a structure built in mud-brick and baked bricks. In the outer face of the walls and in the collapse materials were found painted and glazed bricks showing parts of figurative motifs in relief very similar to bricks from Babylon's Ishtar Gate.

The aim of this paper is threefold: first to characterize the mineralogical and chemical composition of the bricks and glazed coatings; then to understand the raw materials origin; furthermore to verify whether the production of polychrome glazed bricks followed techniques of Babylonian and Elamite traditions. Non-invasive (visible reflectance spectrometry, X-ray and micro X-ray fluorescence) and micro-invasive analytical techniques (optical microscopy, environmental scanning electron microscopy with energy dispersive spectroscopy, X-ray diffraction, X-ray fluorescence spectroscopy) were chosen in order to provide the higher set of significant data, limiting as much as possible future sampling and investigations. The results of the studies showed that the baked bricks of Tol-e Ajori were produced using local clays from an area near to the site. As regards the production technique, glazed coatings are alkaline and are similar to those found in bricks from the Achaemenid monuments at Susa: calcium antimoniate for white; lead antimoniate for yellow and orange; copper based compounds and oxides of iron for the green; copper based compounds and cobalt for the blue.

ABC-P2

Contributo Ritirato

ABC-P3

Study on emissions from domestic biomass burning of pellet of regional origin (FVG)

Sabina Licen[a], *Sergio Cozzutto*[b], *Gianpiero Barbieri*[b], *Arianna Tolloi*[a] ,
Gianpiero Adami[a], *Pierluigi Barbieri*[a,b]

a Dipartimento di Scienze Chimiche e Farmaceutiche, Università degli Studi di Trieste, Via L. Giorgieri 1, 34127, Trieste, Italia
b ARCo SolutionS Srl Spin off dell'Università di Trieste, Via Giorgieri 1, 34127, Trieste, Italia

barbierp@units.it

Sustainibility of biomass burning for heating purposes relies on both low emissions of toxic compounds and on the organization of supply chains able to provide these renewable fuels of local origin. Three types of biomasses grown in the region Friuli Venezia Giulia were considered in this study: conifers (mainly *Picea abies*), broad-leaved trees (mainly Robinia *pseudoacacia*) and grapevine shoots.

The wooden residues collected were in the form of wooden chips and have been converted in pellet. The pellets were characterised by moisture content, ashes content and calorific value.

Four one hour burning tests for every pellet type were performed on a domestic pellet stove (9 kW, average pellet feed 2.2 kg/h) collecting on line data on O2, CO, CO2, NOx, HC concentrations. Total PM was collected by isokynetic sampling from a dilution tunnel (modified US-EPA method 5G) on quartz fiber filters; PAHs and levoglucosan were analyzed on PM by solvent extraction and GC-MS. During the burning tests BTEXs were sampled on Tenax cartridges and analyzed by TD-GC-MS.

The results were compared with data obtained using commercial pellets in the same conditions by means of Positive Matrix Factorization implemented in the R computational and visualization environment.

ABC-P4

Emissions embodied in international trade: a method to allocate trade-related emissions in the greenhouse gas inventories

Simone Bastianoni[a], *Dario Caro*[a], *Federico Maria Pulselli*[a], *Simone Borghesi*[b], *Valentina Niccolucci*[a]

a Department of Earth, Environmental and Physical Sciences, Ecodynamics Group, University of Siena, Pian dei Mantellini 44, 53100 Siena, Italy
b Department of Political and International Sciences, University of Siena, Via Mattioli 10, 53100 Siena, Italy

bastianoni@unisi.it

The Intergovernmental Panel on Climate Change (IPCC) has defined a comprehensive method for taking into account greenhouse gases (GHG) emissions released from different countries. The geographical or producer-based perspective currently used in the IPCC framework does not consider (and may therefore encourage) delocalization of production from industrialized to other countries, thus allocating responsibility for emissions associated with goods and services, consumed in one country but produced elsewhere, exclusively to the producer. Here, we propose a formalization (named NCI method), in order to evaluate GHG emissions associated with goods and services that are traded internationally, based on a systemic approach that places the responsibility on consumer countries, and weighs imported and exported goods by applying national carbon intensity factors. An assessment of the degree of approximation of this method can be realized by comparing our results with data obtained from multi-regional input output analysis considering the nine largest net importing/exporting countries already investigated by Davis and Caldeira (2010) [1]. It emerges that the NCI method gives, in general, a realistic picture of the emissions embodied in international trade and consequently of emissions due to consumption for the largest net importing/exporting countries with differences with respect to multi-regional input output analysis below 5% except for the case of U.K. (10%). The analysis performed suggests that the adoption of a consumption-based accounting could be an important tool in the climate change challenge to reduce global emissions.

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ABC-P5

High Silica Zeolites for the Removal of Polar Organic Contaminants from Water

V. Bosi[a], *E. Sarti*[a], *L. Pasti*[a], *A. Martucci*[b]

[a]*Dep. of Chemistry and Pharmaceutical Sciences, University of Ferrara, Ferrara, Italy*
[b]*Dep. of Physics and Earth Sciences, University of Ferrara, Ferrara, Italy;*

luisa.pasti@unife.it

Efficient methods for the removal of polar organic contaminants, a contaminant class that includes many pharmaceutically active compounds, is an emerging concern in the production of safe water. Recent research publications show that the very favorable adsorption kinetics along with the effective and highly irreversible adsorption make high silica zeolites [1, 2], cheap and environmental friendly materials, applicable for the treatment of contaminated water. Here, we report on the adsorption properties of organophilic synthetic zeolites differing in topology, SiO_2/Al_2O_3 ratio, channel systems and free window apertures with respect to commonly used drugs. In particular, the interaction between different drugs, such as ketoprofen, hydrochlorothiazide and atenolol (ATN) and organophilic zeolites was systematically investigated by considering the effect of surrounding pH, ionic strength, and thus chemical state of drugs, in order to evaluate the role of hydrophobic and electrostatic forces in the interaction between the pharmaceutical molecule and the adsorbent.

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ABC-P6

Active biomonitoring using moss (*Hypnum cupressiforme*) of metals in the atmospheric deposition of the urban area of Taranto (Sorthern Italy)

Micaela Buonocore, *Nicola Cardellicchio, Antonella Di Leo, Cristina Annicchiarico, Santina Giandomenico, Lucia Spada*

CNR- Institute for Coastal Marine Environment, Via Roma 3, 74123 Taranto, Italy

buonomicaela@libero.it

The purpose of this study was to evaluate the atmospheric deposition during a time frame of three years of 14 metals through a species of bryophyte, *Hypnum cupressiforme*, in four stations in Taranto area, applying active biomonitoring techniques using moss bags, to include the Taranto city in a national network of biomonitoring. The metals analyzed were chosen in relation to toxicity and specific situations of industrial pollution and vehicular traffic. Monitoring started in the summer of 2006 and was carried out in the summer of next two years. The summer season has been chosen in relation to the lower intensity of the winds and therefore a greater impact of atmospheric deposition. The stations were chosen in areas more and less affected by industrial pollution. The results obtained show that, even though the statistical analysis it is possible to determine the extent of contamination, establish correlations between various metals and to determine the influence of industrial emissions also on the city center. All studies show that biomonitoring through mosses allows to define, with low costs and in a short time, maps of the atmospheric depositions of persistent contaminants on a regional or over national scale [1,2]. It is possible also to get very detailed information about air quality. Moss-monitoring with *Hypnum cupressiforme,* not only offers a more cost-efficient method available to researchers with less available technology, it also allows a more time-efficient way to reveal qualitative and quantitative differences in metal concentrations at discrete locations and on local and landscape scales.

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[2] K.LaaKsovirta, H. Olkaoknen,*Ann. Bot. Fenn*., **14,** (1997) 112.

ABC-P7

La contaminazione da mercurio in sedimenti e specie ittiche del Mar Piccolo di Taranto: valutazione del bioaccumulo e del rischio sanitario

M. Calò, C.Annicchiarico, M. Buonocore, N.Cardellicchio, A. Di Leo,
S.Giandomenico, L. Spada

CNR, Istituto per l'Ambiente Marino Costiero "Cerruti", Via Roma 3, 74123 Taranto

md0ra@libero.it

Lo scopo del presente lavoro è stato quello di valutare il livello di contaminazione da mercurio nei sedimenti marini e in alcune specie ittiche catturate nel bacino del Mar Piccolo di Taranto, Sito di Interesse Nazionale per le bonifiche. I risultati ottenuti sugli organismi sono stati valutati dal punto di vista ecotossicologico e confrontati con le vigenti normative Nazionali e Comunitarie; è stato stimato, inoltre, il rischio associato al consumo dei prodotti ittici confrontando "l'esposizione calcolata" con la dose settimanale tollerabile (PTWI) raccomandata dal comitato congiunto "FAO/WHO Expert Committee on Food Additives" (JECFA). Relativamente ai sedimenti, i risultati confermano una notevole contaminazione da mercurio con un valore massimo pari a 3.7 mg/kg p.s., osservato nel I seno del bacino, in corrispondenza di un'area adibita ad attività cantieristica navale. Per quanto riguarda i pesci, la specie maggiormente interessata al bioaccumulo è risultata la spigola (*D. labrax*), che ha mostrato, inoltre, superamenti del limite imposto dalla normativa Europea n. 1881/2006 (0.5 mg/kg p.u.) [1] con valori pari a 0.6 e 0.9 mg/kg p.u. L'esposizione settimanale derivante dal consumo di questa specie ittica è risultata, in diversi casi, superiore al PTWI indicato dal JECFA, specialmente nei bambini. In questo scenario, risulta necessario, per minimizzare i rischi e massimizzare i benefici derivanti dal consumo di prodotti della pesca, approfondire ulteriormente gli studi inerenti i livelli di contaminazione da mercurio nel biota, con particolare attenzione alle categorie più a rischio come ad esempio bambini e gestanti.

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ABC-P8

Il Fotosensore di datazione archeologica (DAPhS)

Luigi Campanella[a], *Lorenzo Nigro*[b], *Susanne Heidi Plattner*[a], *Federica Polimeni*[a], *Federica Spagnoli*[b]

a Dipartimento di Chimica, Università di Roma Sapienza, Piazzale A. Moro 5, 00185, Roma, Italia
b Dipartimento di Scienze dell'antichità, Università di Roma Sapienza, Piazzale A. Moro 5, 00185, Roma, Italia

luigi.campanella@uniroma1.it

Il tempo cancella purtroppo molti dei segni originali e ne produce degli altri, da un lato rendendo così difficile la determinazione dell'età e dall'altro, invece, consentendo attraverso le misure di questi segni di risalire all'età di un oggetto. I metodi di analisi di datazione sono ben noti, andando dai radioattivi all'ir, dalla dendrocronologia al NMR, dalla termografia ai metodi enzimatici. Alla ceramica, il reperto archeologico maggiormente diffuso, non si adatta la maggior parte di questi metodi, per cui si è sempre alla ricerca di metodi innovativi.

Qui si propone un metodo fotosensoristico basato sulla misura del potenziale di superficie di un campione da datare esposto all'azione fotodegradativa della radiazione uv attiva su una sospensione fotocatalitica di TiO_2. La disponibilità di campioni per cui è possibile verificare archeologicamente la datazione ha consentito di validare il metodo rispetto a valutazioni archeologiche e archeometriche e di correlare il segnale misurato con specifiche caratteristiche dei campioni analizzati.

Breve descrizione del metodo: un campione polverizzato di ceramica (alcuni mg) è sospeso in una sospensione acquosa di TiO_2 e irradiato da una lampada uv che attiva il catalizzatore TiO_2, iniziando la degradazione radicalica. Il campione subisce fotodegradazione di cui si monitora il procedere mediante misure di potenziale (E) nel tempo (t). Il processo e i relativi dati t-E sono influenzati da variazioni composizionali presenti di per sé in ceramiche diverse e indotte da processi post-deposizionali. Le differenze di maggiore interesse riguardano il contenuto in carbonato e in ioni metallici. Per ogni tipo di ceramica e sito con materiale ceramico di età nota si costruisce una curva di calibrazione che permette poi la datazione di campioni di età ignota.

ABC-P9

Fibers innovative burning and reuse by Self-propagating High temperature Synthesis (SHS)

V. Caratto[a,b]*, C. Belfortini*[b]*, L. Musi*[b]*, L. Gaggero*[a] *and M. Ferretti*[b]

a Dipartimento di Scienze della Terra, dell'Ambiente e della Vita,, Università degli Studi di Genova., Corso Europa 26, 16132, Genova , Italia b Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Genova, Via Dodecaneso 31, 16146, Genova , Italia.

valentina.caratto@unige.it

The Asbestos-Containing Waste (ACW) represents, beside the urban solid waste, the most conspicuous typology in our country and the first among toxic wastes.

In the perspective of reducing the environmental issue and to explore recycling of the breakdown products, we experimented the use of Self-propagating High temperature Synthesis (SHS), exploiting the highly exothermic and fast self – propagating high temperature alumino-thermic reactions [1,2]. Different ACWs have been selected and preventively characterized by optical microscopy, SEM-EDS and XRPD analysis. The reactions were based on the couple Fe_2O_3/Mg varying some parameters as ACW abundance (from 45% to 65% weight), size of the pellet (diameter 13 and 25 mm, height from 7 to 60 mm) and weight of samples (from 2 to 100 g). All samples were characterized after combustive reaction by SEM-EDS and XRPD analysis. Experiments have demonstrated efficiency in destroying the fibrous habit of chrysotile transforming the composition to non fibrous silicates (fig 1).

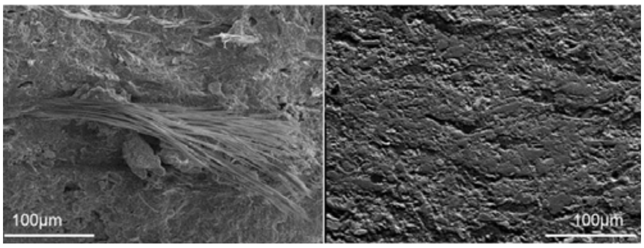

Fig.1: SEM Microphotograph left Asbestos-Containing Waste (Etenit) and right SHS treated pellets

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ABC-P10

Dry cleaning methods for conservation treatment of paintings: characterization and application

Antonella Casoli [a], *Valentina Emanuela Selva Bonino* [a], *Laura Bergamonti*[a], *Giovanni Predieri* [a], *Pier Paolo Lottici* [b], *Oscar Chiantore* [c], *Chiara Riedo* [c], *Dafne Cimino* [c], *Ilaria Saccani* [d]

[a]*Dipartimento di Chimica, Università degli Studi di Parma, Parco Area delle Scienze 17/a, 43124 Parma*
[b]*Dipartimento di Fisica e Scienze della Terra, Università degli Studi di Parma, Parco Area delle Scienze 7/A , 43124 Parma*
[c]*Dipartimento di Chimica, Università degli Studi di Torino, Via P. Giuria, 7 - 10125 Torino*
[d]*Associazione CESMAR7, Via Mentana 5, 37128 Verona, Italia.*

antonella.casoli@unipr.it

The project concerning *Dry cleaning* methods finds its origin in the conservation of modern unvarnished oil and acrylic surfaces.
In particular, the unvarnished oil surfaces show high sensibility, both respect aqueous solutions and organic solvents (leaching, opacity,..) that cause discoloration and superficial skin of medium, in addition to colors alterations, brightness and opacity changes and loss of adhesion.
From these considerations, among conservators of modern paintings, grow the interest on so-called *"dry methods"* or *"semihumids",* that allow to avoid or limit contact between solutions and substrates or let effectively to control the amount of reagent.
By the light of results obtained by RCE *Netherlands Cultural Heritage Agency* [1], our study was focused on a selection of materials available in Italian large-scale retail trade: aim of research is their chemical- physical characterization. In fact these products are not produce for conservation or fine art practice, on the contrary they derive from different fields.
The aim of this project is to develop and test cleaning strategies for unvarnished oil and acrylic paintings, especially water sensitive, as well as unvarnished under bound paint surfaces. Emphasis was given to the cleaning power of the materials in balance with the optimum preservation of the paint surfaces.

[1] M. Daudin-Schotte, M. Bisschoff, I. Joosten, H. van Keulen, and K.J. van den Berg, "Dry Cleaning Approaches for Unvarnished Paint Surfaces", *Smithsonian contributions to museum conservation*, 2013, **3**, 209-219.

ABC-P11

QSAR study of Fragrance Biodegradability for Greener Chemicals

S.Cassani[a], *S.Kovarich*[a,b], *L.Ceriani*[a, c], *R. Boethling*[d], *E.Papa*[a], *P.Gramatica*[a]

a DiSTA, Università dell'Insubria, Varese, Italia
b S-IN Soluzioni Informatiche srl, Vicenza, Italia
c International Centre for Pesticides and Health Risk Prevention, Azienda Ospedaliera Luigi Sacco, Milano, Italia
d Office of Pollution Prevention and Toxics, US Environ. Protection Agency, Washington, USA

stefano.cassani@uninsubria.it

Fragrances are emerging contaminants widely used as ingredients in many consumer and personal care products as well as food additives. Their environmental occurrence is of potential concern for humans and wildlife. Information on biodegradability is needed to assess risk from human and environmental exposure to these substances, and to assist in the design of safer alternatives following green chemistry principles [1]. *In-silico* approaches, such as quantitative structure-activity relationships (QSARs), can be used to predict biodegradability of untested fragrances as well as support experimental data in a weight of evidence approach. The objective of this work is to propose valid QSARs for the prediction of ready biodegradability that are specifically applicable to fragrance material. QSAR classification models were developed based on data measured for 189 fragrances. Models were validated for their robustness and external predictivity, and the structural applicability domain was verified. A comparison was carried out between the here presented QSARs and BIOWIN models implemented in the EPI Suite tool [2]. In conclusion, we here present robust and predictive QSARs for the prediction of ready biodegradability of fragrances, based on transparent algorithms and on descriptors that are either commercially or freely calculable. The proposed models can be applied for the screening of fragrance chemicals, to support experimental data and to design safer alternatives that are less persistent than existing ones, as also required by REACH Reglation and in line with the green chemistry principles.

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ABC-P12

Priority setting of PFCs and Personal Care Products in QSARINS-Chem

S.Cassani, N.Chirico, A.Sangion, A.Fracasso, P.Gramatica

DiSTA, Università dell'Insubria, Via J.H.Dunant 3, Varese, Italia

stefano.cassani@uninsubria.it

The screening and the prioritization of hazardous chemicals is a useful procedure for the identification of critical substances and the optimization of experimental tests. This procedure became of particular relevance within the REACH, which encourages the use of alternative *in silico* methods. Among these, QSAR models can predict missing data for the unknown activities and properties, necessary to prioritize existing or not yet synthesized chemicals. The prioritization of two classes of emerging pollutants (Poly- and Perfluorinated compounds, PFCs, and Personal Care Products, PCPs) is here summarized. The interest on PFCs and PCPs is mainly due to the huge lack of information for the majority of these compounds. Regarding PFCs, the QSA(P)R models for the prediction of PBT Index [1], inhalation and oral toxicity in Rat and Mouse, vapor pressure and solubility in water, implemented in the new version of QSARINS software (QSARINS-Chem module), [2-3] were applied to 770 PFCs, verifying the Applicability Domain. More than 550 PCPs, such as flavor and fragrance agents, parabens, phthalates and UV filters, have been screened for their cumulative PBT behavior, acute toxicity on fish and soil sorption on organic carbon (Koc) by the corresponding models included in QSARINS-Chem, using also some chemometric method as Principal Component Analysis and MultiCriteria Decision Making. These new data availability can be used in screening and ranking approaches to prioritize the most hazardous compounds, focusing the necessary experimental tests only on the highlighted PFCs and PCPs.

[1] E. Papa, P. Gramatica, *Green Chem.* 2010, **12**, 836-843. (Hot Article)
[2] P. Gramatica, N. Chirico, E. Papa, S. Cassani, S. Kovarich. *J. Comput. Chem. (Software News and Updates)*, 2013, **34**, 2121-2132.
[3] P.Gramatica, S.Cassani, N. Chirico. *J. Comput. Chem. (Software News and Updates)*, 2014, Early View, DOI: 10.1002/jcc.23576.

ABC-P13

ArCo and Saving Oseberg Projects: chemical investigations to preserve archaeological wooden objects

F.Modugno [a], *D.Tamburini* [a], *J. J. Łucejko* [b], *H. Kutzke* [c], *S.Braovac* [c], *M.P. Colombini* [a,b]

a Department of Chemistry and Industrial Chemistry, University of Pisa; b Institute for the Conservation and Valorization of Cultural Heritage, Sesto Fiorentino, FI, Italy; c Department of Conservation, Museum of Cultural History, University of Oslo, Norway

perla@dcci.unipi.it

Museums and preservation centres specialized in the treatment of archaeological organic materials, have to face phenomenon of wood degradation which raise questions regarding treatment of wooden wet archaeological objects.

Many forms of deterioration which appear on wooden objects after conservation treatments are related to the presence of unstable inorganic salts in the wood. After drying, salts crystallize and oxidize causing swelling and cracking of wood and lead acidification of the material ($pH < 2$).

One of the most well-known cases of acid attack on wood is the Swedish warship Vasa (17th century) in the museum of Stockholm. A similar case exists within the Oseberg collection, the most important archaeological findings in Norway, which were treated by alum salts in the early 1920's. Other European countries have not escape to this problem for some of their own collections and studies on the different possible solutions are ongoing. Currently there is no consensus regarding the most suitable treatments to prevent salt damage because the long-term behavior of unstable concretions with different consolidants is not well known.

To investigate these problems and answer these questions two projects started: the ArCo project- Ageing Study of Treated Composite Archaeological Waterlogged Artefacts (2013 – 2015) has been recently funded in the framework of JPI - JHEP Joint Pilot Transnational Call for Joint Research Projects on Cultural Heritage and the Saving Oseberg (2014-2016) project funded by the Norwegian State and the University of Oslo.

For the chemical characterisation of wood and its degradation products the Department of Chemistry and Industrial Chemistry of the University of Pisa (Italy), has applied DE-MS and Py-GC/MS. DE/MS Also synchrotron infrared spectroscopy has been employed.

The preliminary analysis on samples from the Oseberg collection highlight extensive oxidation of wood components due to the acidity caused by alum treatment.

ABC-P14

Antibacterial chemical formulation for the household waste management

R. Cucciniello[a], *I. Zarrella*[a], *F. Rossi*[a], *O. Motta*[b], *A. Proto*[a]

[a] *Dipartimento di Chimica e Biologia,* [b] *Dipartimento di Scienze Umane Filosofiche e della Formazione, Università di Salerno, Via Giovanni Paolo II,132,84084, Fisciano, Italia*

ilaria.zarrella@gmail.com

A wide range of events underlined the need for renewed action in relation to infectious disease. As a significant part of this there is awareness of the importance of placing prevention through hygiene at the core of national strategies aimed at infection control[1]. For this reason a growing attention is focused on domestic setting in the chain of infection transmission through the community[2].

The aim of this study was to formulate a product that could aid in solving the problem of bacterial proliferation during the household waste storage. For this reason harmless and natural components that are known for their antimicrobial properties are used. The antimicrobial activity of the new microbicide mixture was evaluated over a range of concentration in two type of tests, both in the liquid phase and in vapour diffusion. Confirmed the efficacy as antimicrobial agent in liquid phase in direct contact with the microbe (*Escherichia coli*), its durable effect as vapour phase was tested. The perfect combination between more volatile agents (2-propanol and limonene) and less volatile agent (cinnamaldehyde) gives rise to an antimicrobial mixture useful to control the microbial growth (*Staphylococcus aureus, Escherichia coli, Debaryomyces hansenii or Penicillium citrinum*) up to 4 weeks. The natural flavour and the synergic antibacterial and antifungal function of the natural components of this mixture makes it attractive in the management of domestic waste inhibiting the microbial proliferation and shooting down the foul smell.

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ABC-P15

Catalytic materials for the hydrogenation of glycidol to value-added products

R. Cucciniello[a], *C. Pironti*[a], *M. Di Serio*[b], *A. Proto*[a], *C. Capacchione*[a]

[a] *Dipartimento di Chimica e Biologia, Università di Salerno, Via Giovanni Paolo II 132 , 84084, Fisciano (SA),Italia*

[b] *Dipartimento di Scienze Chimiche, Università di Napoli, Via Cintia-Complesso Monte S. Angelo 21 ,80133,Napoli, Italia*

rcucciniello@unisa.it

The ring-opening reaction of terminal epoxides, to the corresponding alcohols, is a transformation of considerable importance both in organic chemistry and in industrial processes[1]. Catalytic hydrogenation using heterogenous catalysts is a prominent route to prepare glycols from glycidol (2,3-epoxy-1-propanol), a by-product in the acrolein preparation process[2].

Glycidol represents an important feedstock for glycols productions, such as 1,2-propandiol and 1,3-propandiol (PDO). PDO is actually produced with good performances only through fermentation of sugars, but this procedure in not economically advantageous.

In this work we report the glycidol conversion to glycols by hydrogenation using several catalysts based on transition metals (Rh, Pd, Pt, Cr, Ni) exploring the effect of the reaction conditions on selectivity to PDO. Reactions were conducted in a closed steel reactor under mild conditions of temperature and hydrogen pressure. Moreover, an active metal catalyst support were synthesized and employed in glycidol conversion, showing a significant effect on selectivity to PDO, compared to commercial available catalyst supports.

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ABC-P16

Aragonite crystals grown on bones by reaction of CO_2 with nanostructured $Ca(OH)_2$ in presence of collagen. Implications in archaeology and paleontology

Irene Natali[a$], *Paolo Tempesti*[a], *Emiliano Carretti*[a], *Mariangela Potenza*[a], *Stefania Sansoni*[b], *Piero Baglioni*[a], *Luigi Dei*[a].

[a]*Department of Chemistry "Ugo Schiff" and CSGI Consortium, University of Florence, via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy*
[$]*Present address: CNR-ISAC, Area della Ricerca CNR, via Gobetti 101, I-40129 Bologna Italy*
[b]*Private conservator, via Galeno 6, 20126 Milan, Italy*

luigi.dei@unifi.it

The loss of mechanical properties affecting archaeological or paleontological bones is often caused by demineralization processes that are similar to those driving the mechanisms leading to osteoporosis. One simple way to harden and to strengthen demineralized bone remains could be the *in situ* growth of $CaCO_3$ crystals in the aragonite polymorph – metastable at atmospheric pressure –which is known to have very strong mechanical strength in comparison with the stable calcite. In the present study the controlled growth of aragonite crystals was achieved by reaction between atmospheric CO_2 and calcium hydroxide nanoparticles in the presence of collagen within the deteriorated bones. In a few days the carbonation of $Ca(OH)_2$ particles led to a mixture of calcite and aragonite, increasing the strength of the mineral network of the bone. Scanning Electron Microscopy coupled with Energy Dispersive x-rays Spectroscopy (SEM–EDS) and Fourier Transform Infra-Red (FT-IR) spectrometry showed that aragonite crystallization was achieved. The effect of the aragonite crystals formation on the mechanical properties of the deteriorated bones was investigated by means of x-rays microtomography, Helium porosimetry, Atomic Force Microscopy (AFM) and Vickers micro-hardness techniques. All these data enabled to conclude that the strength of the bones increased of a factor 50-70% with respect to the untreated bone. These results could have immediate impact for preserving archaeological and paleontological bone remains.

I. Natali, P. Tempesti, E. Carretti, M. Potenza, S. Sansoni, P. Baglioni, L. Dei, Langmuir, 2014, **30**, 660-668.

ABC-P17

Biodisponibilità e bioaccumulo di PCB e metalli in molluschi bivalvi

C. Annicchiarico[1], G. Assennato[2], M. Blonda[2], M. Buonocore[1], N. Cardellicchio[1], A. Di Leo[1], S. Giandomenico[1], L. Spada[1], N. Ungaro[2]

[1]CNR - Istituto per l'Ambiente Marino Costiero, via Roma 3, 74123 Taranto, Italy.
[2] ARPA Puglia, Corso Trieste 27, 70126 Bari

dileo@iamc.cnr.it

Da studi pregressi e da caratterizzazioni effettuate nell'area del Mar Piccolo di Taranto, è emerso che i policlorodifenili (PCB) e i metalli pesanti (in particolare il mercurio) rappresentano i contaminanti presenti a concentrazioni ritenute "pericolose" nei sedimenti superficiali di alcune aree del bacino, localizzate prevalentemente nel primo Seno. La contaminazione di organismi bentonici e di organismi filtratori, come i mitili allevati, ha messo in evidenza la necessità di valutare i fenomeni di rilascio di questi inquinanti da sedimenti contaminati nella colonna d'acqua e la conseguente diffusione per effetto di correnti, moti ondosi, etc, in tutto il bacino. Tra le ipotesi più accreditate, infatti, vi è quella secondo cui la risospensione di particelle fini di sedimento possa essere responsabile della diffusione della contaminazione anche in aree meno inquinate. In questo modo i sedimenti si comporterebbero come "sorgente secondaria di contaminazione". Relativamente ai processi di mobilizzazione e di trasporto di inquinanti, le ipotesi sono dunque legate alla possibilità che gli stessi possano diffondere nella colonna d'acqua non solo per gradiente di concentrazione, ma anche a seguito di fenomeni di risospensione di varia entità e natura indotti da escursione mareale, bioturbazione, attività umane (es. traffico marittimo, pesca), etc. Per valutare la possibilità di trasferimento di metalli (Pb, Cd, Zn, Cu, Hg, Ni, Cr, V, Fe, Mn, Se, Sn) e di policlorobifenili (PCB) da sedimenti a molluschi bivalvi, nel presente studio sono stati programmati esperimenti di bioaccumulo. Le prove sono state condotte sia in laboratorio che in situ in corrispondenza di un'area con sedimenti contaminati del Mar Piccolo, dove è stato allestito un esperimento di "mussel watch", con risospensione periodica dei sedimenti. Le prove di bioaccumulo (in situ ed in laboratorio) hanno evidenziato un incremento nel tempo delle concentrazioni di PCB e metalli dimostrando come anche inquinanti lipofili o insolubili possono essere resi biodisponibili per gli organismi da processi chimico fisici che riguardano i sedimenti marini.

ABC-P18

Inquinamento indoor: biomasse a confronto.

Monica Filice[a]*, Pierantonio De Luca*[b]*, Giancarlo Costantino*[b]

a Activa Società Cooperativa, Via dell'Uguaglianza 1 , 87040,Castrolibero (CS), Italia
b Dipartimento di Ingegneria per l'Ambiente e il Territorio e Ingegneria Chimica (DIATIC),
Università della Calabria, Ponte P. Bucci ,87036, Rende, Italia

filice@activasc.com, pdeluca@unical.it

La biomassa è un combustibile molto in uso per il riscaldamento degli edifici residenziali, in quanto risorsa rinnovabile è disponibile e accessibile in molti mercati locali. Generalmente la combustione di biomassa produce sia particelle di diversa granulometria-morfologia [1,2] sia inquinanti gassosi, inclusi monossido di carbonio, monossido di azoto, aldeidi, formaldeidi e idrocarburi policiclici aromatici [3].

Il seguente studio è focalizzato sulla caratterizzazione chimico-fisica di particelle (PMx) prodotte dalla combustione di biomasse a diverso grado di umidità (ulivo/quercia). Individuata una abitazione-campione ubicata nel comune di Lamezia Terme (CZ), avente come unico sistema di riscaldamento un caminetto a legna, il monitoraggio è stato condotto in due fasi: (1) avvio della combustione, (2) combustione con fiamma costante (3, 6, 9 h *fire on*). Al fine di simulare la presenza di abitanti, il campionatore è stato posto al centro dell'ambiente oggetto di studio (altezza 1.60 m, volume aria inalata 1 m^3/h). La massa di particolato raccolta è stata discretizzata in dimensione e composizione chimica mediante microscopia elettronica a scansione e microanalisi. I risultati mostrano che dalla quercia all'ulivo l'emissione si modifica sia in concentrazione sia in distribuzione dimensionale delle particelle. La concentrazione varia da un valore minimo di circa 30 $\mu g/m^3$(ulivo, 3 h) ad un valore massimo superiore a 100 $\mu g/m^3$(quercia, 9 h di accensione caminetto). La distribuzione dimensionale mostra che entrambe le biomasse utilizzate producono elevate quantità di particelle fini e ultrafini, con maggior presenza di PM_{10} in seguito a combustione di quercia.

[1] Filice M. , De Luca P. , *15th International Symposium on Environmental Pollution and its Impact on Life in the Mediterranean Region*,2009, Bari
[2] Filice M. , De Luca P. ,*4° Convegno sul Particolato Atmosferico* ,2010, Venezia
[3] Qiu G., *Renewable Energy,* 2013, **50**, 94–102.

ABC-P19

Inquinamento indoor/outdoor: il ruolo del riscaldamento domestico.

Monica Filice[a], *Pierantonio De Luca*[b], *Ilaria Naccarato*[b]

a Activa Società Cooperativa, Via dell'Uguaglianza 1 , 87040,Castrolibero (CS), Italia
b Dipartimento di Ingegneria per l'Ambiente e il Territorio e Ingegneria Chimica (DIATIC),
Università della Calabria, Ponte P. Bucci ,87036, Rende, Italia

filice@activasc.com, pdeluca@unical.it

Il grande dibattito sui combustibili, le fonti di energia rinnovabile, il risparmio energetico e la riduzione delle emissioni di anidride carbonica (Obiettivi 2020) tocca settori quali quelli dell'edilizia in termini di rifacimento dell'involucro edilizio, efficienza energetica e introduzione di sistemi integrati per la produzione di energia in sito. La riduzione delle emissioni di anidride carbonica in scala globale parte dalle amministrazioni locali (Piani di Azione per l'Energia Sostenibile) fino a coinvolgere i singoli nuclei familiari (consumi di energia, emissioni da riscaldamento).
Lo studio, condotto nel territorio del comune di Castrolibero nell'autunno/inverno 2013, è stato finalizzato alla valutazione del contributo degli impianti di riscaldamento sulla qualità dell'aria indoor/outdoor. Sono stati analizzati i fumi di 200 caldaie [1] alimentate a metano e GPL (5% di penetrazione territoriale), monitorata la concentrazione di PM10 outdoor e indoor in presenza/assenza riscaldamento domestico. Il monitoraggio in aria urbana mostra che il ruolo degli impianti di riscaldamento è rilevante, in quanto la concentrazione impianti on/off (autunno/inverno) fa variare la concentrazione giornaliera da 16 a 37 $\mu g/m^3$ (24h). Il monitoraggio all'interno di un ambiente confinato mostra concentrazioni giornaliere pari a 20 $\mu g/m^3$ ricche di particelle ultrafini (image analysis mediante microscopia elettronica a scansione), mentre la caratterizzazione dei fumi emessi da una caldaia-tipo mostra emissioni medie pari a 11.7 vol % O_2, 44.5 ppm CO e 61.6 ppm NO_X [1]. Tutti questi dati sottolineano la potenzialità degli ambienti domestici in termini di emissioni inquinanti.

[1] Naccarato I., *Le emissioni da combustione per il riscaldamento delle civili abitazioni. Caso di studio: il Comune di Castrolibero*, Tesi di Laurea, 2012-2013.

ABC-P20

Effetti della risospensione sulla mobilizzazione e distribuzione di policlorobifenili (PCB) e metalli nei sedimenti del Mar Piccolo di Taranto

C.Annicchiarico[1], *G. Assennato*[2], *M. Buonocore*[1], *N.Cardellicchio*[1], *M. Blonda*[2],
A. Di Leo[1], *S. Giandomenico*[1], *L. Spada*[1], *N. Ungaro*[2]

[1]*Consiglio Nazionale delle Ricerche (CNR), Istituto per l'Ambiente Marino Costiero "Cerruti", Via Roma 3, 74123 Taranto*
[2] *ARPA – Puglia Corso Trieste 27, 70126 Bari*

santina.giandomenico@iamc.cnr.it

Nell'ambito dello studio relativo ai processi di mobilizzazione e di trasporto di inquinanti nel Mar Piccolo di Taranto, sono stati condotti esperimenti di "risospensione simulata" in laboratorio al fine di valutare il rilascio, in particolar modo di metalli (Pb, Cd, Zn, Cu, Hg, Ni, Cr, V, Fe, Mn, Se, Sn) e policlorobifenili (PCB), nella fase acquosa disciolta e particellata della colonna d'acqua.

Normalmente, sono i primi centimetri di sedimento superficiale ad essere coinvolti nei processi di risospensione e, potenzialmente, nei processi di scambio. Tuttavia nei sedimenti analizzati nel presente studio, la frazione pelitica fine superava il 70%; tenuto conto però che il bacino di Mar Piccolo è caratterizzato da fondali poco profondi, da un'intensa attività di traffico marittimo ed in generale da una forte presenza antropica, nei processi di risospensione sono coinvolti strati di sedimento anche relativamente più profondi.

In generale, i risultati ottenuti, evidenziano la presenza di importanti fenomeni di mobilizzazione degli inquinanti, soprattutto dei PCB, dal sedimento all'acqua con incrementi significativi, sia nella fase disciolta che in quella particellata,. I processi di risospensione di sedimenti contaminati nel Mar Piccolo di Taranto rappresentano, pertanto, un punto cruciale nel trasferimento degli inquinanti nella catena trofica, soprattutto di contaminanti lipofili e scarsamente degradabili.

ABC-P21

Determination of toxic metals in marine biomonitors by multivariate analysis of voltammetric and spectroscopic data

Clinio Locatelli, Dora Melucci, Lara Nobili

Dipartimento di Chimica Ciamician, Università di Bologna, Via Selmi 2, 40126, Bologna, Italy

E-mail clinio.locatelli@unibo.it, dora.melucci@unibo.it

This work proposes an analytical procedure regarding the voltammetric determination of mercury(II), copper(II), lead(II), cadmium(II) and zinc(II) by square wave anodic stripping voltammetry (SWASV) in matrices employed as possible biological monitors for trace metal, but also involved in food chain as fishes, mussels, clams and algae. A critical comparison with spectroscopic measurements is also discussed.

The voltammetric measurements were carried out using, as working electrodes, a gold electrode (GE) [simultaneous determination of Hg(II) and Cu(II)] and a stationary hanging mercury drop electrode (HMDE) [simultaneous determination of Cu(II), Pb(II), Cd(II) and Zn(II)], and a platinum electrode and Ag/AgCl/KClsat electrode as auxiliary and reference electrodes, respectively. The analytical procedure has been verified on standard reference materials. For all the elements in the certified matrices, the precision as repeatability, expressed as relative standard deviation (sr) was of the order of 3-5 %. The accuracy, expressed as relative error (e) was of the order of 3-7 %.

Once set up on the standard reference materials, the analytical procedure was transferred and applied to fishes, mussels, clams and algae sampled in five sites located in the Adriatic Sea (Italy) between the Goro Bay and the Ravenna Lagoon. Multivariate analysis of data by principal components analysis allowed to explore data: similarities among samples and correlation of variables was evidenced.

ABC-P22

Real-Time Determination of Black Carbon with Photoacoustic Extinctiometer (PAX)

Naim Malaj[a], *Franco Cofone*[c], *Ugo Cosentino*[b], *Irene De Franco*[a], *Andrea Piazzalunga*[a], *Demetrio Pitea*[b], *Francesca Sprovieri*[c], *Massimiliano Vardè*[c]

a Dipartimento di Scienze Ambiente e Territorio e Scienze della Terra, Università di Milano-Bicocca, Via Pietro Bucci , 87036, Rende, Italia.
b Dipartimento di Scienze Ambiente e Territorio e Scienze della Terra, Università di Milano-Bicocca, Piazza della Scienza 1, 20126, Milano, Italia.
c CNR - Istituto sull'Inquinamento Atmosferico, UOS di Rende, Polifunzionale UNICAL, 87036, Rende, Italia.

naim.malaj@unimib.it

Black carbon (BC) is a light-absorbing, carbon-containing constituent of particulate matter (PM) formed by the incomplete combustion of fossil fuels, biomass and biofuels. BC is directly emitted into the air (mainly from diesel road-vehicles, non-road mobile machinery, ships, residential heating and open biomass burning) and acts as a black body to scatter and adsorb solar radiation, warming the atmosphere and affecting the human health [1]. BC acts over a much shorter period than classic greenhouse gases such as carbon dioxide because of its shorter life time in the air [2]. Therefore, controlling BC emissions could potentially have significant immediate beneficial effects on global climate. The conventional techniques employed for the determination of BCare often time-consuming and less accurate while the recently developed techniques are near real-time but have some limitations related with their selectivity. In the present work, which is part of the project SNIFF (Sensor Network Infrastructure For Factors), we have used a recently introduced Photoacoustic Extinctiometer (PAX) system to monitor the mass concentration of BC in an urban site. PAX is a real-time, selective, sensitive, high-temporal-resolution and accurate instrument that measures *in-situ* light absorption and scattering of aerosol particles from which then derives the extinction, single scattering albedo and the mass concentration of BC. The sampling site was located near an industrial area and between two busy roads: the motorway and the main street connecting the whole Campus of University of Calabria which includes a highly frequented bus terminal. The data obtained show high levels of BC for the hours in which the frequency of road-vehicles and domestic heating are intense in the measuring area.

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ABC-P23

S.I.C.A.M.O.R.
Sviluppo di indagini chimiche applicate al mantenimento delle opere e al restauro

N. Marchettini[a], *A. Atrei*[b], *F. Benetti*[a], *E. Carretti*[c], *L. Dei*[c], *E. Gaggelli*[b], *F. Giambi*[c], *E. Gliozzo*[a], *C. Guerranti*[a], *C. Migliorini*[b], *A. M. Papini*[c], *G. Perra*[a], *M. Potenza*[c], *L. Rosi*[c], *G. Sabatino*[c], *I. Turbanti Memmi*[a], *M. Uva*[b], *D. Valensin*[b], *G. Valensin*[b]

[a] *Dipartimento di Scienze Fisiche, della Terra e dell'Ambiente, Università di Siena, Pian dei Mantellini 44 e Strada Laterina 8, 53100, Siena, Italia*
[b] *Dipartimento di Biotecnologie, Chimica e Farmacia, Università di Siena, Via Aldo Moro 2, 53100, Siena, Italia*
[c] *Dipartimento di Chimica "Ugo Schiff", Università di Firenze, Via della Lastruccia, 3-13, 50019, Sesto Fiorentino, Firenze, Italia*

nadia.marchettini@unisi.it

In questo lavoro vengono presentati i risultati conseguiti nel progetto di ricerca "*Sviluppo di Indagini Chimiche Applicate al Mantenimento delle Opere e al Restauro*" (S.I.C.A.M.O.R.) - PAR FAS 2007/2013, finanziato dalla Regione Toscana. L'obiettivo del progetto è stato quello di sviluppare una metodica innovativa di indagine della composizione chimica di manufatti artistici, basata sull'uso combinato di tecniche sensibili alle proprietà di superficie e al volume. Nel presente progetto sono state applicate tecniche di recente impiego nello studio dei dipinti su tavola, la tecnica Time-of-Flight Ion Mass Spectrometry (ToF-SIMS), la spettroscopia di risonanza magnetica nucleare portatile e la tecnica immunoenzimatica Dot-ELISA, accoppiata alla tecnica AccQ•Tag Ultra High Performance Liquid Chromatography (UPLC). Questi metodi sono stati applicati per la caratterizzazione dei materiali, del degrado e delle tecniche artistiche di dipinti medievali senesi su tavola, al fine di pianificare idonee strategie per il restauro di opere d'arte della Pinacoteca Nazionale di Siena. I risultati conseguiti tramite le tecniche ToF-SIMS, NMR portatile e test Dot-ELISA sono stati confrontati con quelli ottenuti tramite tecniche consolidate nello studio dei dipinti, quali la microscopia elettronica SEM-EDS, la microspettroscopia Raman e la cromatografia liquida ad alta pressione.

ABC-P24

Assessment of brick kiln workers exposure to dust bound PAHs in Punjab province of Pakistan

T. Martellini[a], *A. Cincinelli*[a], *A. Kamal*[b], *R. N. Malik*[b]

a Dipartimento di Chimica "Ugo Schiff", Università di Firenze, Via della Lastruccia, 3, 50019 Sesto Fiorentino, Firenze, Italia

b Environmental Biology and Ecotoxicology Laboratory, Department of Environmental Sciences, Faculty of Biological Sciences, Quaid-i-Azam University, Islamabad, 45320, Pakistan

tania.martellini@unifi.it

The aim of this study was to evaluate the health risks of brick kiln workers exposed to dust bound PAHs in Punjab province (Pakistan). Surface dust samples were collected from 39 different brick kiln units located in Chung, Gujranwala and Sohdra villages. In these rural areas, bricks are still made using traditional technology consisting in hand molding, sun drying and firing in clamps. The practice of firing clay bricks consumes huge amounts of fuel in terms of wood/coal, and with the increasing prices of coal, a large number of cheaper fuels (i.e firewood, old rubber tyres, discarded motor oil, poultry farm droppings, etc.) are being used and contributing to the emissions of toxic gases, smoke, particulate matter and hazardous organic compounds, such as PAHs, in the atmosphere. The fate of PAHs in the environment is of great concern due to their known carcinogenic and mutagenic properties. The median and mean concentration of ∑PAHs were 956 and 1528 ± 1416 ng g^{-1}dry weight (d.w.), respectively, and ranged between 16.1 (observed in Gujranwala) to 6757 (observed in Sohdra) ng g^{-1}dry weight. Source identification using diagnostic ratios and principal component analysis identified coal and wood combustion as the major PAHs sources. The cancer risk model (CR-Model 1) and the Incremental Lifetime Cancer Risk model (ILCR-Model 2) were used to evaluate the cancer risk assessment, suggesting that brick kiln workers (including adults and children) were exposed to high-potential carcinogenic risk via both ingestion and dermal contact pathways. Brick kiln workers and a non-occupationally exposed group (CN) were recruited for comparative analysis of urinary biomarkers of PAHs exposure (i.e. 1-hydroxypyrene (1-OHPyr), α-naphthol and β-naphthol blood level of superoxide dismutase (SOD) as biomarker of oxidative stress and other hematologic parameters of both groups. This study emphasizes the need of introducing higher level of mechanization, more refined alternative technologies and social programs can improve not only the working conditions, but also to reduce child labour and increase occupational safety and health measures in brick kiln industry.

ABC-P25

Gellan enzymatic hydrogel for selective paper artworks cleaning process

E. Cervelli[a], *G. Petrella*[a], *C. Mazzuca*[a], *L. Micheli*[a], *C. Cristini*[a], *S. Iannuccelli*[b], *S. Sotgiu*[b], *A. Palleschi*[a], *G. Palleschi*[a].

[a]*Dipartimento di Scienze e Tecnologie Chimiche, Università degli studi di Roma "Tor Vergata", Via della ricerca Scientifica snc – 00133 Rome, Italy*

[b]*Laboratorio di restauro ICRCPAL, Ministero per i Beni e le Attività Culturali, Via Milano 76 - 00184 Rome, Italy*

laura.micheli@uniroma2.it

Paper artworks are difficult to restore, due to their inherent fragility, their degradation processes and their multi-component composition. Moreover, often the ancient paper artworks are strengthened by gluing external materials (like wooden or cardboard lining paper) to the original piece.. This step adds further problems, because the used glue undergoes to structural transformations that cause a loss in compactness, yellowing and an acidity increase, finally accelerating the degradation processes of the artwork itself. As a consequence, the removal of glues from wooden and paper artworks is of capital importance for the preservation of the integrity of the artworks themselves. We present an innovative alternative to the traditional removal systems (solvents or localized enzymatic packs on the support to be cleaned). To this end, we have prepared rigid Gellan hydrogel (removable totally in one step) loaded with hydrolytic enzymes. In this system, the enzyme works as selective cleaning agent, hydrolyzing not easily removable glues into smaller fragments soluble into the gel, which, in turn, plays the role of support and removal matrix for the enzymatic products. Gellan hydrogel carrying alpha-amylase or proteinase K enzymes has been applied on several paper samples soiled with starch paste or animal glues respectively. Fluorescence microscopy, SEM, FTIR-ATR, HPLC have been used to establish the cleaning efficacy of the proposed method.

ABC-P26

Caratterizzazione del nano-particolato atmosferico mediante indagini Raman video imaging confocale.

Zelica Minniti[a], *Matteo Pappalardo*[a], *Vito Librando*[ab].

a Dipartimento di Scienze Chimiche, Università di Catania, Viale A. Doria 6, 95125, Catania, Italy.
b CRAM3RA: Centro di Ricerca per l'Analisi, il Monitoraggio e le Metodologie di Minimizzazione del Rischio Ambientale, Viale A. Doria 6, 95125, Catania, Italy.

envch1@unict.it

Nel presente lavoro vengono esposti e discussi i risultati ottenuti dalla caratterizzazione del nano-particolato atmosferico (PM), campionato nella città di Catania, mediante l'ausilio di tecniche non convenzionali come la spettroscopia Raman. Questo approccio innovativo rispetto alle più classiche tecniche di estrazione, purificazione e analisi, ha fornito un valido ed immediato strumento. Il protocollo sviluppato e le analisi condotte hanno permesso di comprendere meglio i vantaggi e gli svantaggi del metodo selezionato e l'applicabilità in future analisi sul nano particolato. In particolare l'utilizzo di strumentazione d'avanguardia come il micro Raman alpha300 R+, ha consentito di effettuare indagini Raman video imaging confocale, generando immagini costituite da 65.536 singoli spettri. I risultati ottenuti sono risultati ottimi permettendo così la caratterizzazione della componente organica e inorganica del nano particolato atmosferico frazionato. Inoltre, operando con tale tecnica non distruttiva, che non ha previsto alcuna manipolazione o processazione chimica dei campioni, l'analisi condotta ha rispecchiato quanto più verosimilmente le condizioni reali in cui il campione si trova quando interagisce in atmosfera con altri composti e con gli organismi viventi.

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[3] N. P. Ivleva, U. McKeon, R. Niessner, U. Pöschl *Aerosol Sci. Tech.*, 2007, **41**, 655-671.

ABC-P27

Fotodegradazione di esteri ftalici su pitture murali tramite irradiazioni UV

Salvatore Barreca[a], *Roberta Indelicato*[a], *Santino Orecchio*[a], *Andrea Pace*[a]

Dipartimento di Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche, Università di Palermo, Viale delle Scienze, I-90128 Palermo, Italy

santino.orecchio@unipa.it

Gli esteri ftalici (esteri dell'acido ftalico), rappresentano una particolare classe di inquinanti organici ubiquitari, molto resistenti alla bio-degradazione, capaci da fungere da interferenti e distruttori endocrini e dannosi a causa del loro effetto mutageno e cancerogeno.

Molti composti di questa classe di sostanze per decenni, e probabilmente ancora oggi, sono stati utilizzati nelle pitture murali utilizzate sia in ambito domestico che industriale [1].

Considerando quindi che attualmernte, le attività di demolizione e ristrutturazione rappresentano una cospiqua fetta di mercato delle attività edilizie, e che spesso i lavoratori impiegati in queste attività sono soggetti in maniera continua e prolungata all'esposizione a questa classe di inquinanti, in questo lavoro riportiamo i risultati circa la foto degradazione dei 6 più comuni esteri ftalici utilizzati nelle pitture murali.

La fotodegradazione è stata eseguita mediante irradiazione diretta utilizzando una sorgente di 254 nm. Le percentuali di degradazione sono state valutate mediante comparazione degli estratti del campione irradiato con quello tale e quale. Le analisi sono state effettuate mediante GC-MS.

Degradazioni pari al 50 % di ogni singolo estere ftalico sono state osservate nella prima ora di irradiazione con valori massimi pari all 82% nell'arco delle 8 ore di irradiazione.

Inoltre, studi sulle velocità di degradazione hanno evidenziato cinetiche del primo ordine con valori di costanti *k* comprese tra 0.221 e 0.737 h^{-1}.

[1] S. Orecchio, R. Indelicato, S. Barreca, *Microchemical,* 2014, **114**, 187-191.

ABC-P28

Effect of composition of model membranes on interaction with Glyphosate herbicide

Matteo Pappalardo, Zelica Minniti, Vito Librando

Dipartimento di Scienze Chimiche e CRAM3RA, Università di Catania, Via A.Doria 6, 95125, Catania

mpappala@unict.it

Pesticide Glyphosate is one of the worldwide used herbicide because of its effectiveness and low persistence in the environment [1]. Moreover, its solubility and its ionic nature, evidenced in numerous studies since the 70s, suggest that this compound could not be harmful to humans. However, these studied are based on the results of long-term carcinogenicity tests with rodents, in which the herbicide was fed or injected. Into reality it was observed that the herbicide could be exposed to the man, both in agricultural fields that the place of production. In the last decade, a number of studies have been published and the results indicate that occupational exposure to the pesticide is associated with increased cancer risks [3]. In this work, we study the ability of the Glyphosate to cross a membrane bilayer composed by DOPC and DOPS. Molecular Dynamics calculations were adopted to simulate the diffusion of Glyphosate thought a coarse-grained model of DOPC and DPPS. Due to the ionic nature of the Glyphosate we, also studied, the effect of composition of membrane gradually increasing the percentage of the positive charges DOPS, from 0 % to 70 %. Our preliminary results suggest that Glyphosate, under certain condition, is able to cross the model membranes, opening new perspectives for assessing the impact of this herbicide on human health.

[1]RM.Mann and JR Bidwell, Arch Environ Contam Toxicol., 1999,36,193-9.
[2]GM Williams, R Kroes , IC Munro*, Reg. Toxicol. and Pharm.,* 2000, **31,** 117-165
[3]C. Bolognesi, G. Carrasquilla, S. Volpi, KR Solomon, EJ Marshall, *J. of Toxicol. and Env. Health,* 2009 **72**,986-997

ABC-P29

Misura della componente ionica e della frazione carboniosa ad elevata risoluzione temporale: risultati di una campagna estiva in pianura padana

Andrea Piazzalunga[a], *Paola Fermo*[b], *Gianluigi De Gennaro*[c], *Alessia Di Gilio*[c], *Alessandro Bigi*[d]

[a] *Dipartimento di Scienze dell'Ambiente e del Territorio e di Scienze delle Terra, Università di Milano Bicocca, Piazza della Scienza 1, 20156, Milano, Italia*
[b]*Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milano*
[c]*Dipartimento di Chimica, Università degli Studi di Bari, Via E. Orabona 4,70126 Bari*
[d]*Dipartimento di Ingegneria, Università degli Studi di Modena e Reggio Emila, Via Vignolese 905, 41125 Modena*

andrea.piazzalunga@unimib.it

In questo lavoro saranno presentati i principali risultati di una campagna della durata di 60 giorni condotta a Milano durante l'estate del 2012.

Con l'obiettivo di indagare le variazioni della composizione chimica del particolato atmosferico durante la giornata è stata utilizzata strumentazione ad elevata risoluzione temporale (1 ora). La componente organica ed elementare (OC, EC) della frazione carboniosa è stata determinato tramite l'utilizzo di uno strumento da campo termo-ottico (Sunsent instrument). La componente inorganica (Nitrati, Solfati, Ammonio) è stata determinata sia in fase gassosa che in fase particellare attraverso un sistema di campionamento dotato di due denuder e di una camera di condensazione delle particelle (URG) accoppiato con due cromatografi ionici.

I restati parametri (meteo e gas) sono stati prelevati dalla centralina ARPA più prossima al sito di campionamento.

La disponibilità di dati ad elevata risoluzione temporale sia della composizione della particella che di alcuni precursori gassosi accoppiati con principali dati meteo, permette di indagare sui processi di formazione delle particelle in atmosfera.

ABC-P30

Identifying the emergy basis of ecosystem services

Federico M. Pulselli[a], *Luca Coscieme*[a], *Paul C. Sutton*[b],

Simone Bastianoni[a], *Nadia Marchettini*[a]

a Department of Earth, Environmental and Physical Sciences, University of Siena, Pian dei Mantellini 44, 53100, Siena, Italy
b Department of Geography, University of Denver, 2199 S.University Blvd, CO80208, Denver, United States

federico.pulselli@unisi.it

Ecosystems provide fundamental services, that are defined as the part of ecosystem functions which humans use directly or indirectly. This is also possible by virtue of the ability of ecosystems to capture and process energy from the environment. The energy processes behind the ecosystem service provision can be expressed in terms of emergy. In particular, the correlation between the renewable emergy flows that feed ecosystems and the services they provide is apparent. A comparison between the ability of ecosystems and economies to translate natural resources (measured in emergy terms) into useful services for the society (expressed in monetary values) can be made for national or even regional economic systems. At the global level, we have found that Nature contributes to humans not only more (as already shown by [1]), but in a more efficient way, than all the world economic system.

[1] R. Costanza, R. d'Arge, R. de Groot et al. *Nature*, 1997, **387**, 253-260.

ABC-P31

How to avoid dangerous alternative to banned chemicals in a safer approach: screening of Flame Retardants by the PBT Index

A.Sangion, S.Cassani, P.Gramatica
DiSTA, Università dell'Insubria, Via J.H.Dunant 3, 21100 Varese, Italia

a.sangion@hotmail.it

During the last decades, Brominated Flame Retardants (BFRs) were widely used in various industrial products in order to prevent or slow down a fire. The use of some of these BFRs, such as polybrominated diphenyl ethers (PBDEs), is now restricted or prohibited, due to their hazardous properties regarding Persistence, Bioaccumulation and Toxicity (PBT). So, nowadays PBDEs are replaced by different New Flame Retardants (NFRs) such as new BFRs (NBFRs) or OPFRs (OrganoPhosphorous Flame Retardants). Nevertheless, these substances were commercialized without complete information regarding their PBT properties, that require complex and expensive experiments. However, the PBT assessment is expressly required by REACH. In this study, several compounds proposed and used as ”safer alternatives” to PBDEs, were screened with the cumulative PBT Index model, [1] implemented in QSARINS (QSAR-INSUBRIA), [2] a software for the development and validation of multiple linear regression QSAR models. The results, obtained directly from the chemical structure for the three properties altogether, have been compared with those obtained by the EPA PBT profiler and good agreement between the predictions was found, resulting in a more precautionary assignment of PBT Index. A consensus approach in these screenings is recommended. A priority list of the most dangerous chemicals has been proposed, highlighting that some "safer alternatives" compounds are detected as intrinsically hazardous for their PBT properties. Moreover, this study also shows that the PBT Index could be an effective decision-making tool to evaluate appropriate and safer substitutes, immediately from chemical design in a benign by design approach, thus avoiding expensive synthesis and tests.

[1] E. Papa, P. Gramatica, *Green Chem.* 2010, **12**, 836-843. (Hot Article)
[2] P. Gramatica, N. Chirico, E. Papa, S. Cassani, S. Kovarich. *J. Comput. Chem. (Software News and Updates)*, 2013, **34**, 2121-2132.

ABC-P32

Screening and prioritization of chemicals for REACH: the cumulative PBT Index in QSARINS

A.Sangion, N.Chirico, S.Cassani, P.Gramatica

DiSTA, Università dell'Insubria, Via J.H.Dunant 3, 21100 Varese, Italia

a.sangion@hotmail.it

The limited availability of data for Persistence, Bioaccumulation and Toxicity (PBT) of chemicals is a serious hindrance in the assignment of any chemical to the category of PBTs or vPvB, that require an authorization in REACH for their use and additionally plans for safer alternatives. In the context of screening and prioritization tools for PBT-assessment, explicitly required in REACH, the cumulative PBT Index model, [1] included in QSARINS (QSAR-INSUBRIA), [2] offers a holistic approach to identify chemicals with cumulative PBT properties, directly from their structure. Here, the PBT Index has been applied to screen a big dataset containing large variety of chemicals of environmental concern. Particular attention has been taken in the study and definition of the Applicability Domain, using different approaches such as Descriptors range, Leverage, and Principal Component Analysis of the modeling descriptors, in order to propose reliable predictions. The results of this study, which is based only on the molecular structure features and is not dependent on single threshold values for P, B and T, have been compared with those obtained by the US-EPA PBT Profiler and in other published studies. A good agreement among various approaches has been found, supporting the need of a consensus approach. The discrepancies have been highlighted and commented. A priority list with the most hazardous compounds has been drafted identifying the common structural features among the potential PBT chemicals. The PBT Index has demonstrated to be a practical and reliable solution for PBT-assessment, immediately from the chemical structure, thus even before the synthesis, in a benign by design approach.

[1] E. Papa, P. Gramatica, *Green Chem.* 2010, **12**, 836-843. (Hot Article)

[2] P. Gramatica, N. Chirico, E. Papa, S. Cassani, S. Kovarich. *J. Comput. Chem. (Software News and Updates)*, 2013, **34**, 2121-2132.

ABC-P33

Componenti organiche e inorganiche del particolato atmosferico nel mar Glaciale artico

G. Sangiorgi[a], M.G. Perrone[a], L. Ferrero[a], G. Rovelli[a], F. Marazzi[a], A. Molinelli[a], E. Bolzacchini[a], S. Becagli[b], R. Traversi[b], R. Udisti[b], W. Walczowski[c], T. Zielinski[c]

a Dipartimento di Scienze dell'Ambiente e del Territorio e di Scienze della Terra, Università degli Studi di Milano-Bicocca, Piazza della Scienza 1, 20126, Milano, Italia
b Dipartimento di Chimica, Università degli Studi di Firenze, Via della Lastruccia 3, 50019, Sesto Fiorentino, Italia
c Istituto di Oceanologia, Accademia Polacca di Scienze, Powstańców Warszawy 55, 81-712, Sopot, Polonia

giorgia.sangiorgi1@unimib.it

La composizione chimica dell'atmosfera Artica è fortemente influenzata dalla meteorologia. Alcuni risultati mostrano la presenza di fenomeni di trasporto su lunga distanza di inquinanti atmosferici (es. Idrocarburi Policiclici Aromatici, IPA) provenienti dalle zone antropizzate di Eurasia e Nord America.[1]

Per studiare l'atmosfera del mar Glaciale Artico, sono state organizzate due campagne di misura del particolato atmosferico totale (PTS) a bordo della nave scientifica OCEANIA (prof. T. Zielinski), che lo ha percorso da Tromsø (Norvegia) verso nord fino alle isole Svalbard (Norvegia) durante le estati 2011 (n=24) e 2012 (n=14). I campioni sono stati analizzati per determinare alcuni marker di sorgente: IPA (combustione), alcani lineari (sorgente mista antropica e naturale), ammine alifatiche (metabolismo ossidativo del fitoplancton), ioni inorganici e acidi mono- e dicarbossilici (sorgenti primarie e secondarie).

Mentre la concentrazione media del PTS e di alcuni analiti (es. alcani) è risultata molto simile tra le due campagne (per il PTS, 5-8 $\mu g\ m^{-3}$), il livello della somma degli IPA è risultato più alto durante l'estate 2011 ($27.0 \pm 17.7\ pg\ m^{-3}$) rispetto all'estate 2012 ($6.3 \pm 5.0\ pg\ m^{-3}$). Questo è da mettere in relazione alla diversa provenienza delle masse d'aria durante i due periodi di campionamento.

[1] C.J. Halsall et al. *Environ. Sci. Technol.*, 1997, **31**, 3593-3599.

ABC-P34

Photocatalytic activity of immobilized nanostructured TiO_2 under solar light

E. Sanguineti[a,b], V. Caratto[b,c], M. Sturini[d], I. C. D'Oria[a,c], M. Ferretti[a,b]

[a] Department of Chemistry and Industrial Chemistry, University of Genova, via Dodecaneso 31, 16146, Genoa, Italy; [b] CNR-Spin Genoa, corso Perrone 24, 16156, Genoa, Italy; [c] Department of Earth, Environmental and Life Science, University of Genova, corso Europa 26, 16132, Genoa, Italy; [d] Department of Chemistry, University of Pavia, via Taramelli 12, 27100, Pavia, Italy

elisa.sanguineti@unige.it

Titanium dioxide (TiO_2) in anatase form has attracted much interest for its efficiency in the photodegradation of environmental pollutants, especially the emerging ones [1]. Recently, efforts have been made to immobilize TiO_2 onto various solid supports for avoiding the problems related to losses of the photocatalyst in the environment and its post-treatment separation and recovery.

In the present study, TiO_2 was immobilized on glass beads (σ=4.6 mm) and the efficiency of the supported catalyst was tested in removing a commercial dye, methylene blue (MB), from aqueous solution under simulated solar light. The effects of different pre-treatments of the beads, coating procedures and re-use of the material on the degradation rates were investigated. At the optimal operating conditions it was possible to reduce the concentration of 10 mg L^{-1} MB of 92% in 60 min. The immobilized photocatalyst is still active after repeated cycles: in fig. 1 the photodegradation profiles of MB at various irradiation times at the eighth cycle of use of the coated glass bead are shown.

Considering the promising results, tests are in progress to apply the TiO_2-coated glass beads in removal of fluoroquinolone antibiotics from wastewater.

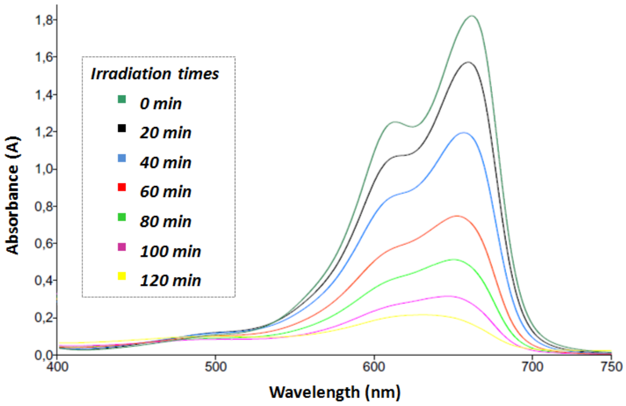


Fig. 1 MB spectra vs. photoreaction time using TiO_2 coated glass beads.

[1] M. Sturini, A. Speltini, F. Maraschi, A. Profumo, L. Pretali, E.A. Irastorza, E. Fasani and A. Albini, *Appl. Catal. B-Environ.*, 2012, **119-120**, 32-39.

ABC-P35

Investigation of mineral carbonation for ex situ carbon dioxide storage

E. Sanguineti[a], *M. Ferretti*[a], *L. Gaggero*[b], *V. Caratto*[a,b], *C. Belfortini*[a]

[a] Department of Chemistry and Industrial Chemistry, University of Genoa, Via Dodecaneso 31, 16146, Genova, Italy, [b] Department of Earth, Environment and Life Sciences, University of Genoa, Corso Europa 26, 16132, Genova, Italy

elisa.sanguineti@unige.it

The increase of anthropogenic CO_2 concentration in the Earth's atmosphere has been linked to global warming which in turn has driven international efforts to explore mitigation strategies to CO_2 emissions. Among them carbonation of alkaline minerals appears to be a realistic option for carbon sequestration; this process mimics natural rock weathering and involves the permanent storage of CO_2 under the thermodynamically stable form of calcium or magnesium carbonates [1].

In this laboratory scale study, we investigated the mineralogical changes occurred to serpentinite, basalt and syenite bulk rock compositions in a three-phase system (CO_2-water-finely powdered sample). Stainless steel vessels were filled up to 50% volume by a slurry of sample and distilled water (1:1); CO_2 was injected to a pressure of 4 MPa and then the sealed vessels were heated at 100°C and 150°C for different times (25, 50, 100, 250 h). The dried slurries were characterized by XRPD, SEM-EDS, FE-SEM and calcimetry.

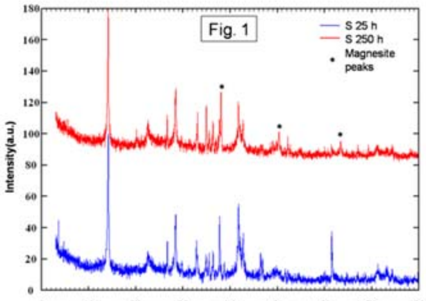


Fig. 1

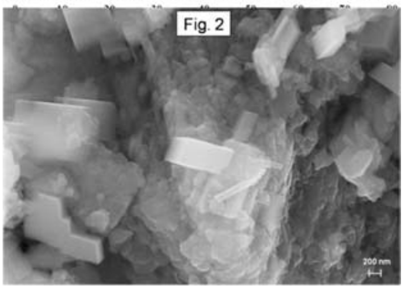


Fig. 2

Enhanced aqueous carbonation of serpentine demonstrated promising results: magnesite peak appeared in XRPD patterns (Fig. 1) and FE-SEM showed neat euhedral lens-shaped polycrystalline aggregates of magnesite after 250 h exposure (Fig. 2).

[1] J. Kaszuba, B. Yardley and M. Andreani *Rev. Mineral Geochem.*, 2013, **77**, 153-188.

ABC-P36

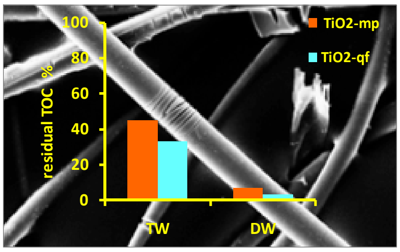
Immobilized TiO_2 for the photocatalytic mineralization of emerging pollutants

Michela Saracino[a,c], Federica Bezzi[b], Claudio Mingazzini[b], Massimo L. Capobianco [a], M. Luisa Navacchia[a], Alberto Zanelli[a]

[a] Consiglio Nazionale delle Ricerche (CNR), Istituto per la Sintesi Organica e la Fotoreattività (ISOF) e Proambiente s.c.r.l., 101, via P. Gobetti, 40129 Bologna, Italy;
[b] ENEA - Unità Tecnica Tecnologie dei Materiali Faenza (UTTMATF), 186, Via Ravegnana, 48018 Faenza, Italy;
[c] Università di Bologna, Dipartimento di Chimica Industriale "Toso Montanari", 4, viale Risorgimento, 40134 Bologna, Italy.

michela.saracino@isof.cnr.it

This research work describes the UV photo-catalytic degradation[1] of a mixture of five emerging pollutants (carbamazepine, diclofenac, benzophenone-3, benzophenone-4 and triton x-100), selected for their ecotoxicity concern [2-3] as well as for the variety of their chemical functional groups. The photocatalytic treatments have been carried out both in deionized (DW) and tap water (TW), and by using a homemade TiO_2 supported on quartz fiber produced through a sol-gel method (TiO_2-qf), in comparison with the Aeroperl P25/20 purchased from Evonik (TiO_2-mp). Furthermore it has also been explored the reuse of the TiO_2 -qf. The effectiveness of the photocatalytic treatments have been determined following the disappearance of the parent molecules by HPLC and evaluating the degree of mineralization through the Total Organic Carbon (TOC) analysis. The figure shows a SEM image of the quartz fiber coated with TiO_2 in the background, and the comparison of residual TOC at the end of the treatments (240 min). The mineralization process was slighlty faster with TiO_2-qz than TiO_2-mp, and significatively faster in DW than in TW.



[1] S. Horikoshi, N. Watanabe, H. Onishi, H. Hidaka, N. Serpone *Appl. Catal., B: Environ.*, 2002, **37**, 117–129.
[2] B. Ferrari, N. Paxéus, R. Lo Giudice, A. Pollio, J. Garric *Ecotoxicol. Environ. Saf.*, 2003, **55**, 359–370.
[3] Z. F. Zhang, N. Q. Ren, Y. F. Li, T. Kunisue, D. W. Gao, K. Kannan *Environ. Sci. Technol.*, 2011, **45**, 3909-3916.

ABC-P37

Application of chitosan, under different conditions, for textile dye removal from aqueous solutions by adsorption processes

P.Cosma[a,b]*,V.Rizzi*[a]*,P.Semeraro*[a]*, A.Agostiano*[a,b]*,A. Longo*[a]*, P.Fini*[b]
E.Franco[c]*, R.García*[c]*, M.Ferrándiz*[c]*,E. Núñez*[d]*, J.Antonio Gabaldón*[d]*,*
I.Fortea[d]*,E.Pérez*[e]*, M. Ferrándiz*[e]

[a] *Università degli Studi "Aldo Moro" di Bari, Dip. Chimica, Via Orabona, 4- 70126 Bari, Italy*

[b] *Consiglio Nazionale delle Ricerche CNR-IPCF, UOS Bari, Via Orabona, 4- 70126 Bari, Italy*

[c]*Biotechnology Department. Textile Industry Research Association (AITEX), Plaza Emilio Sala, 1- 03801 Alcoy, Spain*

[d]*Departamento Ciencia y Tecnología de Alimentos, UniversidadCatólica San Antonio de Murcia, Avenida de losJerónimos s/n, 30107 Guadalupe, Murcia, Spain*
[d] *Colorprint Fashion, SL, Avda. Fco. Vitoria Laporta, s/nApdo. Correos 104, 03830 Muro de Alcoy (Alicante), Spain*

pinalysa.cosma@uniba.it

Water is one of the most very important human resources and has economic, social, political and environmental importance throughout the world [1]. In recent years, various pollutants are entering aquatic systems for the rapid industrialization and urbanization [2]. Consequently, the treatment of wastewater is a subject of fundamental importance. Biological treatments, membrane processes, advanced oxidation processes, chemical and electrochemical techniques [3], and adsorption procedures have become a widely used technology for the removal of both inorganic and organic material In this work we summarize the ability of chitosan films inbinding different textile dyes, varying conditions and modifying the procedure to prepare chitosan film.

[1] H.H.G. Savenije. *J.PhysChem Earth* 2002, **27**,741–4.
[2] R. Van der Oost, J. Beyer and P.E. Vermeulen.*Environ Toxicol Pharm* 2003,**13**,57–149.[3] V.V. Goncharuk, D.D. Kucheruk, V.M.Kochkodan and V.P. Badekha.*Desal.* 2002,**143**,45–51.

ABC-P38

Sunlight-promoted photocatalytic H_2 evolution from aqueous suspensions of cellulosic biomasses: a systematic study

Enrico Annovazzi, Andrea Speltini, Michela Sturini, Daniele Dondi, Federica Maraschi, Antonella Profumo, Armando Buttafava

Dipartimento di Chimica, Università di Pavia, Via Taramelli 12 , 27100, Pavia, Italia

andrea.speltini@unipv.it

Being the most abundant biopolymer on the Earth, cellulose (CLS) is now attracting the interest of the scientific community with regard to its conversion into biofuels [1] and H_2 [2]. This work presents a systematic study of CLS as a sacrificial biomass for photocatalytic H_2 evolution from water. The idea is indeed to couple a largely available and not expensive biomass, and water, with a renewable energy like solar radiation. Aqueous CLS suspension irradiated under either UV-A or sunlight in the presence of Pt/TiO_2 behaves as a H_2-evolving system. The effects of irradiation time, catalyst and CLS concentrations, pH and water salinity are studied. The mechanism of the photocatalytic process relies on the TiO_2-mediated CLS hydrolysis. The polysaccharide depolymerisation generates water-soluble species, e.g. 5-hydroxymethylfurfural (HMF), readily oxidized following the glucose photoreforming. The formation of "coloured" byproducts from HMF self-polymerization (i.e. humins) involves a sort of "in situ dye sensitization" that allows an effective photoreaction even under solar light, with yields up to 89% with respect to those under UV-A. The procedure is successfully extended on non-food/waste cellulosic biomasses, i.e. alfalfa and rice husk. Cellulosic biomasses suspended in water improves the H_2 yields that resulted up to 10-fold higher than those observed by water splitting. Being part of a natural cycle, co-evolved CO_2 does not contribute to the greenhouse effect.

[1] S. Xiao, B. Liu, Y. Wang, Z. Fang and Z. Zhang *Biores.Technol.*, 2014, **151**, 361-366.
[2] P. Azadi, S. Khan, F. Strobel, F. Azadi and R. Farnood *Appl.Cat.B:Environ.*, 2012, **117-118**, 330-338.

ABC-P39

Conta delle particelle, anemologia, analisi gravimetrica e chimica per la caratterizzazione del PM in un hot spot industriale

Arianna Tolloi_[a], Sabina Licen [a], Sergio Cozzutto [b], G. Adami [a], Pierluigi Barbieri [a,b]

a Dipartimento di Scienze Chimiche e Farmaceutiche, Università degli Studi di Trieste, Via L. Giorgieri 1, 34127, Trieste, Italy
b A.R.Co. Solutions s.r.l. Dipartimento di Scienze Chimiche e Farmaceutiche, Università degli Studi di Trieste, Via L. Giorgieri 1, 34127, Trieste, Italy

ARIANNA.TOLLOI@phd.units.it

Gli impatti sulla qualità dell'aria di sorgenti puntuali possono risultare di difficile controllo nel caso in cui le emissioni non siano convogliate bensì diffuse ed in presenza di più possibili fonti di inquinamento relativamente vicine. Per valutare gli impatti su bersagli sensibili risulta importante acquisire informazioni sulle variazioni delle caratteristiche del particolato con elevata frequenza temporale, in corrispondenza alla registrazione di intensità e direzione dei venti che possono veicolare polveri ad un sito recettore.

Si riporta un approccio che descrive l'integrazione tra dati registrati da un contatore ottico di particelle ad otto canali d'acquisizione tra 0,3 e 10 micrometri, da una stazione meteorologica con anemometro sonico, che vengono arricchiti da informazioni su filtri campionati da una stazione Hydra Dual Channel di FAI Instruments, equipaggiata con impattori per la selezione del PM_{10}, su cui sono state effettuate determinazioni gravimetriche ed analisi chimiche per valutare la presenza di idrocarburi policiclici aromatici. I dati raccolti nell'arco di un semestre sono stati razionalizzati grazie allo sviluppo di modelli che ottimizzano la stima della densità delle particelle rilevate al sito recettore, per diverse direzioni di provenienza del vento ed in corrispondenza di diversi cicli produttivi di una sorgente industriale prossima all'abitato considerato. Si propongono modelli che correlano le anomalie registrate per parametri critici per la salute umana, come la concentrazione del benzo[a]pirene nel PM_{10} con la direzione di provenienza delle masse d'aria, e vengono identificate situazioni di anomalia associate a numerosità di particolato submicronico, ignorate dalle evidenze gravimetriche.

[1] A. Tittarelli, Atm. Environ., 2008, **42**, 8543–8548 and references there in.
[2] C. Colombi, Atm. Environ., 2013, **470**, 166–178.

ABC-P40

Analysis of black crusts from several European monuments: A challenge to deepen understanding the relationship among microstructure, microchemical features and pollution sources

<u>Silvestro A. Ruffolo</u>[1], Valeria Comite[2], Mauro F. La Russa[1], Cristina M. Belfiore[1,2], Donatella Barca[1], Alessandra Bonazza[3], Gino M. Crisci[1], Antonino Pezzino[2], Cristina Sabbioni[3]

[1] *Università della Calabria, Dipartimento di Biologia, Ecologia e Scienze della Terra (DiBEST), Via Pietro Bucci 87036, Arcavacata di Rende (CS), Italy*

[2] *Dipartimento di Scienze Biologiche, Geologiche e Ambientali – Sezione di Scienze della Terra, Università di Catania, Corso Italia 57, 95129 Catania, Italy*

[3] *Istituto di Scienze dell'Atmosfera e del Clima, ISAC-CNR, Via Gobetti 101, 40129 Bologna, Italy*

silvestro.ruffolo@unical.it

Most of the historical buildings located in urban environment suffer several degradation phenomena related to the high pollution level. Undoubtedly, the formation of black crusts plays a crucial role in the decay of the stone materials. Their formation is demonstrated to occur mainly on carbonate building materials, whose interaction with a sulphur oxide enriched atmosphere leads to the transformation of calcium carbonate into gypsum which, together with embedded carbonaceous particles, consequently forms the black crusts on the stone surface. In order to better understand the composition and the formation dynamics of this degradation product, as well as to identify the pollutant sources and evaluate their impact on the stone material, an analytical study was carried out on black crust samples collected from different European built Heritage, i.e., the Corner Palace in Venice, the Cathedral of St. Rombouts in Mechelen, the Church of St. Eustache in Paris and the Tower of London. For a complete characterization of the black crusts, several techniques were used, including LA ICP-MS, FT-IR and SEM. This battery of tests provided information about the nature and distribution of mineralogical phases and elements within the crusts and crust-substrate interface, contributing to the identification of the major pollution sources responsible for the deterioration over time of these monuments. In addition, the obtained results revealed a relation among the height of sampling, the surface exposure and the concentration of heavy metals. Finally it has been provided information about the origin of the concentration gradients of some metals.

Chimica Analitica

Plenary

ANA-PL1

Spectroscopy Under Ice

Carlo Barbante

Institute for the Dynamics of Environmental Processes –CNR ,University of Venice, Italy

Department of Environmental Sciences, Informatics and Statistics, University of Venice, Italy

Centro Linceo Interdisciplinare B. Segre, Accademia Nazionale dei Lincei, Rome, Italy

Polar ice caps are among the best archives of atmospheric composition of the past. Analysing the snow layers continuously deposited during centuries and millennia, it is possible to reconstruct the chemical composition of the atmosphere of our planet. Many chemical species are entrapped in gaseous or particulate phases into the snow and ice and thanks to sophisticated analytical techniques we are able to quantify their fluxes on the Earth's surface. In addition, ice caps sometime conceal enormous undisclosed subglacial lakes, buried under hundreds meters of ice, which have preserved fossil liquid water for millions of years.

The analysis of these matrices, the purest water on the Earth's surface, poses a real challenge to analytical chemists that have to develop ultrasensitive analytical methods and stringent protocols to avoid sample contamination.

In this talk I will review the recent developments in high-resolution analysis of ice cores and in the field of speciation analyses of these ultra-clean matrices. In particular I'll present a novel method coupling a high-performance liquid chromatography with ion chromatography and inductively coupled plasma mass spectrometry, which allows the determination of iodine (I) and bromine (Br) species (IO_3^-, I^-, Br^-, BrO_3^-). Iodine and bromine species participate in key atmospheric reactions including the formation of cloud condensation nuclei and ozone depletion. Additional examples on the state of the art in this field of research will also include the iron speciation analysis using Collision Reaction Cell-Inductively Coupled Plasma-Mass Spectrometry (CRC-ICP-MS) that we have recently applied to Antarctic ice samples. This has shown the importance of moving a step forward from the traditional elemental analyses in snow and ice cores, applying the elemental speciation approach to these extremely diluted chemical matrices.

Chimica Analitica

Keynote

ANA-K1

Advanced Sensors for Air Pollution Monitoring: Progress and Future Perspectives

Nicola Pirrone, Antonella Macagnano, Emiliano Zampetti, Andrea Bearzotti, Roberto Pilloton

CNR - Istituto sull'Inquinamento Atmosferico (www.iia.cnr.it), 00016 Monterotondo (Roma)

pirrone@iia.cnr.it

In recent years the need to develop more advanced air quality monitoring systems has been the focus of major international programmes and conventions (i.e., UNEP, UNECE-LRTAP, AMNET, GEF). In the framework of the Group on Earth Observation (GEO) and specifically as part of the GEOSS program, there is a need to develop global scale monitoring systems in order to track the evolution of environmental quality with changing environmental pressures. In order to achieve this objective with affordable investment and running costs, there is a need to develop advanced sensors for air quality monitoring and more in general for environmental monitoring (i.e., for top soil and precipitations) capable to produce data that are comparable to those provided by adopting standard methods and technologies. The progress made in developing nanotechnologies, based on nanocomposite materials along with advances in micro electronics allows to design and develop sensors that have high performance in terms of sensitivity, detection limits, response time and selectivity for different molecules. These new sensors may represent in the near future a good alternative in building citizens observatories and powering monitoring networks also in areas that do not provide adequate infrastructures as required for standard monitoring technologies. The most recent efforts to develop advanced sensors and smart sensing systems for air quality control (AQC) cover several aspects including the designing and developing of new sensor materials, the manufacturing of new gas sensors, new transducers, portable gas sensor systems, wireless technology and sensors networking supported by intelligent algorithms and distributed computing, the definition of new protocols, standards and methods comprising conventional analysers together with sensor technologies. Today several European Networks (www.cost.eu), involving interdisciplinary platforms (i.e., COST Actions TD1105, MP 0901, MP1206, ES1004, ES1002, ES0602) are devoted to explore and improve several aspects of the advanced monitoring systems, keeping in mind protocols and standardisation methods. The present paper will highlight progress and future perspectives in air quality monitoring and environmental quality control.

ANA-K2

Fractionated solid phase extraction of free and conjugated estrogens in milk and determination by liquid chromatography – tandem mass spectrometry

Chiara Cavaliere, Patrizia Foglia, Roberto Samperi, Riccardo Zenezini Chiozzi, Aldo Laganà

Dipartimento di Chimica, Università degli Studi di Roma "La Sapienza", p.le Aldo Moro 5 ,
00144, Roma

chiara.cavaliere@uniroma1.it

Milk is one of the most important products in human diet, especially cow milk type. Milk is known to contain naturally occurring estrogens such as estrone, estradiol, estriol, and their glucuronated and sulfated metabolites. Due to the continuous demands and consumption of milk in human life, in the modern diary industry about 75% of milk is produced from pregnant cows. During gestation state the concentration of natural estrogens is relatively high, therefore relevant quantities of estrogens and their conjugated forms can occur in milk, leading to consumer health problems.

Although conjugated estrogens are considered biologically inactive, however in the human colon they could be reverted by hydrolysis to the original active estrogenic form by the effect of bacterial enzymes, which makes their determination in milk of great interest. Nonetheless, nowadays the analysis of estrogens is commonly focused only on the analysis of the free estrogens; sometimes conjugated forms are estimated by difference from the analysis of total estrogens content before and after enzymatic hydrolysis, with a high degree of uncertainty.

We developed a solid phase extraction (SPE) procedure, using graphitized carbon black as adsorbent material, to obtain from a single cartridge two fractions containing free and conjugated estrogen forms, respectively. The two fractions were then analyzed separately by ultra-high performance liquid chromatography coupled to electrospray (ESI)-tandem mass spectrometry. Ammonia was added post-column to improve free-estrogen negative ESI ionization.

ANA-K3

Tools for the characterization of natural dissolved organic matter in surface waters

D. Vione, M. Minella, E. De Laurentiis, C. Minero

University of Turin, Department of Chemistry, Via P. Giuria 5, 10125 Turin, Italy

davide.vione@unito.it

Dissolved organic matter plays a very important role in aqueous systems, including most notably: *(i)* the carbon cycle, with important implications for the CO_2 budget of water environments [1]; *(ii)* the absorption of sunlight, with the ability to protect living organisms from the harmful effects of UVB radiation [2], and *(iii)* the production of reactive transient species that are involved in the degradation of xenobiotics and of natural organic compounds [3].

Several techniques can be used to characterize natural organic matter. NMR spectroscopy has allowed important discoveries about the structure of soil humic substances. Further advances were obtained more recently by use of LC-MS and of GC-MS, the latter requiring chemical modification of the sample [4]. All these techniques, to which FT-IR can also be added, are extremely useful but require extensive sample pre-treatment and concentration, in soil extracts and *a fortiori* in the case of natural waters. For this reason, the characterization of organic matter in surface waters is most frequently carried out by use of spectroscopic techniques, namely UV-vis absorption and fluorescence spectroscopy that require virtually no sample pre-treatment [5]. Although limited to the chromophoric fraction of dissolved organic matter (the so-called CDOM), these techniques can provide important insights into its origin and valuable information concerning structure and photochemical reactivity [6].

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ANA-K4

Investigation on Reactivity of Silver Nanoparticles Obtained During Bacteria Respiration and Fermentation Processes. A Scanning Electrochimical Microscopy Approach

Dario Battistel[a], *Franco Baldi*[b], *Salvatore Daniele*[b]

a Dipartimento di Scienze Ambientali, Informatica e Statistica, Università Cà Foscari Venezia, Calle Larga S. Marta, 2137, 30123 Venezia, Italy
b Dipartimento di Scienze Molecolari e Nanosistemi, Università Cà Foscari Venezia, Calle Larga S. Marta, 2137, 30123 Venezia, Italy

dario.battistel@unive.it, *sig@unive.it*

In this work, a procedure for studying the reactivity and oxidation state of bio-generated silver nanoparticles (AgNPs) embedded in branched exopolysaccharide (EPS), (Ag-EPS), produced by bacteria cultures, during respiration and fermentation processes, is reported. Size, dispersion and chemical properties and silver ion release from the bio-generated AgNPs were investigated by using scanning electrochemical microscopy (SECM) and voltammetry. The AgNPs were produced under either aerobic ($AgNPs^{aer}$) and anaerobic ($AgNPs^{anaer}$) conditions. The oxidation state of the silver in the Ag-EPS materials was investigated by using SECM, operating in the feedback mode, in a solution containting K_3IrCl_6 as redox mediator, and using a platinum disk electrode 12.5 μm radius as SECM probe. Information on both reactivity of AgNPs and release of Ag(I) species from the Ag-EPS samples were investigated by combining SECM and anodic stripping voltammetry. The measurements were performed on Ag-EPS modified glass-slide spots immersed in a 0.1 M KNO_3 aerated-aqueous solution. Under these conditions, Ag(I) species, eventually present in the samples or fomed by corrosion of Ag(0)NPs, were determined.

ANA-K5

Organic electronic devices as ultrasensitive label-free biosensing platforms

Maria Magliulo, Kyriaki Manoli, Donato de Tullio, Preethi Seshadri, Gerardo Palazzo, Luisa Torsi

Department of Chemistry, University of Bari, Via Orabona, 4, I-70126 Bari, Italy

maria.magliulo@uniba.it

Bio-systems interfaced to an organic electronic device is presently one of the most challenging research activity that has relevance not only for fundamental studies but also for the development of highly performing bio-sensors [1]. Completely novel approaches either involving OFET devices comprising a Functional Biological Interlayer (FBI-OFET) or Electrolyte gated-OFET (EGOFET) integrating bio-recognition elements were recently proposed by our group. Specifically, in the FBI-OFET device configuration a biological layer, acting as biosensor recognition element, is fully integrated into the device structure, right at the interface were the OFET two-dimensional transport occurs [2]. A FBI-OFET integrating bacteriorhodopsin (bR) nano-assembled lamellae is proposed for an in depth study of the photo-induced proton translocation process detected by its impact on the device electronic transport. In the EGOFET biosensing platforms the bio-recognition layer is deposited directly on the organic semiconductor or on the gate surface using strategies that allow a well-oriented immobilization of the biological molecules [3]. Both the structures have been successfully employed for the detection of biological molecules reaching low detection limits.
The specific features of the proposed configurations as well as their performances in terms of device operation, selectivity and sensitivity will be presented.

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ANA-K6

Capillary electrophoresis and HPLC of biomolecules in agro-food matrices

Corradini Danilo

National Research Council, Institute of Chemical Methodologies, Area della Ricerca di Roma 1, 00015 Montelibretti, Rome, Italy.

danilo.corradini@cnr.it

The plethora of natural organic compounds produced in plants by secondary metabolism comprise food ingredients and biomolecules with pharmacological activity employed in phytotherapeutic medicine. The identification and quantification of these target compounds in plants and agro-food matrices is a challenging task, continuously requesting the development of more robust, efficient and sensitive instrumental analytical techniques. This communication discusses fundamental and practical aspects of both reversed phase high performance liquid chromatography (RP-HPLC) and capillary zone electrophoresis (CZE) employed for the analysis of plant biomolecules. The two analytical separation techniques display complementary capability in separating plant secondary metabolites, as it is discussed for the analysis of phenolic compounds in plant extracts. The observed differences in selectivity have been ascribed to the presence of multifunctional moieties displayed by most of these compounds, which are expected to influence to different extents the dissimilar separation mechanisms operating in CZE and in RP-HPLC. The presentation evaluates and discusses the influence of a variety of experimental conditions employed in CZE and in RP-HPLC on the separation performance of secondary metabolites and other biomolecules extracted from plants and agro-food matrices. Also discussed is the practical application of either CZE or RP-HPLC to the study of metabolites in transgenic food and in edible plants, as well as the determination of phenolic compounds by these analytical separation techniques in agro-food matrices during the transformation of raw ingredients into food and in the production of so-called functional foods, functional ingredients and nutraceuticals.

ANA-K7

Enzyme-based Nanoarchitectures for Electrochemical Detection of Nucleic Acids

Diego Voccia, Francesca Bettazzi, Ilaria Palchetti

Dipartimento di Chimica, Università degli Studi di Firenze, Via della Lastrucia 3, 50019 Sesto Fiorentino, Italia

ilaria.palchetti@unifi.it

Different nanoarchitectures, rich in enzyme labels, are herein investigated for signal amplification in the electrochemical detection of nucleic acids and in particular of miRNAs. miRNAs are naturally occurring small RNAs (approximately 22 nucleotides in length) that act as regulators of protein translation. Because many diseases are caused by the misregulated activity of proteins, miRNAs have been implicated in a number of diseases including a broad range of cancers, heart disease, immunological and neurological diseases. Consequently, miRNAs are intensely studied as candidates for diagnostic and prognostic biomarkers. The proposed research is focused on the determination of miRNAs specific of lung tumors (mir-221, mir-222) and colorectal tumors (miR-92a).

The proposed method is based on thiolated DNA capture probes immobilized onto gold electrode surfaces, or gold nanostructured carbon surfaces. Total RNA is extracted from the sample, biotinylated, and then hybridized with the specific capture probes. The biosensing platform is then incubated with enzyme-rich nanoarchitectures and exposed to a proper substrate.

Dendritic amplification, accomplished by the use of streptavidin and biotinylated alkaline phosphatase, and enzyme-decorated liposomes are used as labels to amplify the miRNA-sensing, by their association to the probe-miRNA hybrid generated onto the transducer. Differential pulse voltammetry and faradaic impedance spectroscopy were employed to characterize these different amplification routes.

ANA-K8

Development of innovative analytical methods and devices for food quality and safety control

Fabio Terzi[a], *Barbara Zanfrognini*[a], *Stefano Ruggeri*[a], *Laura Pigani*[a], *Chiara Zanardi*[a], *Renato Seeber*[a], *Nicolò Dossi*[b], *Rosanna Toniolo*[b], *Gino Bontempelli*[b]

a Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emila, Via G. Campi 183, 41125, Modena, Italy
b Dipartimento di Chimica degli Alimenti, Via Cotonificio 108, Università di Udine, 33100, Udine, Italy

fabio.terzi@unimore.it

We report here on the joint efforts of two research groups working in analytical chemistry. Conveying the expertise of the two groups aims at developing innovative analytical tools for rapid, simple and capillary control of food quality and safety. Most of the approaches commonly adopted make use of sophisticated methodologies and instrumentation, based on both separation techniques and molecular or mass spectrometry. They often require non trivial and time-consuming sample pre-treatments, and the use of expensive apparatus. The innovative analytical approach is based on amperometric sensing systems exploiting recent progresses in the fields of material science, in the wide sense. They meet with the request for simplicity, low cost and potential wide diffusion, however possessing high sensitivity, selectivity, and robustness. Similar devices are capable to operate on samples either directly or after a minimal pre-treatment. The two research groups possess complementary expertise. The group from Modena possesses acknowledged experience in developing novel electrode systems based on unconventional materials. In particular, conducting polymers and metals and metal-oxides under the form of bulk materials and (nano)particles have been developed and employed even in real matrices. The group from Udine recently developed pencil leads suitable to draw conductive patterns on paper-based devices, also using room temperature ionic liquids. In such systems fluidics and electrochemical detection are integrated on the same substrate and exploit the electrode materials developed in Modena.

ANA-K9

Medaglia Canneri

Mass spectrometry based strategies in lipidomics

F. Palmisano

Dipartimento di Chimica & Centro Interdipartimentale SMART, Università degli Studi di Bari Aldo Moro, Via E.Orabona, 4 - 70126 Bari, Italia

francesco.palmisano@uniba.it

Lipids are essential cellular constituents that have multiple distinct, yet critical, roles in cellular activity, ranging from simple energy storage to complex signaling functions.
Lipidomics can be viewed as ‘‘the full characterization of lipid molecular species and of their biological roles with respect to expression of proteins involved in lipid metabolism and function, including gene regulation”[1]. The combination of all these complex aspects is a very challenging task, but the first step is, obviously, the identification and quantitation of each distinct chemical entity present in cells lipidome. Significant achievements in our understanding of lipidomics have been greatly facilitated by recent advances in, and novel applications of, mass spectrometry techniques based on soft ionization methods. Electrospray ionization mass spectrometry (ESI/MS) techniques permit the analysis and quantitation of a significant fraction of cellular lipidomes directly from crude extracts of biological samples (shotgun lipidomics). The shotgun approach is complemented by liquid chromatography-ESI/MS/MS, that provides structural information and the separation of isomeric/isobaric species. LC-ESI/MS/MS can be used for a global lipidome analysis or for targeted analysis of very low abundance molecular species (e.g. second lipid messengers). Novel approaches combining CID with ozone induced dissociation (OzID) demonstrated the ability to differentiate regioisomers and to assign carbon-carbon double bond positions to individual acyl chains at specific sn-positions (top-down lipidomics).
Although not yet commonly accepted, MALDI MS represents a complementary method of lipid analysis even if some classes (e.g. cardiolipins, poly-phosphoinositides and sulfatides) are more tricky analytes than other ones; here further methodological developments, particularly in the field of matrix engineering, are required. Nevertheless, MALDI MS drawbacks are compensated for by several important advantages typical of a high throughput analytical technique. Finally, the recent introduction of MS imaging techniques has led to a strong renaissance of interest in MALDI MS focused in the field of lipidomics, as lipids are abundant in tissues and ionize also particularly well.
In this lecture, the analytical challenges posed by lipidomics will be shortly reviewed and selected applications from the Author’s lab will be illustrated.

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ANA-K10

Proteomica presente e..........futuro!!

Piero Pucci

Dipartimento di Scienze Chimiche e CEINGE Biotecnologie Avanzate, Università di Napoli Federico II, Napoli, Italy.

pucci@unina.it

La moderna ricerca sulle proteine utilizza una filosofia globale che contrappone al classico studio di una singola proteina, l'analisi su larga scala di migliaia di proteine simultaneamente (proteomica). Tuttavia, il proteoma risulta differente da individuo ad individuo, da cellula a cellula e varia notevolmente in corrispondenza di stimoli. Inoltre, la maturazione dell'RNA e le modifiche post-traduzionali hanno portato a riformulare il dogma "un gene, una proteina" che non riflette più la reale natura di un proteoma.

Gli studi di proteomica sono indirizzati verso due aree principali, la proteomica di espressione che tende alla determinazione quantitativa delle proteine espresse in varie condizioni sperimentali mediante l'uso di tecniche di marcatura con coloranti fluorescenti (DIGE) e la proteomica funzionale che ha come obiettivi principali la definizione della funzione biologica di proteine sconosciute e la definizione dei meccanismi cellulari a livello molecolare.

Questi studi hanno modificato in modo radicale il nostro modo di intendere l'universo delle proteine dimostrando che i profili di espressione proteica sono determinati dalla regolazione concertata di numerosissimi geni. Inoltre, i processi cellulari vedono la partecipazione di una moltitudine di proteine che si assemblano in modo rapido e transiente a formare grandi complessi funzionali che poi dissociano liberando singoli componenti proteici. Una singola proteina può assemblare con partners diversi a costituire complessi funzionali diversi, ognuno dotato di una propria specifica funzione biologica. Ne consegue che una proteina possiede una sola attività ma può avere molte funzioni biologiche.

Inoltre, le strategie e le tecnologie sviluppate per l'identificazione di proteine sconosciute durante le analisi proteomiche stanno pian piano affermandosi anche in campi diversi, quali le investigazioni scientifiche sulla scena del crimine e nei beni culturali per la definizione dei materiali proteici utilizzati nell'antichità in vari ambiti dell'arte umana.

E' prevedibile che il futuro della Proteomica sia indirizzato verso il calcolo accurato della concentrazione di proteine in fluidi biologici come alternativa alle metodiche esistenti. Strategie mirate di spettrometria di massa tandem in modalità multiple reactionmonitoring (MRM) costituiscono un potente strumento per la determinazione quantitativa altamente specifiche di biomarkers proteici assicurando una assoluta specificità ed una elevata sensibilità nell'analisi di biomarcatori e superando molte delle difficoltà connesse con l'uso di anticorpi.

ANA-K11

La tossicologia analitica nell'ambito del sistema giudiziario italiano: problematiche, risposte, innovazione

M. Vincenti[a,b], *A. Salomone*[b], *E. Gerace*[b], *D. Di Corcia*[b], *V. Pirro*[a,b]

a Dipartimento di Chimica, Università di Torino, Via Giuria 7, 10125, Torino, Italia
b Centro Regionale Antidoping e di Tossicologia "A. Bertinaria", Regione Gonzole 10/1, 10043, Orbassano (Torino), Italia

marco.vincenti@unito.it

Nel corso degli ultimi anni, si è verificato un consistente incremento delle richieste che il sistema giudiziario italiano nel suo complesso ha posto ai laboratori che eseguono analisi chimiche, soprattutto in ambito tossicologico. I motivi di tale incremento sono da ricercarsi sia nella crescente consapevolezza che la Magistratura ha maturato sul ruolo che le indagini chimico-analitiche possono svolgere nell'orientare le indagini e nel fornire elementi probatori, sia negli sviluppi tecnologici e metodologici dell'analisi chimica, che forniscono strumenti sempre più sofisticati, efficaci e rapidi per orientare le indagini e perfino per consentire l'apertura di nuovi filoni di investigazione.

In ambito tossicologico, le analisi chimiche si applicano ad una grande varietà di matrici (sangue[1], urina, capelli[2], pelo, saliva[3], reperti autoptici), di analiti (sostanze stupefacenti e dopanti vecchie e nuove[4], alcol[5], farmaci, veleni, tossine, inquinanti) e di problematiche, ciò che richiede un aggiornamento continuo dei protocolli analitici e la loro rigorosa validazione, ai fini dell'inconfutabilità delle relative risultanze in sede processuale. Unitamente a ciò, al laboratorio di analisi tossicologica sono richiesti tempi di risposta e costi progressivamente più bassi.

La relazione illustrerà questi concetti, traendo esempi di applicazione reale da un'ampia casistica, che si riferisce a reati di violenza sulla persona, di abuso di sostanze lecite e illecite, di avvelenamento, di sofisticazione alimentare e di ambito zootecnico.

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ANA-K12

Green electrosynthesis of ZnO nanoparticles and their application as OTFT modifiers

M. C. Sportelli[a], *R. A. Picca*[a], *K. Manoli*[a], *M. Magliulo*[a], *L. Torsi*[a], *N. Cioffi*[a],
[a] *Dip. Chimica, Università degli Studi Bari Aldo Moro, V. Orabona 4, Bari, Italia*

nicola.cioffi@uniba.it

The applications of ZnO nanoparticles (NPs) and thin films are continuously expanding in several fields [1]. They are highly attractive nanomaterials because of their excellent properties, including biocompatibility, stability, electrochemical activity, high electron mobility [2]. We report on the green electrochemical-thermal synthesis of ZnO NPs in aqueous basic solution in the presence of poly(sodium 4-styrenesulfonate) as dispersing agent [3], improving a previous synthetic procedure [4]. Electroproduced NPs were thermally treated at 300°C or 600°C, to improve ZnO stoichiometry and crystallinity. A detailed morphological and spectroscopic characterization was performed by TEM, UV-Vis, CV, FT-IR, and X-ray Photoelectron spectroscopy (XPS). NPs improved the performance of polythiophene-based Field Effect Transistors (FETs). ZnO NPs were part of the biosensor active layer, and mixed organic-inorganic composites were also developed using Streptavidin, as model protein. ZnO NPs' aptitude at coordinating biomolecules, and their enhancement of device performance [5] were studied.

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ANA-K13

Analyzing multivariate data from designed experiments: a journey into ANOVA-Simultaneous Component Analysis (ASCA)

Marta Bevilacqua[a], *Federico Marini*[a]

[a] *Department of Chemistry, University of Rome "La Sapienza", P.le Aldo Moro 5, 00185, Rome, Italy*

federico.marini@uniroma1.it

During the last years, ANOVA-Simultaneous Component Analysis (ASCA) has been introduced for the exploratory analysis of multivariate data with an underlying experimental design [1]. It consists in partitioning the variation in multivariate data matrix into the contribution of the individual effects according to an ANOVA-like scheme and then in the analysis of the effect matrices using a bilinear decomposition through Simultaneous Component Analysis. Due to its characteristics, ASCA has found many application in the –omics field, e.g. to unravel the effect of diet or treatment on the metabolic fingerprint of individuals, but, more recently, has proved to be valuable also in other areas such as food quality control [2] or environmental chemistry [3].

In this communication, the main characteristics of the method will be presented, together with a detailed description of how the significance of the models obtained can be properly validated. The key concepts behind the methods will be also illustrated by means of real-world examples selected from the authors' own experience and coming from different areas of application.

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ANA-K14

Desirable future developments for the studies on equilibria in solution

Silvio Sammartano[a]

a Dipartimento di Scienze Chimiche, Università diMessina, Viale F. Stagno d'Alcontres, 31, I - 98166, Messina, Italy

ssammartano@unime.it

Over the past twenty-five years, some problems obscured the image of the studies on solution equilibria. Already in the nineties of the last century, Martell and Motekaitis [1] argued : "The proliferation of publications in this field (complex formation in solution), by which investigators would report stability constants for their own sake, without any apparent objective of advancing the concepts and principles of coordination chemistry, or of providing information essential to other fields, has led to a general decline in the prestige of this research area, and work on stability constants gradually came to be regarded as routine".

Other problems arise from substantial limitations of the experimental conditions (different ionic medium, ionic strengths and temperatures), and sometimes by the inadequacy of the experimental techniques.

Moreover, some issues were scarcely considered, such as, for example, the study of secondary interactions (e.g., weak complexes or ion pairs), the study of macromolecules (in particular poly-electrolytes), the analysis of the complexing capacity for classes of ligands, rigorous analysis of the literature data, and the construction of suitable databases.

Finally, studies on the complexing ability should be accompanied by parallel investigations on other parameters, such as acid-base properties of the various systems involved, solubility, and formation enthalpy changes.

In this short note we will try to analyze these problems.

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ANA-K15

Bioluminescent magnetotactic bacteria as powerful bioanalytical tool for lab-on-a-chip analysis

E. Michelini[a], *L. Cevenini*[a], *M. Calabretta*[a], *S. Borg*[b], *D. Schuler*[b], *A. Roda*[a]

[a]*Dipartimento di Chimica "G.Ciamician", Via Selmi 2, 40126, Alma Mater Studiorum-University of Bologna, Italy*
[b]*Ludwig-Maximilians-Universität München, Department Biologie I, Mikrobiologie, Planegg-Martinsried, Germany*

elisa.michelini8@unibo.it

The increasing need for rapid, robust and cost-effective toxicity screening systems led to the development of miniaturized analytical devices exploiting the potentiality of genetically engineered living cells for biosensing. The incorporation of living cells within a miniaturized system offers the advantage of small reagent and sample volume requirements combined with the possibility to move the cells in different areas of the chip designed to carry out specific functions. In an effort to obtain bioreporters with enhanced analytical performance suitable for chip integration, we produced smart whole-cell biosensors using genetically engineered bioluminescent magnetotactic bacteria (BL-MTB). MTB, which have the ability to produce a magnetosome chain, have been genetically engineered to express bioluminescent reporter proteins and used as living biosensors. *M. gryphiswaldense* strain was genetically engineered to constitutively express a click beetle luciferase (CBR, λmax = 610 nm) and used as general toxicity sensor. A microfluidic chip has been fabricated using multilayered black and transparent polydimethyl siloxane (PDMS) in which BL-MTB are incubated for 30 min with the sample, then moved by microfluidics, trapped, and concentrated in detection chambers by an array of NdFeB magnets. The chip is placed in contact with a cooled CCD via a fiber optic taper to perform quantitative bioluminescence imaging after addition of luciferin substrate. Incubation with model toxic compounds (dimethyl sulfoxide, DMSO and taurochenodeoxycholic acid, TCDCA) drastically reduces the bioluminescent signal in a dose-related manner. The generation of bacteria that are both magnetic and bioluminescent combines the advantages of easy 2D cell handling with ultra sensitive detection, offering undoubted potential to develop cell-based biosensors integrated into microfluidic chips.

ANA-K16

pH-triggered nanoswitches based on triplex-DNA

Andrea Idili[a], Alessandro Porchetta[a], Giuseppe Palleschi[a], Francesco Ricci[a]

a Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma, Tor Vergata, Via della Ricerca Scientifica, 00133, Roma

francesco.ricci@uniroma2.it

We have designed programmable DNA-based nanoswitches whose closing/opening can be triggered over specific different pH windows. These nanoswitches form an intramolecular triplex DNA structure through pH-sensitive parallel Hoogsteen interactions. We demonstrate that by simply changing the relative content of TAT/CGC triplets in the switches, we can rationally tune their pH dependence over more than 5 pH units. The ability to design DNA-based switches with tunable pH dependence provides the opportunity to engineer pH nanosensors with unprecedented wide sensitivity to pH changes. With their fast response time (<200 ms) and high reversibility, these pH-triggered nanoswitches appear particularly suitable for applications ranging from the real-time monitoring of pH changes in vivo to the development of pH sensitive smart nanomaterials. Finally, we demonstrate here that these switches can be of utility to build novel DNA-based nanostructures or nanomachines with pH-dependent behavior.

ANA-K17

Indagini sull'efficacia di colture di funghi nella rimozione di vernici da substrati lapidei

Giulia Germinario[a], Inez D. van der Werf [a], Rosa M. Montes-Estelles[b], Josè L. Regidor-Ros[c], Luigia Sabbatini[a]

a Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro", via Orabona 4, 70126 Bari, Italia
b Dipartimento di Biotecnologia, Universitàt Politècnica de València, Camino de Vera 14, 46022 Valencia, España
c Dipartimento di Conservación y Restauración de Bienes Culturales Universitàt Politècnica de València, Camino de Vera 14, 46022 Valencia, España.

luigia.sabbatini@uniba.it

Nell'ambito di un progetto di recupero, conservazione e valorizzazione dei Beni Culturali, la fase di pulitura rappresenta una delle prime e più delicate operazioni. La rimozione di graffiti da monumenti lapidei costituisce tuttora un problema.
Questo studio si incentra sulla possibilità di rimuovere vernici spray da substrati lapidei con metodologie eco-compatibili, utilizzando colture di *Phanerochaete crysosporium*, fungo appartenente alla famiglia dei basidiomiceti, già noto per la sua capacità di degradare la lignina e alcuni composti aromatici inquinanti[1-2]. I test di biopulitura sono stati eseguiti applicando le colture su provini simulanti casi reali, costituiti da un substrato in ceramica bianca su cui sono state applicate delle vernici spray. Alcuni campioni sono stati sottoposti ad invecchiamento. Le vernici sono state analizzate con diverse tecniche analitiche complementari quali la spettroscopia micro-Raman e infrarossa a trasformata di Fourier (FTIR) nonché la pirolisi-gas cromatografia-spettrometria di massa (Py-GC/MS) al fine di determinare la composizione chimica di tutti i componenti presenti (legante, coloranti e/o pigmenti, additivi, etc.)[3-4]. Le prove di biopulitura sono state eseguite variando i terreni e le condizioni di crescita e ne è stata verificata l'efficacia mediante analisi spettrofotocolorimetriche.

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ANA-K18

Fundamental Surface-Analytical Investigations in Tribology: The Challenges of Studying Phenomena at Sliding Interfaces

Filippo Mangolini

Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA, US

mfilippo@seas.upenn.edu

Tribology is the study of interacting surfaces in relative motion and the resulting phenomena of friction, lubrication, and wear. Energy and material losses in moving mechanical components as a result of friction and wear impose an enormous cost on national economies and call for the development of improved engineering systems with reduced friction and wear. Establishing a fundamental understanding of the phenomena occurring at sliding interfaces and controlling the observed tribological performance constitutes a critical step in the rational design and synthesis of new, and improved materials and lubricants that can reduce energy and resource consumption in tribological applications. A key step in developing this understanding lies in applying advanced surface-analytical methods to the study of tribological materials and interfaces

In this talk, I will present recent results focusing on fundamental surface-analytical investigations of: a) the reaction layers formed by environmentally-friendly lubricant additives on metallic surfaces under both thermal and tribological conditions; and b) the structural changes occurring on solid lubricants upon sliding under different environmental conditions.

First, a fundamental understanding of the molecular-level mechanism of action of an environmentally-friendly anti-wear additive (triphenyl phosphorothionate, TPPT) under harsh tribological conditions was achieved through the development of an *in situ* attenuated total reflection (ATR/FT-IR) tribometer. The outcomes of *in situ* ATR/FT-IR tribological tests together with the *ex situ* X-ray photoelectron spectroscopic (XPS) characterization of the reaction layers formed by TPPT on iron upon sliding demonstrated that the unsatisfactory anti-wear properties of TPPT derive from the lack of counter-ions in the reaction layers formed at the buried sliding interface.

Second, a physically-based understanding of the structural transformations occurring in the near-surface region of silicon oxide-doped diamond-like carbon (SiO_x-DLC) surfaces upon sliding as well as the strong environmental dependence of these transformations was gained through the characterization of the tribologically-stressed material by synchrotron-based near edge X-ray absorption fine structure (NEXAFS) spectroscopy. A correlation with previously published, state-of-the-art molecular dynamics simulations will be discussed.

Chimica Analitica

Oral

ANA-O1

Chemical quality of coastal waters under climate change conditions/scenarios

Andrea Critto [a,b]*, Jonathan Rizzi* [a,b]*, Silvia Torresan* [b]*, Alex Zabeo* [b]*, Daniele Brigolin* [a]*, Sandro Carniel* [c]*, Roberto Pastres* [a]*, Antonio Marcomini* [a,b]

a Dipartimento di Scienze Ambientali, Informatica e Statistica, Università Ca' Foscari Venezia, Calle Larga S. Marta 2137, 30123 Venezia, Italia
b Centro Euro-Mediterraneo sui Cambiamenti Climatici (CMCC), Divisione Impatti sui Suoli e sulle Coste, Via Augusto Imperatore 16, 73100 Lecce, Italia
c Istituto di Scienze Marine – Consiglio Nazionale delle Ricerche, Arsenale - Tesa 104, Castello 2737/F, I-30122 Venice, Italy

critto@unive.it

The increase of sea temperature and the changes in marine currents are generating impacts on marine waters such as changes in water biogeochemical and physical parameters (e.g. primary production, pH, salinity) leading to progressive degradation of the marine environment.

With the main aim of analysing the potential impacts of climate change on marine water quality, a Regional Risk Assessment (RRA) methodology was developed and applied to coastal marine waters of the North Adriatic (i.e. coastal water bodies of the Veneto and Friuli Venezia Giulia regions, Italy).

RRA integrates the outputs of regional models providing information on macronutrients (i.e. dissolved inorganic nitrogen e reactive phosphorus), dissolved oxygen, pH, salinity and temperature, etc., under future climate change scenarios with site-specific environmental and socio-economic indicators (e.g. biotic index, presence and extension of seagrasses, presence of aquaculture). The presented approach uses Geographic Information Systems to manage, analyse, and visualize data and employs Multi-Criteria Decision Analysis for the integration of stakeholders preferences and experts judgments into the evaluation process. RRA outputs are hazard, exposure, vulnerability, risk and damage maps useful for the identification and prioritization of hot-spot areas and vulnerable targets in the considered region.

Therefore, the main aim of this contribution is to apply the RRA methodology to integrate, visualize, and rank according to spatial distribution, physical and chemical data concerning the coastal waters of the North Adriatic sea in order to predict possible changes of the actual water quality.

ANA-O2

Dark formation of hydroxyl radicals ($^•$OH) upon aeration of anoxic lake water

M. Minella[a], *D. Vione*[a,b], *E. De Laurentiis*[a], *V. Maurino*[a], *C. Minero*[a]

a University of Turin, Department of Chemistry, Via P. Giuria 5, 10125 Turin, Italy
b University of Turin, NatRisk Centre, Via L. Da Vinci 44, 10095 Grugliasco (TO), Italy

marco.minella@unito.it

The hydroxyl radical ($^•$OH) is a highly reactive transient causing the degradation of most dissolved organic and inorganic substrates (e.g. pollutants) [1]. It is formed photochemically in surface waters, by irradiation of photosensitisers such as chromophoric dissolved organic matter (CDOM), nitrite and nitrate [2-3].

Here we report for the first time that $^•$OH can also be produced in the dark by aeration of anoxic lake water. Many lakes located in temperate environments are stratified during summer, as the warmer and oxygenated surface layer (epilimnion) floats above the colder and often anoxic deep water (ipolimnion). Lake circulation is an important phenomenon that ensures oxygenation of the water column. Dark $^•$OH formation was measured in anoxic water (taken from the ipolimnion of different lakes during summer stratification) upon exposure to the atmosphere.

It is interesting to compare dark $^•$OH formation with photochemical processes. The cumulated $^•$OH concentration produced in a few hours in air-exposed ipolimnion samples can be obtained by illumination of epilimnion water under fair-weather sunlight for up to 4 months in spring-summer. This is equivalent to $\geq 50\%$ of the yearly sunlight energy received by lake water. Dark $^•$OH production is thus a new environmental process that could be very important in the $^•$OH *budget* of lake environments. It could play a key role in the self-depollution potential of the lakes and in carbon biogeochemical cycles, increasing the bioavailability and mineralisation of dissolved organic matter.

This is an exciting new discovery that could deeply modify the current understanding of the processes taking place in lake water.

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ANA-O3

A new technique for the determination of Trichloroethylene diffusion matrix in water

Federico Rossi[a], *Adriano Intiso*[a], *Raffaele Cucciniello*[a], *Oriana Motta*[b], *Nadia Marchettini*[c] *and Antonio Proto*[a]

a Dipartimento di Chimica e Biologia, Università di Salerno, Via Giovanni Paolo II 132 , 84084, Fisciano (SA), Italia
b Dipartimento di Scienze Umane, Filosofiche e della Formazione, Università di Salerno, Via Giovanni Paolo II 132 , 84084, Fisciano (SA), Italia
c Dipartimento di Scienze Fisiche della Terra e dell'Ambiente, Università di Siena, Pian dei Mantellini 44, 53100, Siena, Italia

frossi@unisa.it

Trichloroethylene (TCE) is one of the most diffuse halogenated aliphatic organic compounds. Because of its properties, TCE is widely used in industrial cleaning and degreasing applications and, together with Perchloroethylene (PCE) and Trichloroethane (TCA), is the most frequently detected volatile organic pollutants in ground water [1]. In order to study the fate of TCE in water and to devise effective remediation strategies, a series of advection-diffusion (dispersion) models, where the diffusion coefficient of TCE (D_{TCE} is an important parameter, have been developed. However, D_{TCE} in water has never been experimentally determined and only theoretical values ($\simeq 1 \times 10^{-5}$ cm^2 s^{-1} at 25 °C) are present in the literature [2]. In this paper we present a method based on the Taylor dispersion technique [3] which allow for measuring D_{TCE} in a broad range of temperature and, in principle, in any solvent. We found that at 25 °C $D_{TCE} = 7.3 \pm 0.1 \times 10^{-6}$ cm^2 s^{-1} and the value increases almost linearly with the temperature, while, in the limit of the experimental error, is independent from [TCE] for dilute solutions.

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ANA-O4

Development of molecularly imprinted membranes for selective recognition of toxic compounds

Laura Donato and Enrico Drioli*

Research Institute on Membrane Technology, ITM-CNR, c/o University of Calabria,
Via P. Bucci, Cubo 17/C, 87030 Rende (CS), Italy

l.donato@itm.cnr.it.

Molecularly imprinted membranes (MIMs) represent a special format of molecularly imprinted polymers having bio-mimetic molecular recognition properties. In fact, owing to the presence of specific recognition sites in their matrix, they are able to recognize and separate a molecule of particular interest (template) from a mixture of similar chemical compounds. The molecular recognition is achieved thanks to the chemical and spatial complementary existing between the template and the recognition sites of the membrane. Combining the advantages of both, the imprinting technique and the oldest membrane technology, MIMs signed a new pathway for the detection, of targeted compounds like drugs [1], optical isomers [2], organic pollutants [3] and other. In this work were developed MIMs for specific recognition of the pesticide dimethoate (DMT) and the primary amine 4,4'-methylendianiline (MDA). Membranes were prepared *via* the phase inversion inversion technique using polyacrylonitrile and its copolymers with different functional co-monomers (acrylic acid, methacrylic acid, itaconic acid and acrylamide) *ad hoc* synthesized by the water-phase precipitation polymerization process.

The recognition properties of the membranes were evaluated by rebinding tests performed in a dead-end filtration cell using aqueous or organic solutions of DMT and MDA, respectively. Results showed that all the imprinted membranes exhibit specific binding for the templates and could be used in solid-phase extraction processes such as removal of genotoxins from organic solvents and pesticides from water samples.

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ANA-O5

Photodegradation of paracetamol under conditions relevant to sunlit surface waters

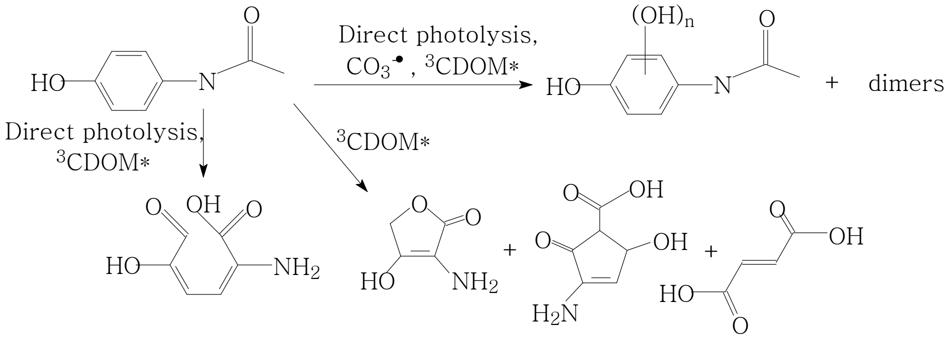
D. Vione[a], E. De Laurentiis[a], M. Minella[a], V. Maurino[a], C. Minero[a],
C. Prasse[b], T. A. Ternes [b]

a University of Turin, Department of Chemistry, Via P. Giuria 5, 10125 Turin, Italy
b Federal Institute of Hydrology (BfG), Am Mainzer Tor 1, 56068 Koblenz, Germany

davide.vione@unito.it

Photochemical reactions are important pathways for the transformation of xenobiotics in surface waters [1], and they involve direct and indirect photolysis. In the latter case sunlight is absorbed by photosensitisers (nitrate, nitrite and chromophoric dissolved organic matter, CDOM), which produce reactive transients such as hydroxyl ($^{\bullet}OH$) and carbonate ($CO_3^{-\bullet}$) radicals, singlet oxygen ($^1O_2$) and CDOM triplet states ($^3CDOM^*$), inducing pollutant degradation [2].

In this work we show that the anti-pyretic drug paracetamol can be transformed in surface waters by direct photolysis and reaction with $CO_3^{-\bullet}$ and $^3CDOM^*$. The dissolved organic carbon (DOC) is a key parameter in directing phototransformation, because reaction with $CO_3^{-\bullet}$ would prevail in low-DOC and reaction with $^3CDOM^*$ in high-DOC waters. The substrate lifetime varies from a few days to some months, depending on water conditions. The paracetamol intermediates formed in the main phototransformation processes, identified by LC-MS, are reported in the scheme below.



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ANA-O6

The harmful effects of antifouling biocides in Southern Adriatic sea

P. Massanisso[a], G. Ansanelli[b], G. Di Landa[b], S. Schiavo[b], C. Minopoli[b], A. B. Lanza[b], M. Pezza[a], A. Salluzzo[b], S. Manzo[b]

a ENEA,UTPRA-GEOC, CR Casaccia, Via Anguillarese 301, 00123, Rome, Italy
b ENEA, UTTP-CHIA, CR Portici. P. le E. Fermi, 1, 80055 - Portici, Naples, Italy,

paolo.massanisso@enea.it

Antifouling (AF) paints are routinely used to prevent any living organisms from undesirably adhering to the submerged surfaces of ships, boats and aquatic structures; they act realising effective biocides from the coated surface.

Formulations containing organotin tributyltin, (TBT) were the most successful against biofouling but they were banned in 2008 [1], due to their detrimental impact on sea life. Currently, most antifouling paints contain copper or zinc as an active ingredient and a “booster” biocide, such as Irgarol and Diuron, to strengthen the effectiveness of the formulation [2]. The toxicity of AF biocides can also be exerted on non-target species, after their release in water column. Likewise, copper and zinc at high concentrations and in a bioavailable form can be toxic to algae and other water organisms. Therefore these AF agents need to be monitored in order to assess the possible environmental damage related to their use

The CARISMA project, funded by the Italian Ministry of Foreign Affairs, aims to appraise the quality of the Southern Adriatic sea between Italy (Apulia region) and Albania and, in particular, the impact due to the use of biocidal antifouling coatings. Under this project, a survey at the main hot spots of contamination (e.g. ports and marinas) was conducted at the end of summer nautical season.

Analysis of Irgarol, Diuron, TBT and some heavy metals in marine environment (sediment, mussel and seawater) were complemented with ecotoxicological assays. The Albanian and Italian ports showed different degree of contamination, highlighting the most critical situation in one port of Apulia.

For that reason, there is an urgent need for further investigation in order to evaluate the spread of antifouling biocides in the marine environment and to distinguish the possible sources of these dangerous pollutants.

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ANA-O7

Determination of pharmaceutical and herbicide compounds in soil samples using the QuEChERS methodology

L. Rivoira[a], R.M. De Carlo[a], C. Ancillotti[b], L.Ciofi[b],
M. Del Bubba[b], M.C. Bruzzoniti[a]

a Department of Chemistry, University of Torino, Via Pietro Giuria, 5 - 10125 Turin
b Department of Chemistry, University of Florence, Via della Lastruccia, 3 – 50019 Sesto Fiorentino (Florence)

luca.rivoira@unito.it

QuEChERS is a recently developed approach for the extraction of organic compounds, in particular pesticides, from fruit and vegetables [1]. Since the last six years, QuEChERS method has been applied for analyzing compounds of environmental concern (mainly pesticides) in environmental matrices [2]. In this work, a modified QuEChERS approach was optimized for the extraction of five molecules of environmental concern from soil samples. The analytes considered were bentazone and atrazine (belonging to the herbicides class), phenytoin and carbamazepine (anticonvulsant medicines) and 5-(p-hydroxyphenyl-),5-phenylhydantoin (HPPH), a metabolite of phenytoin [3]. Several QuEChERS-based procedures were compared for the extraction of the above-mentioned compounds from a soil sample. The composition of the solvent ($CH_3CN:H_2O$) was optimized in terms of organic modifier percentage and pH values. In addition, the effect of the clean-up step was also studied, evaluating the performance of the QuEChERS method with different sorbents (mainly PSA and C18 resins). The recoveries were evaluated by an optimized RPLC separation with both UV and pulsed amperometric detection (PAD). According to the results obtained, with the optimized QuEChERS procedure, the recoveries, obtained applying a matrix-matched calibration and evaluated for concentrations ranges of 200-2000 µg/kg, were included between 83.3±11.4% (HPPH) and 122.5±8.9% (atrazine) for the UV detection and between 108.7±6.1% (carbamazepine) and 120.4±2.6% (HPPH) for the PAD method.

Method validation was performed evaluating linearity, limits of detection (LODs) and quantification (LOQs), intra-day and inter-day repeatability. The LODs obtained ranged from 4.1 µg/Kg (bentazone) to 492 µg/Kg (phenytoin) for the UV detection and from 4.3 µg/Kg (HPPH) and 11.4 µg/Kg (bentazone).

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ANA-O8

Influence of the composition of the liquid phase on the performance of separations in reversed phase liquid chromatography and in capillary electrophoresis of biomolecules

Danilo Corradini, Isabella Nicoletti

National Research Council, Institute of Chemical Methodologies, Area della Ricerca di Roma 1, 00015 Montelibretti, Rome, Italy.

danilo.corradini@cnr.it

This communication discusses the influence of the composition of the liquid phase on the performance of separation of biomolecules by either capillary electrophoresis (CE) or reversed phase high performance liquid chromatography (RP-HPLC). Appropriate selection of the background electrolyte solution (BGE) in CZE or the mobile phase in RP-HPLC involves the evaluation of the equilibrium in solution that might take place between the analytes and the components of the liquid phase. The ionogenic nature of several biomolecules, such as phenolic compounds and other plant secondary metabolites, requires the control of the protonic equilibrium in solution, which is performed using suitable buffering agents incorporated into the BGE or the mobile, respectively. The constituents of the buffer solutions do not limit their action at controlling the protonic equilibrium. They also might interact with the analytes, with the result of altering either their electrophoretic mobility or their chromatographic retention, respectively. In addition, the components of the BGE influence the generation of the electric double layer at the interface between the inner surface of fused silica capillaries and the electrolyte solution, which originates the electroosmotic flow in CZE. The discussion include the results of a study performed to identify the N-acylhomoserine lactone signalling molecules released by several nitrogen-fixing bacteria such as *Azospirillum brasilense*, *Herbaspirillum seropedicae*, *Burkholderia ambifaria,* and *Gluconacetobacter diazotrophicus,* which are of interest in plant microbiology to study pathogenic or symbiotic interactions of bacteria with plant hosts. The AHLs, extracted from cell-free spent culture supernatants of the selected bacteria, are separated ad identified by HPLC-ESI-MS, using a narrow bore reversed phase column.

ANA-O9

Studio di caratterizzazione di fitocomposti mediante LC-MS/MS

Fabio Gosetti[a], Ugo Chiuminatto[b], Rita Mastroianni[c], Simona Martinotti[a], Elia Ranzato[a], Emilio Marengo[a]

a Dipartimento di Scienze e Innovazione Tecnologica, Università del Piemonte Orientale,
Viale T. Michel 11, 15121, Alessandria (AL), Italia
b AB Sciex, Viale Lombardia 218, 20047 Brugherio (MB), Italia
c Merck Serono, Via Ribes 1, 10010 Colleretto Giacosa (TO), Italia

fabio.gosetti@unipmn.it

Con il termine fitocomposti si intende una categoria di sostanze bioattive non nutrienti di origine vegetale che sono fortemente connesse alla riduzione del rischio della maggior parte delle patologie croniche [1]. La loro azione benefica sulla salute si basa principalmente sulle loro proprietà antiossidanti e sulla stimolazione del sistema immunitario. Alcune di queste sostanze polifenoliche, presenti in piante e alimenti, possiedono persino proprietà antimutageniche ed antiproliferative in grado di inibire l'insorgenza e al tempo stesso la diffusione di tumori [2-3].

In questo studio è stato preso in considerazione l'estratto acquoso di una pianta orientale che pare abbia sulla popolazione autoctona proprietà benefiche nei confronti di disturbi gastrointestinali, mal di denti, bruciori di stomaco, iperlipidemia e controllo del diabete di tipo 2. E' stata effettuata una caratterizzazione della frazione volatile mediante GC-MS, del contenuto di metalli mediante ICP MS, e della frazione polare mediante UHPLC-QTOF MS/MS, al fine di poter effettuare un' impronta digitale dell'estratto e presumere quali potessero essere i potenziali principi attivi. Dalle analisi sono state identificate diverse specie principalmente appartenenti alle classe delle procianidine e prodelfinidine oligomeriche. Infine l'estratto è stato testato in vitro su linee cellulari tumorali fornendo soddisfacenti risultati sull'inibizione profilerativa delle cellule stesse.

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ANA-O10

Quantitative analysis of biogenic amines in food by tandem mass spectrometry

F Mazzotti, L Di Donna, A Napoli, D Taverna, D Aiello, G Sindona

a Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Via P. Bucci Cubo 12/D, 87036, Rende, Italia

fmazzotti@unical.it

Biogenic amines (BA) are basic nitrogenous compounds formed mainly by decarboxylation of aminoacids or by amination and transamination of aldehydes and ketones. Biogenic amines may also be considered as carcinogens because of their ability to react with nitrites to form potentially carcinogenic nitrosamines.[1,2]
Here we present a simple methodology for the simultaneous determination of BAs, based on the use of labeled internal standard, chemical derivatization and LC-MS/MS analysis under MRM condition. The derivatization reagent is the 4-methoxybenzoic acid OSu (N-Hydroxysuccinimide) activated, which reacts mainly with the primary amines, and the internal standard are the analogous amines deirvatized with 4-methoxy-d_3-benzoic acid. The quantitative analysis have been performed under MRM condition monitoring the transitions that lead to the ion at *m/z* 135 for the analyte and to the ion at *m/z* 138 for the labeled internal standard. The addition of a labeled internal standard prior to analysis helps to minimize the matrix effects providing a large improvement of precision and accuracy. The derivatization process is easily obtained in mil condition. The examined analytes are separated by UHPLC stage before the mass analysis, the chromatographic run is necessary in order to eliminate the excess of derivatizing reagent. The developed methodology has been applied to blank sample, spiked at different concentration and a different food matrices. The calculated analytical parameters of accuracy, recovery and RSD% for all amines highlight the reliability of the proposed approach.

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ANA-O11

Analisi sperimentale e modellazione del processo di estrazione del limonene da bucce di "Limone di Rocca Imperiale IGP" con CO_2 supercritica

Giuseppe Di Sanzo [a], *Roberto Balducchi* [c], *Oliviero Maccioni* [d], *Silvia Mazzuca* [e], *Antonio Brucci* [a], *Alessandra Meluso* [b], *Ramona Agostini* [b], *Vincenza Calabrò* [b].

c ENEA, C.R. TRISAIA, Unità Tecnica Tecnologie Trisaia, Rotondella (MT)
a ENEA, C.R. TRISAIA, Lab. di Sviluppo Sostenibile della Produzione Primaria, Rotondella (MT)
d ENEA, C.R. CASACCIA, Lab. di Radiazioni Biologia e Biomedicina, S.Maria di Galeria (RM)
b Dipartimento di Modellistica per l'Ingegneria, Università della Calabria, via P. Bucci, cubo 39/c, I-87030 Rende (CS)
e Dipartimento di Chimica e Tecnologie Chimiche - CTC, Università della Calabria, via P. Bucci, 87030 Rende (CS)
giuseppe.disanzo@enea.it

La regione dell'Alto Ionio in Calabria offre le condizioni climatiche ottimali per la crescita di una varietà di limoni che di recente hanno ottenuto l'IGP come "Limoni di Rocca Imperiale". In quest'ambito la cultivar Femminello mostra qualità organolettiche e salutistiche ottimali che la rendono di grande interesse per l'industria agrumaria e per gli utilizzi anche in campo medico e farmacologico. Un ruolo cruciale, in tale ambito, è svolto dal limonene, utilizzato in campo farmacologico ed alimentare per le sue proprietà biologiche. Più recentemente è stata anche scoperta una possibile applicazione medica per la cura del cancro al seno, al pancreas e al colon e per la cura dell'AIDS. Il presente lavoro si propone come obiettivo lo studio ed il controllo del processo di estrazione con CO_2 supercritica del limonene da bucce essiccate di "limoni di Rocca Imperiale IGP", mediante l'utilizzo di un estrattore SPE-ED SFE 2 (Applied Separations) per migliorare la resa di limonene estratto. A tal scopo è stata esaminata la tecnica estrattiva con CO_2 supercritica; essa è una tecnica innocua sia per l'ambiente che per l'uomo e a fine estrazione, non necessita di controlli per la misura del residuo di solvente come previsto dal D.M. 20.05.1976. Lo scopo del presente lavoro è, quindi, quello di migliorare la resa di limonene estratto e la modellazione matematica del processo. Un risultato che si è ottenuto con la modellazione è stato la correlazione/interpolazione dei risultati sperimentali con equazioni di bilancio risolte numericamente che rappresentano l'interpretazione chimico-fisica del processo. Si è voluto, infatti, analizzare quanto più nel dettaglio possibile i meccanismi di trasporto di materia che hanno luogo nel corso dell'estrazione con CO_2 supercritica del limonene e caratterizzarli per la matrice solida in esame. Diventano, pertanto, parametri importanti sia la pressione e la temperatura di estrazione, sia la dimensione e la quantità delle bucce utilizzate, il flusso di CO_2, nonché il grado di maturazione degli stessi limoni. Tali parametri sono risultati fondamentali sia per la conduzione dell'analisi sperimentale sia per l'elaborazione teorica.

ANA-O12

Quality by Design for capillary electrophoresis method development: analysis of metformin and its impurities

Benedetta Pasquini, Serena Orlandini, Paola Mura, Sergio Pinzauti, Sandra Furlanetto

Department of Chemistry "U. Schiff", University of Florence, Via U. Schiff 6, 50019 Sesto Fiorentino, Italy

benedetta.pasquini@unifi.it

Quality by Design (QbD) principles, recently outlined in ICH Q8 guidance for pharmaceutical development [1], have been increasingly embraced by drug analysis researchers. A QbD method development strategy leads to a deep comprehension of the analytical procedure, and finally to the definition of Design Space (DS), a multidimensional zone where any combination of the variables has been demonstrated to provide assurance of quality of the analytical data [2]. Up to now, only a few examples have been provided concerning capillary electrophoresis (CE). In this study, a comprehensive QbD strategy was applied for developing a CE method for the simultaneous determination of metformin hydrochloride, a biguanide antidiabetic, and its main impurities. Method scouting was aimed to find an operative mode which could assure both a good selectivity and the separation of an impurity of very low basicity from the electroosmotic flow, and led to select capillary zone electrophoresis with the addition of carboxymethyl-β-cyclodextrin. The critical quality attributes (CQAs) were represented by critical resolution values and analysis time. The effects of selected critical process parameters were investigated by a screening asymmetric matrix spanning the knowledge space, and in a subsequent step by response surface methodology. The DS was computed by means of risk of failure maps describing the probability of meeting the specifications imposed on the CQAs. A control strategy was finally designed on the basis of system suitability tests.

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ANA-O13

Development of a SPME-GC-QqQ-MS method for the assay of urinary markers of glutaric acidemias

Antonio Tagarelli, Attilio Naccarato, Emanuela Gionfriddo, Rosangela Elliani, Giovanni Sindona

Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Via Pietro Bucci, Cubo 12/D, 87030, Arcavacata di Rende (CS), Italia

a.tagarelli@unical.it

Glutaric acidemia type 1 (GA-1) is an autosomal recessive inherited metabolic disorder that is caused by a deficiency of glutaryl-CoA dehydrogenase (GCDH). This enzyme takes part in the metabolic pathways of the amino acids lysine, hydroxylysine and tryptophan and its deficiency induces an increase of concentration of glutaric acid, 3-hydroxygluraric acid, and glutaconic acid in the free and conjugated forms in tissues and body fluids [1]. Another disorder characterized by an increased excretion of glutaric acid is glutaric acidemia type 2 (GA-2). The recommended follow-up testing procedure for GA-1 and GA-2 is analysis of urinary organic acids and the follow-up markers are glutaric and 3-OH-hydroxyglutaric for GA-1 and glutaric, 2-OH glutaric, adipic, suberic, sebacic, ethylmalonic, 3-OH isovaleric and isobutyric for GA-2 [2].
The main objective of the work presented here was to develop a rapid and easy method for the analysis of urinary organic acids which are markers for GA-1 and GA-2 by SPME-GC-QqQ-MS after a derivatization step with alkyl chloroformate. The simplicity of the final protocol can be achieved by an easy derivatization reaction carried out directly in urine sample and a following SPME analysis in immersion mode in the same vial without use of toxic solvents and further sample treatment. Five commercially available fibers were examined and, in analogy with other studies [3], the variables affecting the derivatization reaction and the SPME process were optimized by the multivariate approach of "Experiment design". Analyses were performed in single reaction monitoring (SRM) mode using a GC interfaced to a triple quadrupole mass spectrometer (QqQ-MS).

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ANA-O14

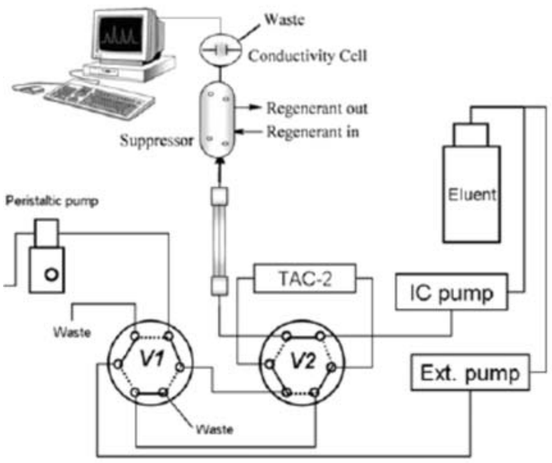
Sviluppo e applicazione di un nuovo metodo in Fast Ion Chromatography (FIC) per la determinazione dei fluoruri in neve e ghiaccio.

Mirko Severi, Silvia Becagli, Daniele Frosini, Miriam Marconi, Rita Traversi, Roberto Udisti

Dipartimento di Chimica "Ugo Schiff", Università di Firenze, Via della Lastruccia 3, 50019, Sesto Fiorentino, Firenze, Italia

mirko.severi@unifi.it

Le carote di ghiaccio rappresentano un importante strumento per la ricostruzione dei cambiamenti passati del sistema climatico. Per esempio, i record ottenuti da carote di ghiaccio di numerose specie chimiche intrappolate nella neve e nel ghiaccio offrono la possibilità di indagare i cambiamenti di concentrazione di vari composti chiave presenti nell'atmosfera come aerosol o come gas. E' stato sviluppato un nuovo metodo per la determinazione quantitativa dei fluoruri nelle carote di ghiaccio a livelli di sub-µg L^{-1} accoppiando una tecnica di analisi in flusso (CFA) con un metodo in Fast Ion Chromatography (FIC) basato sulla tecnica "hearth cut". Per questo nuovo metodo sono stati valutati: sensibilità, intervallo di linearità (fino a 60 µg L^{-1}), riproducibilità e limite di rilevabilità (0,02 µg L^{-1}). Questo metodo è stato applicato con successo per l'analisi dei fluoruri a livello di tracce in più di 450 campioni di neve recente raccolti durante una traversa scientifica effettuata negli anni 1998-1999 nell'ambito del progetto internazionale ITASE (International Trans-Antarctica Scientific Expedition).



ANA-O15

Aree sorgente di polveri minerali nel PM_{10} campionato a Lampedusa dall'analisi di elementi principali e Terre Rare.

S. Becagli[a], *M. Marconi*[a], *D. M. Sferlazzo*[b], *C. Bommarito*[c], *G. Calzolai*[d], *M. Chiari*[d], *A. di Sarra*[e], *D. Frosini*[a], *J.L. Gómez-Amo*[e], *F. Lucarelli*[d], *D. Meloni*[e], *F. Monteleone*[c], *S. Nava*[d], *G. Pace*[e], *S. Piacentino*[c], *M. Severi*[a], *R. Traversi*[a], *and R. Udisti*[a].

a Dip. di Chimica, Università di Firenze, 50019, Sesto F.no, Italy
b ENEA, Laboratory for Earth Observations and Analyses, 92010, Lampedusa, Italy
c ENEA, Laboratory for Earth Observations and Analyses, 90141, Palermo, Italy
d Dip. di Fisica e Astronomia, Università di Firenze, e I.N.F.N., 50019, Sesto F.no, Italy
e ENEA Laboratory for Earth Observations and Analyses, 00123, Rome,

silvia.becagli@unifi.it

Le polveri minerali sono un componente importante dell'aerosol atmosferico sia in termini di contributo in massa che per il loro impatto climatico. Le differenti aree sorgente di polvere influenzano la composizione mineralogica e miscrofisica delle polveri e quindi il loro impatto radiativo. Inoltre, la diversa composizione mineralogica implica rapporti diversi fra i componenti principali e fra gli oligoelementi, tali differenze possono essere utilizzate per l'individuazione delle aree sorgente di polvere e lo studio dei processi di trasporto.

L'obbiettivo di questo lavoro è l' identificazione delle possibili differenze nella composizione chimica e dei rapporti caratteristici di elementi principali, in tracce e Terre Rare delle aree di origine della polvere dalla composizione chimica del PM_{10} campionato presso l'isola di Lampedusa (35.5°N, 12.6°E).

La composizione chimica dei campioni PM10 è stata determinata mediante cromatografia ionica per i principali ioni, mediante tecnica PIXE (Particle Induced X-Ray Emission) per il contenuto totale degli elementi e ICP-AES per metalli in tracce e Terre Rare. Dall'analisi delle retrotraiettorie delle masse d'aria sono state identificate due principali aree sorgente, corrispondenti alla regione Tunisia - Algeria e Libia. In particolare, le aree sorgente in Algeria e Tunisia sono caratterizzate da valori più alti dei rapporti Ca/Al e (Ca+Mg)/Fe rispetto a quelle di origine libica.

ANA-O16

Determination of percutaneous absorption of silver nanoparticles in humans

C. Bianco[a], M. Crosera[a], P. Krystek[b], S. Kezic[c], F. Larese[d], G. Adami[a]

a Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Trieste,
Via Giorgieri 1, 34127, Trieste, Italia
b Philips Innovation Service, 7, High Tech Campus, 5656 AE Eindhoven,
The Netherlands
c Coronel Institute of Occupational Health, Academic Medical Center, AMC, Meibergdreef 9,
K0-113, 1105 AZ Amsterdam
d Dipartimento Clinico di Scienze mediche, chirurgiche e della salute, Università di Trieste,
Strada di Fiume 447 - Ospedale di Cattinara, 34149 - Trieste, Italia

gadami@units.it

This preliminary pilot project aimed to quantify the silver in the skin sampled from people exposed to nanosilver and verify if there are significant differences in silver uptake after a short repeated exposure (8 hour per day for five days) or after a continuous exposure of five days. A garment containing silver nanoparticles (50-150 nm) designed for atopic dermatitis treatment was tested on volunteers recruited at the Coronel Institute of Amsterdam (Amsterdam University). The whole stratum corneum (SC) was sampled with the “tape stripping” procedure after different time of exposure. The strips were analyzed with a Scanning Electron Microscope Energy Dispersive X-ray (SEM-EDX) in order to evaluate the presence of silver particles. Three different extraction procedures of silver from the strips were compared and silver was analyzed by means of two different Inductively Coupled Plasma-Mass Spectrometers (ICP-MS). The silver concentration of each strip was plotted as a function of the relative SC depth. We followed the approach based on Fick’s second law of diffusion to estimate the penetration parameters[1,2].

Silver was revealed in all the samples collected both by ICP-MS and SEM-EDX analysis. No significant differences were found between the three methods of extraction. Silver aggregates were revealed even in the deepest layer of SC confirming previous in vitro results. Silver permeation is time dependent and it accumulates in the outer layers of SC.

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ANA-O17

Studio del processo di riduzione del Cr(VI) in terreni contaminati

V. Zelano[a], *E. Pera Caciolo*[a], *M.Ginepro*[a], *A.Bianco Prevot*[a], *D. De Luca*[b]

[a]*Dipartimento di Chimica, Università di Torino, via Pietro Giuria, 5 – 10125 Torino*
[b]*Dipartimento di Scienze della Terra, Università di Torino, via Valperga Caluso, 35 - 10125 Torino*

marco.ginepro@unito.it

L'inquinamento da Cr(VI) ha assunto una grande importanza data la tossicità e cancerogenicità di questa specie. Il Cr(VI) può essere naturalmente ridotto a Cr(III), con tempi di trasformazione in genere molto lunghi e può quindi persistere nel suolo ed essere dilavato causando l'inquinamento di acque superficiali e sotterranee. Studi recenti mostrano l'efficacia di composti organici nella rimozione del Cr(VI) attraverso una complessa rete di processi ossido riduttivi dei quali è difficile discriminare la natura biotica o abiotica. Specie donatrici di e^- come ioni ferrosi, solfuri e sostanza umica sono presenti nei suoli e possono essere coinvolte nella riduzione del Cr(VI). Analogamente alcuni microrganismi del suolo possono promuovere la riduzione enzimatica del Cr(VI) o mediarla attraverso i prodotti della loro attività. In entrambi i casi è fondamentale la presenza/creazione di un ambiente riducente. A questo scopo un approccio promettente è rappresentato dalla tecnica di biorisanamento con nutrienti zuccherini. La presente ricerca si propone di simulare, su scala di laboratorio, il biorisanamento di terreni contaminati da Cr(VI). I riducenti studiati sono stati il glucosio o suoi polimeri e altri composti organici ed inorganici. I parametri monitorati sono stati: pH, contenuto di Cr(VI) e Cr totale, Fe, Ni e Mn. E' stato inoltre valutato l'effetto sul processo di parametri sperimentali quali pH, tempo di contatto, quantità di acqua contenuta nel terreno e contenuto di ossigeno. I risultati ottenuti in presenza di glucosio, uno dei reattivi più utilizzati attualmente nei processi di biorisanamento in situ, mostrano la progressiva scomparsa del Cr(VI) quando si aumentano il tempo di contatto e la quantità di acqua, e si diminuisce la concentrazione di ossigeno. Tuttavia, per lunghi tempi di contatto ed in presenza di elevata quantità d'acqua è stato osservato il rilascio in soluzione da parte del terreno di ioni Fe, Mn e Ni. Sono quindi necessari ulteriori approfondimenti per meglio comprendere il complesso meccanismo che coinvolge il processo di riduzione del Cr (VI) accompagnato al rilascio di altri ioni metallici di rilevanza ambientale.

ANA-O18

Nitrate in central Antarctica: insights on sources and temporal patterns by continuous multi-year sampling

R. Traversi[a], *R. Udisti*[a], *D. Frosini*[a], *S. Becagli*[a], *V. Ciardini*[b], *B. Funke*[c], *C. Lanconelli*[d], *B. Petkov*[d], *C. Scarchilli*[b], *M. Severi*[a], *V. Vitale*[d]

[a] *Dip. di Chimica "Ugo Schiff", Università di Firenze, 50019, Sesto F.no, Italy*
[b] *Lab. for Earth Observations and Analyses (UTMEA-TER) ENEA Rome, Italy*
[c] *Instituto de Astrofisica de Andalucía (CSIC), Granada, Spain*
[d] *ISAC-CNR, Bologna, Italy*

rita.traversi@unifi.it

Since 2005, a continuous, all-year-round aerosol and surface snow sampling has been carried out at Dome C (Central Antarctica, 3233 m a.s.l., about 1100 km far from the coastline) by pre-selected cut-off samplers and multi-stage impactors. Here we present the first multi-year record of nitrate in the atmospheric aerosol (2005-08) and surface snow (2006-08) at Dome C, which can be considered as representative of the Antarctic background aerosol in the high central plateau.

Both aerosol and snow records exhibit a recurring seasonal pattern, with summer sharp maxima and winter minima, although a temporal shift can be observed between aerosol and snow. In fact, aerosol maxima lead of one-two months, possibly due to a higher acidity in the atmosphere in mid-summer, favouring the repartition of nitrate as nitric acid and thus its uptake by the surface snow layers).

On the basis of a meteorological analysis of one major nitrate event, of data related to PSC I extent and of irradiance values, we suggest that the high nitrate summer levels in aerosol and snow are likely due to a synergy of enhanced source of nitrate and/or its precursors (such as the stratospheric intrusions), higher solar irradiance and higher oxidation rates in this season. Moreover we confirm the presence of a substantial contribution of HNO_3/NOx re-emission from the snowpack, which can explain a significant fraction of atmospheric nitrate, maintaining the same seasonal pattern in the snow.

As regarding the data obtained by surface snow specifically, it appears that nitrate is likely to be controlled mainly by atmospheric processes more than source timing, and not on the daily timescale but rather on the seasonal one.

ANA-O19

REEs nel PM10 campionato in Artide come marker di polveri continentali.

R. Udisti[a], *S. Becagli*[a], *G. Calzolai*[b], *F. Frosini*[a], *F. Lucarelli*[b], *M. Malandrino*[c], *S. Nava*[b], *M. Severi*[a], *R. Traversi*[a].

a Dip. Chimica, Univ. Firenze, Via della Lastruccia 3, 50019, Sesto F.no (FI)
b Dip. Fisica e Astronomia, Univ. Firenze e INFN, 50019, Sesto F.no (FI)
c Dip. Chimica, Univ. Torino, 10125 Torino

udisti@unifi.it

Nell'ambito delle Campagne Artiche 2010 e 2011, sono stati raccolti campioni di PM10 a Ny-Alesund (Svalbard, Norvegia) e a Thule (Groenlandia). I campioni sono stati analizzati per IC (composizione ionica) e per ICP-SF-MS (Al, Sc, Cd, Ba, Pb, Si, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Mo e REEs), allo scopo di identificare le sorgenti locali o da long-range dei metalli e delle polveri minerali nei due siti. Sui campioni raccolti nel 2010 a Ny Alesund è stata condotta una analisi statistica multivariata (PMF) per l'identificazione e la quantificazione delle sorgenti. L'elaborazione dei dati ha permesso di appurare che, nei due siti, Pb, Cd, As, Ni, Cu, Zn, Mo, Cr e, in parte, V hanno una dominante origine antropica (EF >10). La differenziazione tra sorgenti antropiche locali e da lunga distanza e' stata effettuata grazie al confronto con il profilo temporale dei nssSolfati (long range trasport durante gli eventi di *Arctic Haze)*. Per i metalli di origine antropica da long-range misurati a Ny Alesund, l'analisi delle retrotraiettorie delle masse d'aria ha suggerito una origine da regioni industrializzate dell'Eurasia (zona di Norilsk e Penisola di Kola); per il sito di Thule, l'origine e' stata individuata nelle emissioni da aree minerarie dismesse nell'Artide Canadese e nella Groenlandia nord-occidentale, nonché dalle aree urbane dell'Ontario e del Quebec. Le REEs sono state utilizzate per l'individuazione delle potenziali aree sorgenti di polveri (PSA). Gli andamenti temporali delle REEs hanno mostrato che, in primavera (trasporti long-range), si hanno le massime concentrazioni delle terre rare leggere (LREE) e degli elementi tipicamente crostali (Al, Si, Ti e Sc); al contrario, in estate (risollevamento di polveri locali), si hanno le massime concentrazioni delle terre rare pesanti (HREE). Attraverso la normalizzazione rispetto alla condrite e considerando vari rapporti diagnostici tra le REEs (LREE/HREE, anomalia dell'Eu, anomalia del Ce, La/Ce, La/Pr, La/Nd e La/Sm), e' stato possibile differenziare e caratterizzare le polveri da trasporti a lungo raggio e di origine locale, fornendo ipotesi sia sulle loro PSA che sulla classificazione mineralogica delle rocce che le hanno originate.

ANA-O20

Determinazione di metalli in tracce nel fitoplancton marino antartico: messa a punto della metodica analitica

S. Illuminati, C.Truzzi, A. Annibaldi, C. Finale, G. Libani, T. Romagnoli, C. Totti, G. Scarponi

Dipartimento di Scienze della Vita e dell'Ambiente, Università Politecnica delle Marche, Via Brecce Bianche, 60131, Ancona, Italia

s.illuminati@univpm.it

È stata messa a punto per la prima volta una metodica per la determinazione di Cd, Pb e Cu nel fitoplancton, con particolare riferimento a quello antartico. Durante la Spedizione Italiana in Antartide dell'estate australe 2011-2012 sono stati effettuati campionamenti di acqua di mare nell'area di Baia Terra Nova, prima, durante e dopo il bloom fitoplanctonico a diverse profondità. I campioni di acqua di mare sono stati separati in varie aliquote, per la determinazione di diverse frazioni di Cd, Pb e Cu (concentrazione totale, frazione disciolta, frazione particellata e frazione associata al fitoplancton). È stata inoltre effettuata l'analisi quali-quantitativa del fitoplancton. L'analisi della componente particellata algale ha richiesto la messa a punto di una procedura di pre-trattamento dei vari campioni che consiste di due fasi: 1) separazione delle cellule fitoplanctoniche dal campione tal e quale, mediante sedimentazione in camera di Utermöhl [1] e aspirazione mediante pasteur collegata a un isolatore di cellule, e 2) digestione al microonde, previa aggiunta di HCl ultrapuro 2:1000 e H_2O_2 ultrapura 1:1000. Le diverse frazioni di Cd, Pb e Cu sono state determinate mediante voltammetria di ridissoluzione anodica con scansione del potenziale ad onda quadra (SWASV) [2]. L'accuratezza della metodologia analitica è stata verificata attraverso l'analisi di un materiale di riferimento certificato per l'acqua di mare (NASS-5) e per il plancton (BCR-414 [3]). Risultati preliminari evidenziano una notevole influenza del fitoplancton sulla distribuzione di Cd, Pb e Cu in acqua di mare, dimostrandone un ruolo significativo nei cicli biogeochimici dei metalli.

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ANA-O21

Contributo Ritirato

ANA-O22

Folding-upon-binding and signal-on Electrochemical DNA Sensor with high affinity and specificity

Alessia Amodio [a,b], *Andrea Idili* [a], *Marco Vidonis* [b], *Matteo Castronovo* [b], *Francesco Ricci* [a]

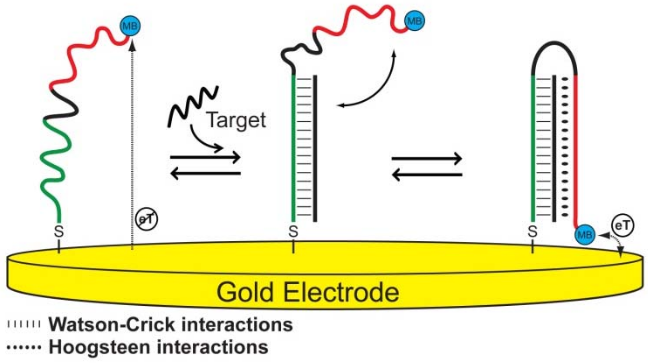
[a] *Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Via della ricerca Scientifica 1, Italy*

[b] *Department of Medical and Biological Sciences, University of Udine, Piazzale Kolbe 4, 33100 Udine, Italy*

alessia.amodio0@gmail.com

Inspired by naturally receptors, based on the use of two recognition elements that simultaneously embrace a single copy of the target, here we have developed and characterized a novel signal-on electrochemical DNA sensor based on the use of a clamp-like DNA probe that binds a complementary target sequence through two sequential events, which lead to the formation of a triplex DNA structure, thus allowing a highly sensitive and specific detection of short DNA sequences.

We demonstrate that this novel target-binding mechanism can improve both the affinity and specificity of recognition compared to a classic, Watson-Crick hybridization-based probe. By using electrochemical signaling to report the conformational change, we demonstrate a signal-on E-DNA sensor with up to 400% signal gain upon target binding.



Moreover, we were able to measure with nanomolar affinity a perfectly matched target as short as 10 bases (K_D = 0.39 nM). Finally, thanks to the molecular "double check" provided by the concomitant Watson-Crick and Hoogsteen base pairings involved in target recognition, such signal-on electrochemical DNA sensor provides excellent discrimination efficiency against a single-base mismatch.

ANA-O23

Oxidative stability of nucleobases

Tonino Caruso, Amedeo Capobianco, Andrea Peluso

Dipartimento di Chimica e biologia, Università di Salerno, Via Giovanni Paolo II, 132 ,
84084, Fisciano, Italia

tcaruso@unisa.it

Differential pulse voltammetry (DPV) and spectroelectrochemistry have provided valuable information about how the inter-base interactions, as H-bonds and π stacking, affect the stability of DNA respect to the oxidative conditions.

DPV measurements have allowed to detect the shift of the oxidation potentials of guanosine (G) and adenosine (A) upon pairing with their complementary bases in apolar solvents.[1,2] The spectrum of the oxidized G-C Watson-Crick complex, recorded at a transparent thin layer electrode during oxidation at controlled potential, has provided an estimate of the energy distribution of low lying electronic states of oxidized DNA.[3,4]. Similar information has been obtained on oligonucleotides containing A and G in different sequences and ratios. They have shown multiple signals, characteristic of π stacked molecular systems, [5] which have allowed to infer the strength of the stacking interaction.[6]

Finally, we evaluated the differences in oxidative stability in the presence of modified nucleobases and the relative association constants of hydrogen-bonded base pairs, by NMR titrations, in order to detect the DNA damages.

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ANA-O24

Carbon black modified GC electrode for the detection of antioxidants compounds of extravirgin olive oil

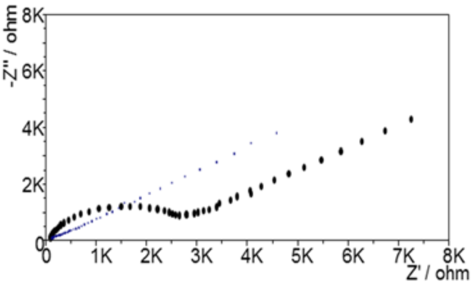
D. Compagnone[a], *M. Del Carlo*[a], *D. Innocenzi*[a], *F. Arduini*[b], *D. Moscone*[b], *G. Palleschi*[b], *L. Agüí*[c], *V. Serafín*[c]

[a] *Facoltà di Bioscienze, Università di Teramo, Via Lerici 1, 64023, Mosciano San Angelo, Italia*
[b] *Dipartimento di Scienze e Tecnologie Chimiche, Università Di Roma "Tor Vergata" Via della ricerca scientifica 00133 Roma, Italia*

c Department of Analytical Chemistry, Faculty of Chemistry, University Complutense of Madrid. 28040-Madrid. Spain

dcompagnone@unite.it

Polyphenols and tocopherols are the main antioxidant compounds found in olive oils. Both polyphenols can be detected by HPLC methods. Alternatively, electrochemical methods can be used especially based on the oxidation to graphite electrode surface. In this presentation the use of Carbon Black (CB) as electrode modifier of both glassy carbon and screen printed electrodes was used to limit the electrochemical fouling of the electrode surface. In the Figure we can show the characterization with IES of electrode surface, with and without CB (line blue and black respectively). The firts results obtained demonstrated a good reproducibility in PBS medium for different polyphenols (n=3, tyrosol 6.9%, Catechol 4.2%, Mixed 1.5, 1.0 % respectively). Also, preliminary experiments have been carried out in organic medium (DMSO/isopropanol) in order to develop an extraction free protocol for the simultaneous electrochemical detection of polyphenols and tocopherols.



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ANA-O25

Electrochemical immunosensor for hepatitis a virus (HAV) determination in food and clinical samples

A. De Stefano[a], *L. Micheli*[a], *M. De Santis*[a], *D. Donia*[b], *M. Divizia*[b], *G. Palleschi*[a]

a Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma "Tor Vergata" Via della Ricerca Scientifica, 00133, Roma, Italia
b Dipartimento di Medicina Sperimentale e Chirurgia, Università di Roma "Tor Vergata", Via Montpellier, 1, 00133, Roma, Italia

alessia.de.stefano@uniroma2.it

Hepatitis A is an acute infectious disease of the liver due to a *picornavirus*, Hepatitis A virus (HAV). Globally, the disease are believed to occur in around 1,4 million people a year eating or drinking contaminated food or water.

Current legislation for water, shellfish (EC 2073/2005 EC B53/2004) and plant (EC 2073/2005) does not provide for any limitation due to the presence of HAV and other enteric viruses in the irrigation and housing water. In addition, there will be no official method for the detection of these viruses. Currently, the environmental presence of HAV virus is only determined after the outbreak. The diagnosis is based on the patient's symptoms and more specifically through the search for anti-HAV IgG antibodies in blood.

In this work we show the development of a disposable electrochemical immunosensor for the detection of *HAV* antigens in food matrices and/or in the environment. This rapid and low-cost analysis method can involve the use of a portable instrument to perform measurements directly in the field.

This electrochemical immunosensor is based on competitive enzyme-linked immunosorbent assay (ELISA) format using screen printed electrodes. Results showed a working range between $1 \cdot 10^{-6} - 1 \cdot 10^{-2}$ IU/mL. The proposed system was applied to food and drinking water. The results obtained on real samples by the proposed immunosensor were compared with those of the qRT-PCR analysis, levels in different samples.

ANA-O26

The use of integrated Michaelis-Menten equation in analytical determination of inhibitors

Aziz Amine[a], *Stefano Cinti*[b], *Fabiana Arduini*[b], *Danila Moscone*[b], *Giuseppe Palleschi*[b]

[a]*Laboratoire Génie des Procédés et Environnement, Faculté de Sciences et Techniques, Université Hassan II - Mohammedia, B.P.146, Mohammadia, Morocco*
[b]*Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Via della Ricerca Scientifica, 00133 Rome, Italy*
.

azizamine@yahoo.fr

There is a large and growing interest in the enzyme inhibition field in order to identify pollutants or drugs that act as enzyme inhibitors. Many drugs based on enzyme inhibition have been commercialized for cancer, diabetes type II and neurologic disorders. Diagnosis of enzyme inhibition and determination of inhibition constant are often found in papers dealing with bioassays and biosensors. Although the huge number of papers published in this field, analyzing all reaction time-course of progress curve of enzyme inhibition is scarce. The advantages of progress curve analysis versus initial velocities will be highlighted in this work. Indeed, the plot of "half time reaction" versus inhibitor concentration contains additional information about kinetic of the enzyme and linear range of the inhibitor. Simplified equation and a graphical method were proposed, valid for all type of reversible inhibition, for the estimation of inhibition constant Ki and determination of inhibitor concentration. A practical examples of inhibition of catalase by cyanide and cholinesterase by fluoride will be presented.

ANA-O27

Studio di mieli toscani monoflorali mediante tecniche chimiche cromatografiche e spettroscopiche

Erica Parri[a]*, *Marco Mattonai*[a], *Mario Cifelli*[a], *Annalaura Restivo*[a], *Ilaria Degano*[a], *Alessandro Lenzi*[b], *Maurizio Zandomeneghi*[a], *Valentina Domenici*[a] *e Erika Ribechini*[a]

[a] *Dipartimento di Chimica e Chimica Industriale, Università di Pisa., Via Risorgimento 35, 56126, Pisa, Italia*
[b] *Chema Srl, via Ernesto Solvay 44, 57016 Rosignano Solvay, Italia*

erica.parri86@gmail.com

Il miele è uno degli alimenti che caratterizzano la produzione agricola della regione Toscana; la grande variabilità pedoclimatica del territorio regionale permette agli apicoltori di ottenere tipologie di miele di differente origine botanica, a seconda della zona e del periodo di raccolta del nettare da parte delle api. Oggetto di questo studio [1] sono stati circa cinquanta campioni suddivisi per sette diverse varietà di miele monoflorale artigianale toscano, di provenienza certa e derivante da fioriture localizzate in aree geografiche definite: acacia, castagno, girasole, sulla, marruca, erica e trifoglio, di cui sono stati analizzati alcuni dei suoi componenti in tracce, tra cui acidi fenolici e composti flavonoidi. Sono state utilizzate sia tecniche chimico-analitiche micro distruttive (estrazione e purificazione dalla componente maggioritaria zuccherina e separazione mediante cromatografia liquida con rivelatore DAD) che chimico-fisiche non distruttive sul campione nello stato 'bulk' (Fluorescenza Front-Face). L'interesse nella ricerca, identificazione e quantificazione delle specie chimiche sopra elencate è legata sia alla individuazione di marker per l'autenticazione dell'origine botanica del miele sia per dare valore aggiunto al prodotto e supportare studi biologici sulle proprietà terapeutiche del miele, dovute alla presenza di tali composti, di cui è nota la capacità antiossidante.

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ANA-O28

Colorimetric method for the direct determination of total polyphenols in the matrix: application to virgin and extra virgin olive oil

Flavio Della Pelle[a,b]*, Roberta Pasquarelli*[a]*, Alberto Escarpa*[a*]*, Dario Compagnone*[b]*, Michele Del Carlo*[b]

[a]*Faculty of Bioscience and Technology for Food, Agriculture and Environment, University of Teramo, 64023, Teramo, Italy*
[b]*Departamento de Química Analítica, Química-Física e Ingeniería Química. Facultad de Química. Universidad de Alcalá, 28871 Alcalá de Henares, Madrid, España*

flaviod.p.86@hotmail.it

In this work, a simple gold nanoparticles (AuNPs) based colorimetric assay for the total polyphenols content determination of olive oil has been developed. As demonstrated in previous work [1-3] the endogenous polyphenols present in food samples are able to drive the synthesis of AuNPs, reducing the gold (III) to gold (0). This method relies on the formation of AuNPS in organic-aqueous medium, it requires no preparation or extraction of the sample, in fact, it involves the direct use of olive oil. The process of generation of AuNPs is characterized by the spectrophotometric reading, which uses the absorption band of localized surface plasmon (LSPR) at 540 nm. It was also demonstrated that for the proposed method, the compounds naturally present in the food matrix under consideration, extra vergin olive oil and virgin olive oil, are not able to influence the spectrophotometric response. To this purpose tocopherols, acidity, peroxide number and the present pigments (carotenoids and chlorophylls) have been studied. The results obtained were compared with two classical methods for the quantification of total polyphenolic content in food samples, for this purpose 28 olive oil samples have been studied. An excellent correlation ($y=1.0149x-8.1044$; $R = 0.989$) with the colorimetric method of Folin-Ciocalteu (F.C.) was obtained. A good correlation ($y=4.8072x+14.632$; $R = 0.904$) was obtained also with the high performance liquid chromatography method (HPLC-UV/VIS). Both methods (F.C. and HPLC) require the sample extraction.

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ANA-O29

3-hydroxy-3-methyl glutaryl flavonoids (HMG-flavonoids) in bergamot: Recent developments and outlook

L Di Donna[a], L Bartella[a], F Mazzotti[a], G Gallucci[a], G De Luca[a], A Napoli[a], AR Cappello[b], G Sindona[a]

a Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Via P. Bucci, cubo 12/D, 87030, Rende (CS), Italia
b Dipartimento di Farmacia e Scienze della Salute e della Nutrizione, Università della Calabria, Edificio Polifunzionale, 87030, Rende (CS), Italia

l.didonna@unical.it

Bergamot fruit (Citrus bergamia Risso & Poiteau) is known by the ethnopharmacology for its anticholesterolaemic activity. In the last years, two new acyl flavonoids have been characterized in the juice and in other part of the fruit;[1] the main characteristic of such compounds is the presence of the 3-hydroxy-3-methyl glutaryl (HMG) moiety linked as ester to the glycosidic portion of the molecules, which makes them structurally similar to statins. It has been shown that those HMG-flavonoids inhibit in vitro the HMGR enzyme involved in the biosynthesis of cholesterol.[2] More recently, it has been investigated the role of the HMG-flavonoids enriched fraction from bergamot fruit, in comparison with simvastatin, in lowering the values of total cholesterol, LDL-cholesterol and triglycerides in a rat model.[3] The recent developments on the investigation of HMG-flavonoids are here presented. In particular new compounds from bergamot fruit containing the HMG ester have been characterized through high resolution mass spectrometry and nuclear magnetic resonance experiments.

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ANA-O30

Proprietà funzionali del caffè

Daglia M, Di Lorenzo A, Curti V

Dipartimento di Scienze del Farmaco, Università di Pavia, Via Taramelli 12, 27100, Pavia, Italia

maria.daglia@unipv.it

Gli alimenti che, oltre a soddisfare i fabbisogni nutrizionali, esercitano un ruolo protettivo nei confronti del nostro organismo, sono in genere definiti alimenti funzionali e gli specifici componenti responsabili degli effetti protettivi riscontrati, vengono indicati con il neologismo di nutraceutici. Tra i componenti a nota attività nutraceutica vi sono i polifenoli, che sono oggetto di studio per i loro potenziali effetti protettivi contro varie patologie croniche, quali alcune forme di tumore, malattie cardiovascolari e neurodegenerative, diabete, cataratta e patologie associate all'invecchiamento. L'azione protettiva dei polifenoli è stata inizialmente attribuita al loro potere antiossidante e, più recentemente, è stata dimostrata la loro capacità di interagire con il genoma e, di conseguenza, di indurre l'espressione di enzimi antiossidanti e detossificanti o di modulare i processi anti-infiammatori.

Il caffè è la terza bevanda più consumata al mondo, non solo per le sue proprietà sensoriali e per il contenuto in caffeina, che ha effetti tonici e stimolanti, ma anche per le potenziali attività nutraceutiche, dimostrate dai risultati di numerose indagini, che hanno indicato un legame tra il consumo di caffè e lo stato di salute. I risultati delle ricerche condotte negli ultimi venti anni hanno infatti dimostrato che il caffè ha una potenziale attività anticarie dovuta all'attività antibatterica, antiadesiva e anti-biofilm [1], e ha potere antiossidante per le sue proprietà radical scavenger, riducenti e chelanti i metalli pesanti [2]. Risultati più recenti, che hanno mostrato che il caffè agisce sui fattori epigenetici, aprono a nuove aree di ricerca, offrendo interessanti prospettive per la comprensione degli effetti del consumo di caffè sulla salute.

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ANA-O31

Evaluation of oxidized buckypaper as adsorbent for the solid phase extraction of cobalamines from milk

V. Pérez-Fernández, A. Gentili, A. Martinelli, E. Morganti, R. Curini.

Department of Chemistry, Faculty of Mathematical, Physical and Natural Science, Sapienza University of Rome, Piazzale Aldo Moro 5, 00185 Rome, Italy

virginia.perez@uniroma1.it

In nature, each vitamin is represented by several structurally similar forms with different biological potency and/or functions, named vitamers. Vitamin B_{12} includes a group of organometallic compounds with antipernicious anemia activity, known as cobalamins that differ for the β-ligand. They all originates from bacterial synthesis and, therefore, occur only in foods of animal origin such as milk. Knowing the natural distribution of a vitamer family permits to better understand the nutritional properties of a specific food. For B_{12}, the available data is usually the total concentration because, during the extraction procedure, all its homologues are converted in CNCbl which is the most stable form determined by microbiological assay, radioassay or LC-UV. For the speciation of cobalamins, LC is indispensable but it is complicated by the structural similarity of B_{12} homologues. Other analytical difficulties are the low endogenous concentrations, the detection system sensitivity, the strong interaction with proteins, and the instability towards light, oxidants and extreme pH values. Therefore, extraction procedure is a very critical step.

In this work, it has been developed a new analytical method for the determination of four cobalamins (CNCbl, MeCbl, AdoCb, OHCbl) in cow milk. The extraction procedure was based on dilution/precipitation of the milk sample with 50 mM sodium acetate buffer (pH 4.0), followed by SPE combining two types of adsorbents: OASIS HLB commercial cartridges coupled to disks of Buckypaper (BP), a nanoporous felt composed of oxidized multiwalled carbon nanotubes. Recoveries were higher than 60% for all the cobalamins. Apart from the great potential of BP in the extraction of organic compounds, its chemical stability makes this material promising for a potential reuse after an adequate chemical regeneration. The analysis of the extracts was performed by LC coupled to mass spectrometry on a C18 analytical column in less than 10 min. Finally, the validated method was applied to the determination of the natural content of the four homologous B_{12} in cow milk samples.

ANA-O32

NMR-based metabolomic in food characterization

Luisa Mannina[a,b], *Anatoly P. Sobolev*[b], *Noemi Proietti*[b], *Donatella Capitani*[b]
[a]*Dipartimento di Chimica e Tecnologie del Farmaco, Sapienza Università di Roma, Piazzale Aldo Moro 5, I-00185 Rome, Italy*
[b]*Istituto di Metodologie Chimiche, Laboratorio di Risonanza Magnetica "Annalaura Segre", CNR, I-00015 Monterotondo, RM, Italy*

Luisa.mannina@uniroma1.it

NMR spectroscopy has found constantly increasing applications in metabolomics and food chemistry due to its ability to solve spectra of complex mixtures and to recognize and quantify components without chemical separation[1]. ^{1}H high field NMR spectroscopy has shown to be a valuable tool for the qualitative and quantitative analysis of the metabolic profiling of foodstuff. The quantitative analysis of the metabolic profiling along with the application of a suitable statistical analysis has allowed food characterization in terms of geographical origin, genotype and farming. The potential of NMR spectroscopy to detect food adulterations has been also demonstrated. Here, the NMR methodology used to study foodstuffs is discussed reporting some significant applications. [2-4]

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ANA-O33

Mass Spectrometry-based proteomic approach in *Oenococcus oeni* enological starter

Napoli Anna[a], Aiello Donatella[a], Aiello Gilda[a], Cappello Maria Stella[b], Di Donna Leonardo[a], Mazzotti Fabio[a], Materazzi Stefano[c], Sindona Giovanni[a]

a Department of Chemistry and Chemical Technologies, University of Calabria, Via P. Bucci, Cubo 12/D, 87036 Arcavacata di Rende (CS), Italy
b CNR, Institute of Science of Food Production (ISPA), Lecce, Italy
c Department of Chemistry, "Sapienza" University of Rome, Rome, Italy

amc.napoli@unical.it

Oenococcus oeni (*O. oeni*) is an autochthonous alcohol-tolerant, acidophilic lactic bacterium species (LAB) naturally present in grapes.[1] The *O. oeni* population is characterized by genetic and biochemical variability, and it is deeply studied in order to confirm the genetic diversity and enological potential. It is also characterized by high population complexity and plays an important role in the improvement of the organoleptic quality and sensorial properties of wines.[2]

A simple procedure is proposed for selective protein solubilization and trypsin digestion, followed by off-line liquid chromatography−matrix assisted laser desorption ionization mass spectrometry (LC−MALDI MS) analysis of Oenococcus oeni (O. oeni) bacterium. Peptides were identified from tryptic digests using sequencing by tandem mass spectrometry and database searches. Cytoplasmic and membrane related proteins (MRP) were identified in the O. oeni bacterium. MS/MS data analysis points out 13 peptides having one point mutation from 9 proteins. The major microheterogeneity was found for Zn-dependent alcohol dehydrogenase (Zn-ADH, Q04GE6) and 60 kDa chaperonin (GroEL, Q04E64) that are involved in methionine catabolism and post-translational protein folding, respectively. MS/MS data processing also leads to the identification of 34 unique phosphorylation sites from 19 phosphoproteins.

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ANA-O34

DNAzyme switching probes for the quantitative detection of transcription factors

Gianluca Adornetto[a], Alessandro Porchetta[a], Giuseppe Palleschi[a], Kevin W. Plaxco[b], Francesco Ricci[a]

a Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, via della Ricerca Scientifica, 00133 Roma, Italia
b Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106, United States

gianluca.adornetto@uniroma2.it

In recent years, switched-based biosensors, proteins or nucleic acids that reversibly shift between two or more conformations in response to the binding of a specific target ligand, have drawn great attention due to their specific attributes. In particular, the binding-specific conformational changes offer a robust means of transducing a binding event into an output signal that is not easily mimicked by non-specific effects. Furthermore, it is possible to describe the ligand-induced biomolecular switches via a 3-state population-shift mechanism in which the observed affinity depends on the intrinsic affinity of our receptor modulated by the switching constant (K_s). It is possible to control the K_s and then tune, extend, or narrow the dynamic range of biomolecular receptors with different strategies, as, for example, mutational approach outside the binding site. In this work, we present a new class of DNAzyme switching probes for the detection of DNA binding proteins. DNAzymes are auto-catalytic DNA molecules able to show a signal output. In particular, we used a DNAzyme with a peroxidase mimicking catalytic activity, formed by specific G-quadruplex structures in association with the cofactor Hemin. After the binding with a DNA binding protein (Transcription Factor, TF), the induced switch of the probe releases a tail of the molecule able to form the DNAzyme. After the addition of a HRP-substrate (TMB + H2O2), we measure the activity of DNAzyme that is proportional to the concentration of TF. We show here results about the detection of different TFs, as TATA-binding protein.

ANA-O35

Electrochemical sensor for vancomicyn based on electroactive nanoparticles of Molecularly Imprinted Polymers

Elisabetta Mazzotta[a], *Antonio Turco*[a], *Cosimino Malitesta*[a],

Iva Chianella[b], *Sergey A. Piletsky*[c]

[a]*University of Salento, Dipartimento di Scienze e Tecnologie Biologiche ed Ambientali,*

Via Monteroni, Lecce, Italy,[b]*CranfieldUniversity, School of Engineering, Vincent Building, MK43 0AL, Bedfordshire, Cranfield, UK,*[c]*Department of Chemistry, College of Science and Engineering, University of Leicester, LE1 7RH, United Kingdom*

elisabetta.mazzotta@unisalento.it

Molecularly Imprinted Polymers (MIPs) are synthetic receptors containing cavities able toselectively recognize the target analyte, largelyapplied inmolecular recognition and in sensing systems[1]. Their application in sensors requires the improvement of binding kinetics and the complete template removal. The design of MIPs at nanodimensional scale has been demonstrated to enhancingsurface-to-volume ratio thus making binding sites more accessible. DifferentMIP nanostructures have been prepared [1] and applied in sensingdevices. Among these, MIP nanoparticles have attracted great attention and different integration with thetransducer surface have been proposed including their entrapment in electro-synthesizedfilms [1]. In this work we describe an electrochemical sensor based on electroactive MIP nanoparticles (NP) deposited on an electropolymerized film for theindirect electrochemical detection of vancomicyn. Electroactive MIP NP for vancomicyn are synthesized by solid-phase synthesis [2] adding vinyl-ferrocene to polymerization mixture and their entrapment in/on different electrosynthesized polymers is explored. The electrochemical detection of vancomicyn is performed by exploiting the modification of theelectrochemical signal of MIP NP, being possibly ascribed to the interaction MIP NP-vancomicyn influencing the electron transfer of the ferrocene redox sites within nanoparticles.

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ANA-O36

Platinum Nanoelectrodes for the Detection of Hydrogen Peroxide

Alberto Citron, Daniele Veclani, Dario Battistel, Carlo Bragato, Salvatore Daniele

Dipartimento di Scienze Molecolari e Nanosistemi, Università Cà Foscari Venezia, Calle Larga S. Marta, 2137, 30123 Venezia, Italy

sig@unive.it

Platinum materials are widely used electrocatalysts for the oxidation and reduction of H_2O_2. However, the current response to hydrogen peroxide is under mixed kinetic and diffusion control and further complicated by competitive adsorption of oxygen onto Pt active surface sites and the protonation of the adsorbed H_2O_2 complex species. Therefore, a lack of Pt surface sites limits the rate of the electrode process and causes a current depression for higher H_2O_2 concentrations. High surface platinum black and mesoporous platinum microelectrodes have been used for H_2O_2 detection, because they circumvent the problems related to the limited number of active sites. Nanometer sized electrodes, which display intriguing features can be successfully exploited for electroanalysis of hydrogen peroxide in confined environments over nano- and pico-liter levels. Reproducible nanoelectrode fabrication with highly controlled electrode geometry can be achieved by pulling metal micro-wires into glass capillaries with the help of a laser pipette puller. In this paper we report on the voltamperometric behaviour of hydrogen peroxide in phosphate buffer media at disk nanoelectrodes with radii over the range 20- 600 nm, and show that the current responses at these electrodes are larger than those predictable on the basis of the geometric surface area and mass transport coefficient. This is due to the fact that these platinum nanoelectrodes display an effective surface area much larger than their geometric surface area.

ANA-O37

Electrosynthetized Au-MOx nanostructures for gas sensing

Elena Dilonardo[a], Michele Penza[b], Gennaro Cassano[b], Marco Alvisi[b],Cinzia Di Franco[c], Francesco Palmisano[a], Luisa Torsi[a], Nicola Cioffi[a]

1 Dipartimento di Chimica, Università di Bari Aldo Moro, via Orabona 4, 70126 Bari, Italia
2 ENEA-Centro di Ricerca di Brindisi-72100 Brindisi, Italia
c Dipartimento di Interateneo di Fisica, CNR-IFN LIT3, Università di Bari Aldo Moro, Via Amendola 173 70126 Bari, Italia

nicola.cioffi@uniba.it

Nanostructured metal oxides (MOx) are widely used to fabricate gas sensors, since the semiconducting nature of some of them makes possible the change of their electrical conductivity when the composition of the surrounding atmosphere changes. To increase the sensitivity and selectivity of MOx-based sensor layers different strategies have been developed; one of them is doping MOx nanostructures with noble metal nanoparticles (NPs).[1] The functionalization of MOx with metal NPs promotes and optimizes sensing characteristics of pristine oxides,[2] on the basis of their catalytic activity that activates MOx by chemical and/or electrical sensitization. In this work a one-step strategy based on sacrificial anode electrolysis is proposed to obtained stabilized gold Au NPs [3] directly deposited on the surface of MOx nanostructured powders. The resulting nanostructures are proposed as active layer in chemoresistive sensors for pollutant gas detection. The nanostructured materials were firstly thermally annealed under mild conditions and, subsequently, they were morphologically and chemically characterized using TEM, SEM, as well as XPS spectroscopy which revealed the formation of nanoscale gold, and its successful decoration on metal oxide nanoparticles. Au-doped and undoped MOx thin films were tested as active layers for gas sensing application. The effect of the MOx composition and of the Au-doping on the sensor performance were analyzed.

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ANA-O38

Caratterizzazione di un bioelettrodo a trasferimento elettronico diretto basato su un materiale composito GOx/CNTs

S. Cresci[a], *A. Curulli*[b], *G. Favero*[a], *F. Mazzei*[a], *D. Zane*[b]

a Dipartimento di Chimica e Tecnologie del Farmaco, Sapienza Università di Roma,
P.le Aldo Moro, 5 – 00185 Roma
b CNR Istituto per lo Studio dei Materiali Nanostrutturati (ISMN),
Via del Castro Laurenziano, 7 - 00161 Roma

gabriele.favero@uniroma1.it

Un efficace trasferimento elettronico diretto (DET) tra il sito attivo di un enzima redox e il materiale elettrodico permette di ottenere bioelettrodi che possono essere impiegati sia come biosensori di terza generazione che come elettrodi di celle a combustibile biologico (*biofuel cells*). In questa ricerca è stato caratterizzato sia dal punto di vista elettrochimico (voltammetria ciclica, spettroscopia di impedenza elettrochimica) che morfologico (microscopia a scansione elettronica) un bioelettrodo ottenuto dalla compressione meccanica di glucosio ossidasi (GOx) e nanotubi di carbonio (CNTs) [1].

L’analisi voltammetrica ha permesso di evidenziare il DET per la GOx individuando una coppia di picchi redox con un potenziale formale pari a -0,211 V e correnti di picco che presentano un andamento lineare con la velocità di scansione come atteso da un sistema legato; in presenza di glucosio il voltammogramma si modifica secondo un tipico profilo catalitico. Mediante la spettroscopia di impedenza elettrochimica (analisi della risposta in frequenza del sistema in esame) è possibile assimilare il sistema elettrochimico a un circuito equivalente. Tale circuito equivalente consente di ricavare per l’interfase elettrochimica parametri quali resistenza al trasferimento di carica, capacità del doppio strato elettrico e impedenza diffusionale di Warburg. E’ quindi possibile studiare i processi che avvengono all’interfase elettrochimica e che coinvolgono i materiali elettrodici e le specie che danno luogo ai processi redox. Si è osservato così il comportamento del bioelettrodo in tampone fosfato e in soluzioni di glucosio a diverse concentrazioni sia in presenza che in assenza di ossigeno. Sono stati confermati i dati ottenuti in voltammetria e consentendo una taratura analitica in funzione delle concentrazioni di glucosio. I risultati ottenuti hanno permesso di valutare l’impiego del bioelettrodo sia come biosensore a DET per il glucosio sia come anodo per la realizzazione di una *biofuel cell* DET-glucosio/ossigeno.

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ANA-O39

Regiochemical Assignment of Sulfoquinovosyldiacylglycerols by Tandem Mass Spectrometry

S. Granafei[a], G. Valenza[a], I. Losito[a,b], F. Palmisano[a,b], T.R.I. Cataldi[a,b]

[a]Dipartimento di Chimica, [b]Centro Interdipartimentale SMART, Università degli Studi di Bari Aldo Moro, Via E.Orabona, 4 - 70126 Bari, Italia

sara.granafei@uniba.it

Sulfoquinovosyldiacylglycerols (SQDGs), known as plant sulfolipids, are a component of plant photosynthetic membranes for which various functions have been proposed, including orientation of chlorophyll in the chloroplast membranes and stabilization of chloroplast coupling factors against cold inactivation [1]. SQDGs are not, however, restricted to chloroplast membranes of plants. Indeed, their occurrence has been demonstrated in photosynthetic bacteria, where their role is most likely as substitutes for phospholipids under phosphate limiting conditions [2]. Liquid chromatography with mass spectrometry (LC-MS) can directly analyze various lipids as intact molecules and preserve the information inherent in their chemical structures. LC with tandem mass spectrometry (LC-MS/MS) with collision-induced dissociation (CID) provides structural information of lipids, including anionic SQDGs, from their fragmentation patterns [3]. However, regiochemical assignment of fatty acyl chains at the *sn*-1 and *sn*-2 positions of glycerol is not trivial because there exists the need to distinguish between isomeric/isobaric SQDGs such as *cis*-18:1Δ^9 and *cis*-18:1Δ^{11} or *cis*/*trans*-18:1Δ^{11}, and so forth. Thus, complete LC separation is needed for accurately identifying and quantifying SQDGs. Along with the SQDG head group specific product ion at *m/z* 225 ($C_6H_9O_7S^-$), which represents the '*fingerprint*' ion for the identification of this lipid class, the observed spectra under CID-MS/MS of deprotonated molecules, $[M\text{-}H]^-$, exhibit product ions with intense signals due to $[M{-}H{-}RCOOH]^-$ as a result of fatty acid loss from *sn*-1 as well as *sn*-2 position of the glycerol backbone. The identification and regiochemical assignment of deprotonated SQDG lipids from crude membrane lipid extracts from the bacterium *Rhodobacter sphaeroides* and leaves of *Spinacia oleracea* will be presented and discussed.

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ANA-O40

Identification of bioactive fish peptides by "omic" analytical methods

Anna Laura Capriotti[a], *Francesco Gasparrini*[b], *Roberto Samperi*[a], *Serena Stampachiacchiere*[a], *Aldo Laganà*[a]

a Dipartimento di Chimica, Università degli studi di Roma La Sapienza P.le Aldo Moro 5,00185 Roma (Italia)
b Dipartimento di Chimica e Tecnologie del Farmaco, Università degli studi di Roma La Sapienza P.le Aldo Moro 5,00185 Roma (Italia)

annalaura.capriotti@uniroma1.it

Food derived constituents represent important sources of several classes of bioactive compounds. Among them peptides have gained great attention in the last two decades thanks to the scientific evidence of their beneficial health effects. The various functionalities for bioactive peptides have just been described, including anti-oxidative, anti-hypertensive and antimicrobial activity. The need to better understand their positive health effects has prompted the development of analytical strategies for their investigation in complex food matrices. The aim of this work was to carry out a peptidomic strategy developing an advanced analytical techniques for separation and characterization of peptides in food matrices, and to evaluate their potential antimicrobial activity. In this study we compared and evaluated four different experiments for the identification of sarcoplasmic and myofibrillar fish peptides. This study is aimed at the development of a simple and fast method for the identification of peptides that could arise from fish meat if trypsin was the only digestive enzyme acting on fish meat proteins. We tested the use of ultrafiltration membranes with a molecular weight cut-off of 3000 Da. In addition, an innovative multidimensional protein identification approach combining organic monolithic and reversed phase pre-columns was developed and applied to peptides separation and identification to improve the performance and the throughput of bottom up approach.

ANA-O41

New strategies to improve the nebulization process in Direct-EI interface

Laura Magrini[a], Giorgio Famiglini[a], Veronica Termopoli[a], Fabiana Capriotti[a], Hanno Evard[b], Achille Cappiello[a].

a DiSTeVA, University of Urbino "Carlo Bo" LC-MS laboratory, Piazza Rinascimento, 61029, Urbino, Italy;
b Institute of Chemistry Chair of Analytical Chemistry, University of Tartu, Ravila 14a, 50411, Tartu, Estonia.

laura.magrini@uniurb.it

The Direct-EI is a new type of interface that combines liquid chromatography (LC) with electron ionization (EI) mass spectrometry using a single quadrupole analyzer, offering the following main advantages: easy compound identification using on-line spectra libraries; no evident matrix effects; low cost instrumentation. The mechanism of Direct-EI is quite simple and it is based on four steps: 1) aerosol formation, 2) solvent evaporation, 3) solute vaporization and finally 4) electron ionization of the analytes. In this way it is possible to detect and quantify a wide range of substances in a single chromatographic run, including thermally labile ones. To ensure an optimal vaporization of these compounds (such as hormones) we have re-designed the nebulizer for a better heat transfer. The first step was the use of a nebulization gas (N_2) to produce a better and fine spray. The results were not optimal because of the high vacuum instability that affects nebulization and vaporization processes in the presence o a make-up gas. The second step was to increase (without nebulization gas) the heat transfer at the tip of the capillary using a modified metal adapter. The capillary position inside the ion source is fundamental for a good heat transfer: it is advisable to apply high temperature at the top of the capillary and the adapter gave promising results. Validation of the new interface performance will be conducted evaluating linearity, LODs and LOQs, and reproducibility. Matrix effects will be deeply investigated on real samples as well.

ANA-O42

Tracing environmental pollution processes in aquatic systems by Hg isotope ratio determination

A. Berni[a], C. Baschieri[a], C. Durante[a], M.C.Rossi[a], D. Manzini[a],
A. Emili[b], F. Rampazzo[c], D. Berto[c], T. Fortibuoni[c], S. Noventa[c],
S. Covelli[b], A. Marchetti[a]

a Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia, Via G. Campi 183, 41125 Modena, Italy

b Dipartimento di Matematica e Geoscienze, Università di Trieste, Via Weiss 2, 34128 Trieste, Italy.

c Istituto Superiore per la Protezione e la Ricerca Ambientale, Loc. Brondolo, 30015 Chioggia, Italy

alex.berni@unimore.it

Mercury stable isotopes are an excellent tool to distinguish among different sources of this element and to investigate its transformation processes in environmental compartments and in food webs. To do this, an highly precise and sensitive method was set up by using a cold vapor generator system (CVG) to introduce gaseous Hg^0 into a multicollector ICP-MS spectrometer[1], allowing "dry plasma" measurement conditions to minimize any matrix effect on the obtained results. Instrumental mass bias on measures was accounted by simultaneously monitoring $^{205}Tl/^{203}Tl$ from the isotopic SRM NIST 997 and applying the correction algorithm proposed by Yang and Sturgeon[2].

This method was applied to the case study of Grado and Marano Lagoon, Italy and of the northern Adriatic Sea. The lagoon has been subjected to Hg input from both industrial waste (chlor-alkali plant) and residues of long-term mining activity (Idrija mine, NW Slovenia) transported by the Isonzo river and marine currents[3].

Mercury isotopic ratios detected on sediments, fish and mollusk tissue samples show both mass-dependent (MDF) and mass-independent (MIF) fractionation phenomena for Hg. With these data, it has been possible to gain a more detailed characterization of the Hg input sources in the lagoon and to gather information on the uptake processes of the element and its derivatives in living organisms.

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ANA-O43

LC-ESI-MS^n Characterization of Ornithine Lipids from *Rhodobacter sphaeroides*

S. Granafei[a]*, G. Valenza*[a]*, V. De Leo*[c]*, F. Italiano*[c]*, M. Trotta*[c]*,*
F. Palmisano[a,b]*, T.R.I. Cataldi*[a,b]

[a]*Dipartimento di Chimica,* [b]*Centro Interdipartimentale SMART,* [c]*Istituto Processi Chimico Fisici CNR, Università degli Studi di Bari Aldo Moro, Via E.Orabona, 4 - 70126 Bari, Italia*

sara.granafei@uniba.it

Ornithine lipids (OLs) are lipids containing a 3-OH fatty acyl group (R_1), attached through an amide linkage to the α-amino group of ornithine. A second fatty acyl chain (R_2) is ester-linked to the 3-hydroxy position of the first fatty acid. One common observation is that OLs, owing to their zwitterionic nature, are involved in stress response of bacteria [1,2] with outer membrane stabilization. To clarify the involvement of both fatty acyl chains (R_1 and R_2) of OLs, the use of an advanced analytical approach is mandatory. ESI-MS has proven to be highly successful in the analysis of phospholipids and closely related compounds. Indeed, the fragmentation behaviour of OLs by ESI-CID MS/MS has been described by Reid and co-workers [3] using bacterial extracts of photosynthetically grown *R. sphaeroides* and the presence of isobaric/isomeric compounds have been invoked. As far as we know, no liquid chromatography (LC) separation of OLs has been reported yet. The main aim of this work was to investigate the OLs profile by LC-ESI-MS/MS and LC-ESI-MS^3. A reversed phase LC method was devised using a fused-core C18 amide column and a gradient elution with water/methanol both containing 2.5 mM of ammonium acetate. A systematic investigation was performed on bacterial extracts of *R. sphaeroides* and the identification of the following OLs was obtained in detail: 36:1, 36:2, 37:1, 37:2, 38:1, 38:2, 39:1, 39:2. Interestingly, the occurrence of several previously unknown isomeric OLs at *m/z* 677.5 (18:0/18:1, 18:0/18:1*, 20:1/16:0), *m/z* 689.5 (18:0/19:2) and *m/z* 707.5 (20:0/18:0) has been demonstrated.

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ANA-O44

Determination of volatile organic compounds in human breath samples for heart failure monitoring

T. Lomonaco[a], *S. Ghimenti*[a], *F. Detti*[a], *F. Bellagambi*[a], *M. C. Scali*[b],

A. Simioniuc[b], *F. Di Francesco*[a, c], *R. Fuoco*[a]

[a] *Department of Chemistry and Industrial Chemistry, University of Pisa, Via Risorgimento 35, 56126, Pisa, Italy*
[b] *Cardiac, Thoracic and Vascular Department, University of Pisa, Via Paradisa 2, 56124, Pisa, Italy*
c Institute of Clinical Physiology, CNR, Via G. Moruzzi 1, 56124, Pisa, Italy

tlomonaco@ifc.cnr.it

Heart Failure (HF) is a rapidly increasing cardiovascular chronic disease, being the main cause of mortality and poor quality of life in the western societies. According to the European Heart Failure Association, 26 million people experience HF globally and 3.6 million people are diagnosed with HF, every year. Nowadays, the common clinical approaches employed to diagnose and monitor HF are invasive and not suitable to predict adverse effects. From this point of view, breath analysis is an appealing tool for an effective, easy, painless and non-invasive monitoring of patients suffering from HF since the chemical composition of exhaled breath reflects the physiological and pathophysiological conditions.

Aim of this study was the monitoring of the concentration profile of Volatile Organic Compounds (VOCs) in breath samples from 10 HF patients in resting and stress (physical exercise) conditions and the evaluation of the correlation between standard clinical tests (such as ECG, echocardiography, natriuretic peptides in blood) and breath concentration of specific VOCs (e.g. acetone and pentane). Mixed expired breath samples were collected into 3 L Nalophan bags before and immediately after the stress test, simultaneously to blood draw. 250 mL of breath were transferred at 50 mL/min into a Tenax GR adsorption tube. Analysis was performed by a thermal desorption-gas chromatography-mass spectrometry system. The results are critically evaluated and the correlation with standard clinical tests is discussed.

ANA-O45

Correlation between Lyso-phospholipids and thermal history in mussels: an LC-ESI-MS/MS investigation

I. Losito[a,b]*, L. Facchini*[a]*, C. Cianci*[a]*, S. Granafei*[a]*,*
T.R.I. Cataldi[a,b]*, F. Palmisano*[a,b]

[a]*Università degli Studi di Bari "Aldo Moro", Dip. Chimica, Via Orabona, 4- 70126 Bari, Italy*

[b]*Centro Interdipartimentale SMART, Via Orabona, 4- 70126 Bari, Italy*

ilario.losito@uniba.it

As for other seafood products, the beneficial effects of mussel consumption on human health are well recognized, with their bioactive lipids playing a key role even in the development of functional foods or dietary supplements [1]. Unfortunately, the lipid components of mussels are susceptible to alteration due to chemical and/or enzymatic oxidation and/or to hydrolysis reactions, which are processes strictly related to storage conditions, especially storage temperature [2]. Even when commercialized as fresh products, mussels may experience a multi-step thermal history, with refrigeration at 4-6 °C often alternated to storage at higher temperatures (even room temperature). Moreover, when produced in countries such as Chile, New Zealand and others that are far from the main markets (Europe, North America), mussels have to be frozen and stored at very low temperatures (at least -15°C), due to long-range transportation plan requirements. Such thermal treatments are expected to affect the integrity also of phospholipids (PLs), one of the sources of mussel precious polyunsaturated fatty acids, through activation of phospholipases. The present communication will thus focus on the analysis of residual Lyso-phospholipids (Lyso-PLs), selected as direct biomarkers of PL hydrolysis, in mussels resulting from different thermal histories. Recently, hydrophilic interaction interaction liquid chromatography-tandem mass spectrometry (HILIC-MS/MS) was successfully employed to characterize complex phospholipid mixtures [3]; here, the same approach has been employed to identify Lyso-PLs and their distributions in different mussel samples.

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ANA-O46

Mass Spectrometric characterization of two Arginine Kinase of *Leptomatix dactyolpii* wasp venom

Cristiana Labella[a], *Giuliana Bianco*[a], *Patrizia Falabella*[a], *Simona Laurino*[a], *Gerarda Grossi*[a], *Alessandro Buchicchio*[a], *Rosanna Salvia*[a], *Basem Kanawati*[b], *Philippe Schmitt-Kopplin*[b], *Heiko Vogel*[c]

[a]*Dipartimento di Scienze, Università della Basilicata, Potenza, Italy.* [b]*Helmholtz Zentrum München Research Unit Analytical BioGeoChemistry (BGC), Neuherberg, Germany.* [c]*Department of Entomology, Max Planck Institute for Chemical Ecology, Jena, Germany*

cristiana.labella@unibas.it

Mass spectrometry (MS)-based proteomic is currently considered the election tool for protein identification. Here, we describe the identification and analysis of two Arginine Kinases from *Leptomastix dactylopii* (Hymenoptera, Encyrtidae) venom, using mass spectrometry direct injection. *L. dactylopii* is an Hymenopteran endoparasitoid of citrus mealybug Planococcus Citri (*Homoptera, Pseudococcidae*) [1]. At oviposition, parasitoid female injects venom, a complex blend of proteins and peptides inducing a number of physiological alterations in parasitized host [2]

L. dactylopii venom was resolved by two-dimensional electrophoresis (2D-PAGE) and gel tryptic digestion was carried out on the most concentrated proteins. Peptide mixture was analyzed by direct infusion (+)-ESI-FTICR-MS (12T). The two most intense peaks were subjected to collision induced dissociation (CID) and the MS/MS spectrum was useful to obtain sequence informations. In detail, the LVTAVNDIEK sequence was identify for a protein of 40 kDa, GGDLGQVYR for protein of 24 kDa and the VSSTLSGLEGELK for both proteins. These peptides colocalized in a singol translated contig of *L. dactylopii* venom glands trancriptome obtained starting from mRNA extracted from this tissue. Both proteins were annotated by Blast2GO as arginine kinase and considered as a full-length and a truncated form respectively. cDNA coding for the arginine kinase full-length and the truncated form were cloned in a specific expression vector and functional studies are underway.

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ANA-O47

Determination of illicit drugs in oral fluid by micro extraction on packed sorbent coupled with LC–MS/MS

C. Montesano[a], *M. Sergi*[b], *M.C. Simeoni*[b], *D. Compagnone*[b], *R. Curini*[a]

[a]*Dipartimento di Chimica, Sapienza Università di Roma, P.zle Aldo Moro, 5, 00185 Roma*
[b]*Facoltà di Bioscienze e Tecnologie Agro-alimentari e Ambientali, Via C. Leric , 64023 Mosciano Sant'Angelo, Teramo*

camilla.montesano@uniroma1.it

Oral fluid (OF) has gained a great popularity as a valuable biologic specimen for toxicological analysis, especially in DUID investigations, because it can be easily obtained and also because for most drugs there is a good correlation with degree of impairment. Limitations in OF testing are its variable viscosity, pH and flow depending on various physiological variables. In addition external contamination can be an issue; in these cases detection of metabolites can be crucial.

Multi-analyte procedures for determination of drugs in biological specimens are very useful because they allow analysis of several important compounds with a single sample extract injection, thus saving time and resources. For OF testing, where sample volume is limited multi analyte procedures are particularly advantageous. A number of procedures allowing the simultaneous determination of a number of illicit drugs in OF can be found in the literature especially using (ultra) liquid chromatography–spectrometry ((UP)LC–MS/MS) [1] and gas chromatography–MS (GC–MS) [2]. Most of these methods require at least 500 µL of OF and use time-consuming sample.

In this work a procedure for the simultaneous determination of illicit drugs, belonging to the classes of cocaine, amphetamines, natural and synthetic opioids and hallucinogens was developed. The sample preparation is based on microextraction on packed sorbent (MEPS) a novel miniaturized SPE technique.

The method has been fully validated according to the SWGTOX guidelines.

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ANA-O48

Spettroscopia NIR e chemiometria in chimica analitica forense. Nuove droghe di sintesi

S.Materazzi[1], R.Risoluti[1], L.Ripani[2], A.Gregori[2], J.Finamore[1], M.Bevilacqua[1], F.Marini[1], R.Bucci[1]*

[1] Dipartimento di Chimica, "Sapienza" Università di Roma, p.le A.Moro 5 – 00185 ROMA, [2] Reparto Investigazioni Scientifiche RIS – viale Tor di Quinto 119 – 00191 ROMA

roberta.risoluti@uniroma1.it

La spettroscopia nel vicino infrarosso (NIR) e la successiva elaborazione chemiometrica sono uno strumento sempre più utilizzato per la caratterizzazione e determinazione di analiti in matrici complesse nei più svariati settori (alimentare, ambientale, farmaceutico, ecc.) [1-4].

La potenzialità di tale approccio in chimica analitica forense è stata valutata nella determinazione di nuove sostanze stupefacenti di sintesi, alcune delle quali già oggetto di sequestri ma non ancora inserite nella tabella ministeriale degli stupefacenti, in collaborazione con il RIS di Roma. Le simulazioni effettuate su campioni preparati in laboratorio, che rispecchiassero le caratteristiche di recenti sequestri, mostrano che l'applicazione della spettroscopia NIR e la successiva valutazione chemiometrica permettono di determinare la presenza dello stupefacente in matrici reali complesse. Tali risultati, validati su campioni derivanti da sequestri, qualificano la spettroscopia NIR come tecnica rapida di approccio preliminare per possibili applicazioni in campo forense.

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ANA-O49

Strategie analitiche per la ricerca di nuove sostanze psicoattive in campioni biologici

E. Gerace[a], *D. Caneparo*[a], *D. Di Corcia*[a], *A. Salomone*[a] *e M. Vincenti*[a,b]

a Centro Regionale Antidoping e di Tossicologia "A. Bertinaria", Regione Gonzole 10/1,
10043 Orbassano (Torino), Italia
b Dipartimento di Chimica, Università di Torino, Via Giuria 7, 10125, Torino, Italia

enrico.gerace@antidoping.piemonte.it

La carenza di metodiche analitiche atte al riconoscimento di nuove sostanze psicoattive (NSP) in campioni biologici limita la comprensione della reale diffusione di questi composti sul territorio. Nel nostro laboratorio abbiamo sperimentato diverse strategie di ricerca delle NSP, in ragione della tipologia di campioni disponibili e della finalità dell'accertamento.

È stata valutata la reattività crociata verso i catinoni sintetici di due kit immunometrici per la ricerca di amfetamine e metamfetamine per poi applicare a 45 campioni di urina, positivi ai test di screening, un metodo di conferma in GC-MS per la determinazione di 20 composti a struttura catinonica. Per la ricerca dei cannabinoidi sintetici nella matrice cheratinica, 344 campioni reali sono stati testati mediante un apposito metodo in UHPLC-MS/MS validato per la ricerca di 23 composti.
Su 45 campioni di urina, 19 sono risultati positivi a sostanze di struttura catinonica; tra queste vi erano molecole effettivamente inserite nella lista delle sostanze illecite. Dei 344 campioni di matrice cheratinica analizzati, 15 sono risultati positivi ad almeno un cannabinoide sintetico. I più frequenti sono risultati essere il JWH-073 e il JWH-122.

L'ampia varietà di strutture chimiche delle NSP, e loro metaboliti, limita la disponibilità di adeguate strategie di screening. Lo sviluppo di metodiche mirate alla ricerca di catinoni sintetici, e analoghi, si rende dunque necessaria. Nel caso dei cannabinoidi sintetici, l'analisi del capello permette una semplice ricerca delle droghe parenti facilitando l'esecuzione di screening su ampie popolazioni di soggetti.

ANA-O50

How to increase brightness and duration of Luminol chemiluminescence for the detection of latent blood stains? Nanoparticles can help!

S.Priante, M. Attisano, M. Vincenti, G. Martra[*]

Department of Chemistry and [*]Interdepartmental Centre ''Nanostructured Interfaces and Surfaces-NIS'', University of Torino, via P. Giuria 7, 10125 Torino, Italy

gianmario.martra@unito.it

As a consequence of a serendipitous observation occurred when some of us were acting as scientific consultants in a court case, a study of the effect on the Luminol test of the dosage of inorganic nanoparticles (NP), both oxidic and saline in nature, on surfaces supposed to retain latent blood stains was undertaken. Almost independently on the nature of NP, a significant increase and duration of the Luminol chemiluminescence was obtained. In particular, the light emission lasted even for minutes instead of seconds, the typical duration obtained with the best commercial product, Bluestar® Forensic, overcoming the main drawback of the Luminol test. On one hand, FT-IR investigations indicated that the observed behavior is not a consequence of some interaction of the catalytic sites (Fe^{3+} ions in heme groups in hematin) with the surface of the nanoparticles. On the other hand, the analysis of the kinetic of the chemiluminescent decay revealed that it stems from a decrease of the mass transfer rate of Luminol molecules in the liquid phase sprayed on inspected surfaces towards the catalytic sites, because of the presence of a percolation layer formed by pre-dosed NP. The absence of any interference of NP in recovering DNA from the so revealed blood stains and the significant decrease in the occurrence of false positives allowed for a successful patenting of a new kit and method for the exploitation of the Luminol chemiluminescence on crime scenes [1].

[1] G. Martra, S. Priante, M. Vincenti, "Method and a kit for determining human or animal blood on a surface" US8637319 (B2) — 2014-01-28

ANA-O51

Contributo Ritirato

ANA-O52

Nuove droghe sintetiche: progetto RIS-NEWS

Sergio Schiavone

Reparto Investigazioni Scientifiche Carabinieri, Messina

sergio.schiavone@carabinieri.it

In questi ultimi anni, le Nazioni Unite e l'Unione Europea hanno segnalato la comparsa, sul mercato illecito delle sostanze stupefacenti, di nuove sostanze psicoattive (NSP) di origine sintetica, con caratteristiche tossicologiche particolarmente pericolose. Dal 2009 il Sistema Nazionale di Allerta Precoce per le droghe del Dipartimento Politiche Antidroga ha monitorato la situazione sul territorio italiano rilevando circa 280 nuove sostanze circolanti.

Questo mercato utilizza principalmente internet per la pubblicizzazione delle molteplici offerte di nuove sostanze psicoattive, per la raccolta degli ordinativi e dei pagamenti mediante mercato elettronico ed approfitta dei normali corrieri postali per il loro invio a domicilio. Il nuovo mercato delle NSP ha visto la comparsa, dal 2009 su segnalazione dell'Osservatorio Europeo e dei centri collaborativi italiani, di: 84 cannabinoidi sintetici, 60 fenetilammine, 42 catinoni sintetici, 8 triptamine, 6 ketamine, 4 piperazine ed altre sostanze.

In Italia, il sistema nazionale di allarme precoce ha rilevato anche circa 70 casi di intossicazione acuta correlati all'assunzione di NSP che hanno avuto bisogno di cure intensive presso i pronto soccorso. Da segnalare, inoltre, la sempre maggiore diffusione delle droghe da stupro, che interessano soprattutto la popolazione femminile. Il fenomeno sta assumendo notevole rilevanza - affiancandosi ormai a quello delle droghe tradizionali (eroina, cocaina, cannabis, amfetamine) – e pervasività, considerando le numerose offerte sulla rete Internet e, soprattutto, sui social network, particolarmente frequentati dalle giovani generazioni.

L'assunzione delle NSP sfugge ai tradizionali controlli di laboratorio per la carenza di metodi e standard analitici di riferimento, oltre che delle conoscenze tecnico-scientifiche e di tecnologie adeguate per la loro determinazione. Nell'ambito delle iniziative coordinate dal DPA, vi è anche il progetto RIS-NEWS per la condivisione delle informazioni sull'individuazione di NSP da parte dei 4 Reparti Investigazioni Scientifiche (RIS) e dei 28 Laboratori di Analisi di Sostanze Stupefacenti (LASS) dell'Arma dei Carabinieri, che prevede l'organizzazione di corsi semestrali per l'aggiornamento di tutto il personale.

ANA-O53

Characterisation of biochar amended soil by hydropyrolysis

A. G. Rombolà[a], *D. Fabbri*[a], *S. Baronti*[c],*L. Genesio*[c], *F. Vaccari*[c], *W. Meredith*[b], *C.E. Snape*[b]

[a] *C.I.R.S.A., Università di Bologna, Via S. Alberto 163, 48132, Ravenna, Italy*
[b] *Department of Chemical and Environmental Engineering, University of Nottingham, Nottingham NG7 2RD, UK*
[c] *Institute of Biometeorology (IBIMET), National Research Council (CNR), Via G. Caproni 8, 50145, Florence, Italy*

alessandro.rombola@unibo.it

Biochar, a solid product of biomass pyrolysis, attracts research interest due to its potential value for long-term carbon sequestration with additional agronomic benefits. The environmental potential and limitation of biochar in soil applications requires a full understanding of stability and the fate of carbon fractions and trace contaminants, such as PAHs. It is well known that a variable component of biochar is labile (degradable on annual/decadal timescales) and hence, only a proportion of total carbon in biochar provides long-term carbon sequestration. Among the various analytical techniques applied to the determination of the labile fraction and black carbon (BC) in soil, hydropyrolysis (HyPy) combined with GC-MS is an emerging approach not yet applied to biochar amended soils in long term studies. In HyPy, pyrolysis is assisted by high hydrogen pressure to facilitate the reductive removal of labile organic matter (defined as non-BC_{HyPy}), so isolating a highly stable portion of the BC (BC_{HyPy}) that is predominantly composed of >7 ring aromatic domains [1]. The aim of this study was to evaluate the fate of organic carbon of biochar amended soils in a four year field study. A large set of soils were amended with biochar from slow pyrolysis of pruning orchard in a vineyard at a rate of 22 t ha^{-1}. Soils were sampled in three different years after treatment following a randomized block layout with 5 replicates. We used HyPy to remove the labile organic carbon from total organic carbon in biochar and amended soils in order to enable reliable quantification and characterisation of the BC_{HyPy} and non-BC_{HyPy} fractions. The distribution of PAHs generated by HyPy was compared to that of solvent extractable PAHs determined by a validated GC-MS procedure [2] to gather information on the leaching of PAHs from the biochar into the soil.

[1] W. Meredith, P.L. Ascough, M.I. Bird, D.J. Large, C.E. Snape, Y. Sun, E.L. Tilston, *Geochim. Cosmochim. Acta*, 2012, **97**, 131-147.

[2] D. Fabbri, A.G. Rombolà, C. Torri, K.A. Spokas, J. Anal. Applied Pyrol., 2013, **103**, 60-67.

ANA-O54

Analisi di clorobenzeni in campioine di sedimento mediante purificazione fotochimica: nuove frontiere nella Green Analytical Chemistry

Salvatore Barreca[a], *Andrea Pace*[a], *Santino Orecchio*[a]

a Dipartimento di Scienze e Tecnologie Biologiche Chimiche e Farmaceutiche (STEBICEF)
Università di Palermo, Viale delle Scienze Edificio 16, 90128, Palermo, Italia
salvatore.barreca@unipa.it

Negli ultimi anni, l'attenzione di una parte della comunità industriale e scientifica è stata rivolta alla minimizzazione dei rischi ambientali e sanitari sviluppando una nuova branca della chimica analitica, ovvero la *Green Analitycal Chemistry* (*GAC*) [1]. Lo scopo del presente lavoro è stato quello di sviluppare e ottimizzare una procedura analitica per la determinazione di clorobenzeni in campioni di sedimento mediante purificazione fotochimica dell'estratto organico.

Al fine di individuare le migliori condizioni di lavoro, gli estratti organici sono stati irradiati a 350 nm per diverso tempo e in diverse condizioni.

Le analisi sono state condotte mediante GC-MS. L'efficenza della purificazione fotochimica è stata valutata in termini di accuratezza e precisione. I dati ottenuti sono stati paragonati con quelli ricavati applicando la purificazione in colonna prevista dalla metodica APAT.

La procedura è stata validata mediante l'utilizzo di un campione di sedimento fortificato e i dati hanno mostrato variazioni standard percentuali inferiori al 10 % con recuperi compresi tra il 95 e il 130 %.

I limiti di quantificazione erano compresi tra 1.0 e 2.3 ng g^{-1} con valori di limite di rivelabilità < 1.0 ng g^{-1}.

I risultati del presente studio hanno evidenzito che, se paragonate alle classiche tecniche di purificazione, le metodiche fotochimiche rappresentano una valida alternativa per la determinazione di analiti organici fotoresistenti ed inoltre mostrano vantaggi in termini economici, ambiente e di prevenzione dei rischi.

[1] A. Galusza. Z. Migaszewski, J. Namisnik *Trends in Analytical Chemistry*, 2013, **81**, 388-402.

ANA-O55

Elettrodeposizione anodica di IrO_x: caratterizzazione elettrochimica e spettroscopica

Innocenzo Casella[a], Michela Contursi[a]

Dipartimento di Scienze, Universitàdella Basilicata, Viale dell'Ateneo Lucano 10 , 85100 Potenza, Italy.

innocenzo.casella@unibas.it

La preparazione e caratterizzazione di ossidi di iridio (IrO_x) riveste notevole importanza in vari settori delle tecnologie e biotecnologie applicate [1-3]. Inoltre, elettrocatalizzatori a base di iridio hanno mostrato incoraggianti livelli di efficienza catalitica verso alcuni processi di elettroriduzione anche in presenza di alti livelli di avvelenanti organici [4].

La presente comunicazione concerne lo studio e caratterizzazione di film di IrO_x elettrodepositati su carbone vetroso in condizioni anodiche direttamente da soluzioni alcaline di Ir(III), aventi la seguente composizione: 55 mM NaOH, 6 mM $IrCl_6^{3-}$ e 20 mM Cl^-. Il processo di deposizione è stato condotto in condizioni potenziodinamiche, esplorando in particolare, la regione di potenziali compresa tra –0.7 V ed 1 V vs. SCE. Sono state ottimizzate le condizioni voltammetriche e le diverse variabili di deposizione, ed il film ottenuto è stato caratterizzato tramite analisi spettroscopica di superficie (XPS) ed analisi morfologica (SEM).

L'elettrodo a base di ossido di iridio è stato infine testato sia in condizioni stazionarie che di flusso come "sensing probe" per la rivelazione amperometrica di semicarbazide, molecola nota avere una importante attività carcinogenica e mutogena. Preliminari esperimenti hanno mostrato che il film di IrO_x mostra una notevole stabilità chimica sia in ambiente acido (50 mM $HClO_4$) che alcalino (0.1 M NaOH). Il film di IrO_x mostra anche buone proprietà elettrochimiche (conducibilità, stabilità, etc.) in ampi intervalli di potenziali applicati.

[1] J. Lipkowski, P.N. Ross. Eds. In "*Electrochemistry of Novel Materials: Frontiers of Electrochemistry*." Ed. VCH Publishers, Inc., Weinheim, 1994.
[2] L.M. Schiavone, W.C. Dautremont-Smith, G. Beni, J.L. Shay, Appl. Phys. Lett., 1979, 35, 823-832.
[3] S. Negi, R. Bhandari, L. Rieth, F. Solzbacher, Biomed. Mater., 2010, 5, 015007- 016.
[4] Y. Liang, H. Zhang, H. Zhong, X. Zhu, Z. Tian, D. Xu, B. Yi, J. Catal., 2006, 238, 468-477.

ANA-O56

Label-Free impedimetric detection of miRNA using biotinylated conducting polymer modified electrodes

D. Voccia[a], *M. Sosnovska*[b], *F. Bettazzi*[a], *I. Palchetti*[a], *W. Kutner*[b]

a Dipartimento di Chimica, Università degli Studi di Firenze, Via della Lastruccia 3 50019, Sesto Fiorentino, Firenze
b Department of Physical Chemistry of Supramolecolar Complexes, Institute of Physical Chemistry, Polish Academy Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

ilaria.palchetti@unifi.it

Short non-coding RNAs, of approximately 22 nucleotides in length, known as microRNAs (miRNAs, miR) have been recently emerged as new clinical biomarkers. A great deal of effort has been devoted, so far, to developing analytical methods for miRNA analysis that possess appropriate sensitivity, appropriate dynamic range and multiplexing capability without PCR. Label-free biosensors posses attractive features for miRNAs analysis, enabling quantitative miRNA expression profiling without requiring additional assay reagents and with minimal sample pretreatment. Electrochemical impedance spectroscopy (EIS)-based detection is one of the promising candidates for the development of label-free nucleic acid biosensors. In this work, an electrochemical label-free method for miRNA detection, based on electropolymerization of a biotinylated monomer onto the surface of Glassy Carbon Electrodes (GCEs) and disposable Screen-Printed Carbon Electrodes (SPCEs) is presented. A functional biotinylated monomer of bis(2,2'-bithien-5-yl)methane was used. Under potentiodynamic conditions, the monomer polymerizes resulting in deposition of a conducting polymer with an intact biotin moiety available for streptavidin binding. Then, the immobilization of biotinylated DNA capture probes occurred via streptavidin-biotin binding. This layer-by-layer assembling of the (biotin-polymer)-streptavidin-(biotin-oligonucleotide) recognition film was used to determine the label-free target oligonucleotide via complementary nucleobase pairing.

ANA-O57

Development of Screen-Printed Electrodes modified with Carbon Networks

D.Talarico[ab], *M.Dieci*[b], *D.Sordi*[b], *F.Arduini*[a], *G.Palleschi*[a], *D.Moscone*[a]
G.Koper[c]

a Dipartimento di Scienze e Tecnologie chimiche, Università di Roma Tor Vergata, Via della ricerca scientifica, 00133, Roma, Italia
b CarbonX BV, Julianalaan 136, 2628 BL, Delft, The Netherlands.
c Chemical Engineerimg Department, Delft University of Technology, Julianalaan 136, 2628 BL, Delft, The Netherlands.

daria.talarico@uniroma2.it

Screen-printed electrodes (SPEs) are recognized as successful sensors in modern electroanalytical chemistry due to their low background, wide potential window, and easiness of surface modification. In order to improve their analytical performances, SPEs can be pretreated electrochemically, with oxygen plasma or modified with nanomaterials such as carbon nanotubes and graphene. In this work, we used for the first time, Carbon Networks (CNetws), a 3D-hyperbranched carbon nanostructured material composed of junctions and interconnections, to modify the surface of the working SPE. In detail, CNetw dispersions were prepared using different CNetws (pristine CNetws and CNetws treated with acids (H_2SO_4/HNO_3) or plasma (O_3)). The type of CNetws and the solvent to prepare the dispersions were selected. The best dispersion in terms of stability was found with the treated CNetws using a mixture of DMF/H_2O as solvent. The selected dispersion was then used to modify the SPE by drop casting. The CNetws-SPEs were morphologically characterised by SEM analysis demonstrating a homogeneous coverage of the surface of the working electrode. The CNetws-SPEs were challenged with ferricyanide and dopamine demonstrating, in terms of peak to peak separation and current intensity, an improvement compared to the bare SPEs. The CNetws-SPE was used to detect dopamine by square wave voltammetry obtaining a linear range of 0.5-10 μM and a detection limit of 0.1 μM.

ANA-O58

DNA technology for small molecules sensing: a new approach for pesticide detection

Riccardo Rapini[a], *Gözde Aydoğdu*[b], *Giovanna Marrazza*[a]
[a]*University of Florence, Department of Chemistry "Ugo Schiff", Via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy*
[b]*Ankara University, Faculty of Science, Department of Chemistry, Degol street Besevler, 06100 Ankara, Turkey*

giovanna.marrazza@unifi.it

DNA technology, which affords the elaboration of programmable chemical synthesis routes to build complex architectures and functions with molecular precision, has focused the attention on a new generation of robust tools. The development of DNA-based sensors is one of the most representative examples because they can be used for the rapid detections of different kinds of pollutants for environmental monitoring.

In this work, an electrochemical DNA array for acetamiprid, a diffused neonicotinoid insecticide, is presented. The DNA array is based on a dual signal amplified strategy by employing a polyaniline film and gold nanoparticles as a sensor platform and enzyme-linked as a label for sensitive detection. Firstly, polyaniline film and gold nanoparticles were progressively grown on graphite screen-printed electrode surface via electro-polymerization and electrochemical deposition, respectively.

The polyaniline-gold nanocomposite modified sensors were firstly modified with a mixed monolayer of a thiol-tethered DNA aptamer and a spacer thiol. The aptasensor was able to capture the pesticide from the sample solutions. An enzyme-amplified detection scheme, based on the coupling of a streptavidin-alkaline phosphatase conjugate and biotinylated secondary aptamer was then applied. The electro-active enzymatic product was detected by means of differential pulse voltammetry. In this way, the sensor coupled the unique electrical properties of polyaniline, gold nanoparticles and enzymatic amplification. Various experimental parameters of the realized DNA-based nanostructured sensor were studied and optimized using optical and electrochemical techniques.

ANA-O59

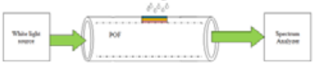
A marker-free sensor for furfural in oil-filled power transformers based on surface plasmon resonance in plastic optical fiber

N. Cennamo[1], L. De Maria[2], G. D'Agostino[3], M. Pesavento[3] and L. Zeni[1]

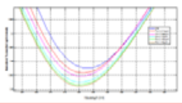
[1]Dep.of Industrial and Information Engineering, Second University of Naples- Aversa – Italy,
[2]Department of Transmission and Distribution Technologies, RSE, Milan, Italy
[3]Department of Chemistry, University of Pavia – Italy

maria.pesavento@unipv.it

Preliminary results about the feasibility of an optical Surface Plasmon Resonance (SPR) based sensor, exploiting a plastic optical fiber (POF) platform, for an early and high sensitivity detection of the chemical agents of interest in oil-filled power transformer are reported. In particular, the on-line detection of furfural (furan-2-carbaldehyde), produced by the degradation of insulating paper-oil could provide an early warning of incipient failures caused by partial discharges, over temperature, hot spot, or of an accelerated aging on dielectric parts of transformer. Oil-filled power transformer is a key component of a Transmission and Distribution (T&D) network, so that its failure can have relevant impact either on maintenance costs and on the new T&D network, due to out-of-services. The selectivity was obtained by using a Molecularly Imprinted Polymer (MIP) layer in contact with the SPR active surface, very specific for one of the most significant indicators of the transformer possible failure, furfural. This particular kind of synthetic receptor has been used instead of the most usual bioreceptors, for example antibodies, in view of the fact that it is widely recognized that bioreceptors poorly perform in non aqueous media. In Figure the optical chemical sensor system [1, 2] and some normalized SPR transmission spectra, obtained at different concentrations of furfural in a transformer oil are reported.



Experimental setup.



SPR transmission spectra obtained on POF sensor, normalized to the spectrum in air before spin coating the MIP layer, for different concentrations of furfural (blue-shifted).

The resonance wavelength linearly depends on furfural concentration in the transformer oil.

[1] N. Cennamo, G. D’Agostino, R. Galatus, L. Bibbò, M. Pesavento and L. Zeni, Sensors and Actuators B, 2013, **118**, 221-226.
[2] N. Cennamo, G. D’Agostino, M. Pesavento and L. Zeni, Sensors and Actuators B, 2014, **191**, 529–536.

ANA-O60

Effects of acetic acid vapour on the ageing of alkyd paint layers: a multi-analytical approach for the evaluation of the degradation processes

Jacopo La Nasa [a], *Ilaria Degano* [a], *Francesca Modugno* [a], *Maria Perla Colombini* [a,b]

a Dipartimento di Chimica e Chimica Industriale, Università Di Pisa, Via Risorgimento 35, 56121, Pisa, Italy
b Istituto per la Conservazione e la Valorizzazione dei Beni Culturali, Consiglio Nazionale delle Ricerche, Via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy

Interactions with volatile organic compounds (VOCs) are one of the main issues within the field of the preventive conservation of artworks. VOCs deriving from wooden frames and museum furniture consist in several aldehydes, formic acid and a high abundance of acetic acid. The aim of this study was to evaluate the interactions between alkyd paints layers and acetic acid that take place during the curing process of the paint layers. A set of reference Winsor & Newton alkyd paint layers was exposed to acetic acid vapour for six months to model these interactions. In order to evaluate the main degradation pathways of the alkyd paint layers during the artificial ageing, a multi-analytical approach based on chromatographic and spectroscopic techniques was used. The combined results describe the main degradation processes of the organic and inorganic components used in the production of the alkyd resin paint tubes [1,2].

[1] La Nasa J, Degano I, Modugno F, Colombini MP. Effects of acetic acid vapour on the ageing of alkyd paint layers: multi-analytical approach for the evaluation of the degradation processes, *Polymer Degradation and Stability,* 2014, *in press*.
[2] La Nasa J, Degano I, Modugno F, Colombini MP. Alkyd paints in art: characterization using integrated mass spectrometry, *Analytica Chimica Acta*, 2013, 797, 64-80.

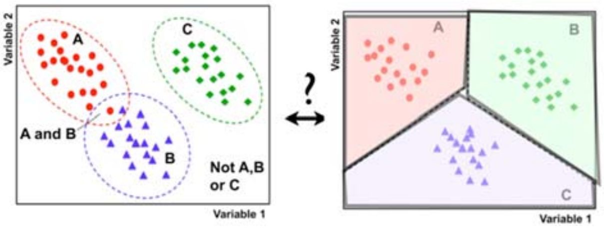
ANA-O61

Class-modelling versus Discriminant classification a survey

M. Cocchi, M. Li Vigni, C. Durante, M. Silvestri, L. Bertacchini

Dip. Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia, Via Campi 183
41125, Modena, Italy

marina.cocchi@unimore.it



The study of complex systems mostly relies on instrumental techniques, especially hyphenated, for the rapid, non-destructive analysis and extensive characterization of the matrix under study. In this perspective, the role of chemometrics is of paramount importance to efficiently extract the information relevant to the problem. In particular, several research tasks require assessing membership to one or more categories. To this aim multivariate classification methods have been developed and can be framed in two main groups: aimed at discrimination, e.g. PLS discriminant analysis, or at class modelling, e.g. SIMCA. In food traceability, authenticity and quality control contexts where the typical questions are: "does sample X, labelled as A, really belong to class A?" or "does sample X follows specifications?", class-modelling techniques are the most suited to deal with.

Notwithstanding the diffuse use of classification models there is a need to refocus on the basic of the methodologies and to define a problem oriented strategy for practitioners, considering as well that there is a clear imbalance between literature and software implementations.

This presentation will offer a survey of the state of art with focus on retrospective on SIMCA and PLS-DA, their multilinear extension (NSIMA and NPLS-DA) and their implementations.

ANA-O62

Multivariate Analysis of TEM Images for the characterization of innovative nano-materials

Mario Li Vigni[a], *Marina Cocchi*[a], *Gigliola Lusvardi*[a], *Gianluca Malavasi*[a]

a Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia.
Via Campi, 183, 41125, Modena, Italia

mario.livigni@unimore.it

The acquisition and analysis of images represents a powerful instrument to obtain, with a single measurement, information on the nature of a sample/system considering different aspects. This is particularly true when multi-channel images (for which, at every pixel, complex information such as a spectrum is collected) are used, where both compositional and texture information can be achieved in a single acquisition, but the image analysis advantage is still significant also when RGB or grey-scale images are acquired. In this case, and as far as microscopy is concerned, it is possible to obtain information on the texture and homogeneity of the sample, both referred to its macro structure, and to its micro structure: local dominions of different physical and chemical nature can be highlighted and measured, in terms of dimensions, when working at pixel level. Multivariate Analysis methods can be used to optimise the evaluation of images in order to extract relevant features to compute both global and local descriptors which can be used to characterise the sample.

In this study, Transmission Electron Microscopy images of nano-structured glasses have been acquired as grey-scale images. The glass materials have been functionalised by the addition of metal oxides, and the study has the two-fold target of quantifying the size distribution of the nano-particles which characterise the material and verify and quantify the degree of encapsulation of metal oxide particles in the silica structure. Grey-scale images are analysed to obtain information about particle dimensions and their distribution (at a > 10 nm scale) and to evaluate the presence of dominions of different crystalline phases (at a ~ 2 nm scale), by using Chemometrics methods based on the identification of neighbourhood pixels correlation, such as MIA [1] and an innovative Wavelet-based image analysis method, Wavelet-MIA.

1 J.M. Prats-Montalban, A. de Juan, A. Ferrer, *Chemom. Intell. Lab. Sys*.

ANA-O63

Local Classification: Locally Weighted – PLS-DA

Marta Bevilacqua[a], *Federico Marini*[a]

[a] *Department of Chemistry, University of Rome "La Sapienza", P.le Aldo Moro 5, 00185, Rome, Italy*

marta.bevilacqua@uniroma1.it

Classification problems occur ubiquitously in chemometrics, from traceability to process monitoring, passing through metabolomics or image analysis. However, the development and widespread availability of more and more efficient instrumental platforms resulted in a corresponding increase in the complexity of the problems and tasks chemists are called to tackle and solve. In the framework of pattern recognition, this consideration translates to the possibility that many sources of variation, other than the class belonging, affect the instrumental signal, resulting in a non-linear separability of the categories in the feature space. Whenever this occurs, the use of non-linear classification methods constitutes an obvious answer to this issue; however, involving an higher number of adjustable parameters, these kind of methods usually have strict requirements in terms of the samples to variables ratio, and are more prone to overfitting. One way of overcoming these limitations, which has already been extensively used also for calibration problems, is to implement the non-linearity through the training of locally linear classifiers [1].

In this study, the possibility of extending the Locally Weighted-PLS approach originally proposed by Centner and Massart [2], to deal with non-linear classification problem was thoroughly investigated. In this context, the effect of applying different weighting schemes (uniform weighting or distance-based weighting) was tested both on spectral-like simulated data sets and on real NIR data, obtaining in all the cases significantly better results with respect to the linear global model.

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ANA-O64

Authentication of *Taggiasca* olives in brine by application of a novel PLS-based class-modelling method on NIR spectra

P. Oliveri[a], *M.I. López*[b], *M.C. Casolino*[a], *S. Lanteri*[a], *L. Medini*[c]

a Department of Pharmacy, University of Genova, Italy
b Department of Analytical and Organic Chemistry, Rovira i Virgili University, Tarragona, Spain
c Special Company for Professional Training and Technological and Commercial Promotion of the Chamber of Commerce of Savona, Albenga, Italy

oliveri@dictfa.unige.it

In the present study, a multivariate screening strategy was developed to verify authenticity of commercial olives in brine of cultivar *Taggiasca*. Two different cultivars were used to assess the strategy; *Coquillo* and *Leccino*. Spectral data were obtained by near-infrared (NIR) spectroscopy and a recently introduced class-modelling method was applied.

This method combines the supervised features of partial least squares (PLS) regression [1], the efficient modelling power of potential function techniques [2] and the analysis of residuals [3]. In more detail, a PLS regression model is developed using as the response a distance-based density estimation. Afterwards, a potential-function class model is built on the scores of training samples on a number of low-order latent variables. To verify compliance of test samples with the class of interest, both the potential-function model and the residual statistics are considered.

Several parameters used in model building were optimised by cross-validation. The final model was validated on two independent external test sets. The performance parameters showed that the new strategy described is able to provide efficient models. An elevate balance between sensitivity and specificity values was achieved if compared with classical class-modelling methods, such as unequal dispersed classes (UNEQ) [4] or soft independent modelling of class analogy (SIMCA) [5].

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ANA-O65

Which distance for similarity/diversity analysis?

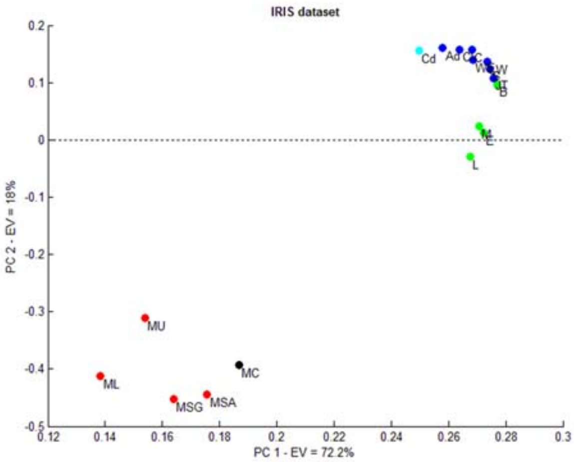
Roberto Todeschini, Viviana Consonni and Davide Ballabio

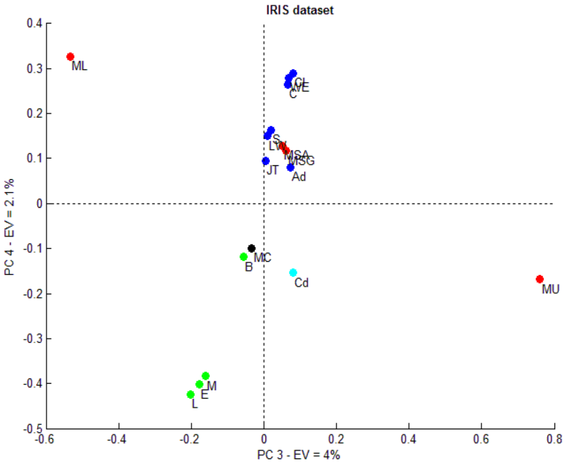
Milano Chemometrics and QSAR Research group

Dept. of Earth and Environmental Sciences, Univ. of Milano-Bicocca – Milano (Italy)

roberto.todeschini@unimib.it

Distance and similarity measures play a key role in most of the common of chemometrics and QSAR/QSPR techniques, such as, for instance, cluster analysis, classification, exploratory data analysis. Several measures of distance for real-valued data are presented and their behaviour compared on different data sets. The studied distance measures are: Euclidean, Manhattan, Lagrange, Lance-Williams, Canberra, Clark, Soergel, Bhattacharyya, Wave-Edge, Jaccard-Tanimoto, Angular and correlation distances. Moreover, the Mahalanobis distance is also considered together with the recently proposed local Mahalanobis distances. PCA, MDS and MST are the main tools used to compare the distances in different data sets. The behaviour of the different distances in the nearest neighbour distributions is also evaluated as a rough approximation of classification performances.





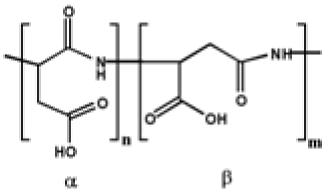
ANA-O66

Acid base properties and sequestering capacity of polyaspartic acid towards divalent metal cations

Clemente Bretti, Rosalia Maria Cigala, Gabriele Lando, Silvio Sammartano

[a] *Dipartimento di Scienze Chimiche - Università di Messina, Viale Ferdinando Stagno d'Alcontres, 31, I-98166 Messina (Vill. S. Agata), Italy.*

cbretti@unime.it



Poly-α,β-D,L-aspartate

In this contribution a study on the acid-base properties and on the complexing ability of the polyaspartic acid (Pasp) towards some metal cations, as Ca^{2+}, Mg^{2+}, Zn^{2+} and Sn^{2+} is reported. The study was performed in $NaNO_3$, KCl, $(CH_3)_4NCl$ and in $(C_2H_5)_4NI$, at different ionic strengths ($0 < I$/mol $L^{-1} \leq 3.0$) and temperatures ($278.15 \leq T$/K ≤ 318.15), using two analytical techniques, potentiometry and voltammetry. On the basis of a previous paper [1], the titration curves of the ligand were modeled assuming a monomeric unit consisting of four aspartyl residues (m = n = 2, so MW=548.28, as Na_4L), see Figure, giving four protonation constants. The dependence on the ionic strength and on temperature was modeled by different equations, such as the Debye-Hückel type equation and SIT approach (Specific ion Interaction Theory). From the analysis of the experimental data it was evidenced that, in $NaNO_3$, the protonation constants increase with increasing the temperature and decrease with increasing the ionic strength. The Ca^{2+}/Pasp, Mg^{2+}/Pasp and Zn^{2+}/Pasp systems were studied only by potentiometry, whereas in the case of the Sn^{2+}/Pasp, the formation of scarcely soluble species was evidenced and the use of voltammetry was necessary, for the use of low metal cation concentration (~ 10^{-7} mol L^{-1}). The general speciation scheme consists of two species, ML and MLH, for the Zn^{2+}/Pasp system we also have the mixed hydrolytic species MOHL, and for the Sn^{2+}/Pasp system four species were found: MLH_2, MLH, ML and MOHL. In all the experimental conditions the stability trend of the complex formation constants is: $Sn^{2+} \gg Zn^{2+} > Ca^{2+} \approx Mg^{2+}$. The sequestering ability of this ligand towards the four metal cations was studied by means of an empirical parameter, $pL_{0.5}$, which allows us to evaluate this capacity cleaned by competitive reaction (*e. g.* protonation of the ligand, hydrolysis of the metal cation).

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ANA-O67

Thermodynamic aqueous properties of molecules of pharmaceutical interest in NaCl aqueous solution

Rosalia M. Cigala, Francesco Crea, Silvio Sammartano, Giuseppina Vianelli

Dipartimento di Scienze Chimiche, Università di Messina, viale Ferdinando Stagno d'Alcontres, 31, I-98166 Messina (Vill. S. Agata), Italy

fcrea@unime.it

Our group has been involved during the last years in studies aimed at the determination of the thermodynamic aqueous parameters of different classes of organic ligands of biological and pharmaceutical interest. Data regarding their thermodynamic properties appear till now few and quite confusing, and no systematic modeling studies regarding their dependence on the experimental conditions (ionic medium, ionic strength and temperature) is reported.

The main scope of our investigation is to give a contribution on the knowledge of the thermodynamic properties (log K^{H}, solubility/distribution and formation enthalpies) and sequestering ability of catecholamine and penicillin derivatives towards some metal ions in aqueous solutions and at different experimental conditions. Whilst data on dopamine and penicillin derivatives were already published[1,2], those regarding epinephrine were for the first time here proposed in $\mathrm{NaCl_{aq}}$ up to $I = 3.0$ mol $\mathrm{L^{-1}}$ and at $T = 298.15$ and 310.15 K. The interactions and the sequestering ability towards some metal ions ($\mathrm{Cu^{2+}}$, DET, $\mathrm{UO_2^{2+}}$, $\mathrm{Mg^{2+}}$, etc.) were studied up to $I = 1.0$ mol $\mathrm{L^{-1}}$. The different speciation schemes were compared among them and the sequestering ability was estimate by means of the $\mathrm{pL_{0.5}}$ parameter. The dependence of such thermodynamic parameters on the ionic strength was modeled by means of an extended Debye-Hückel equation and of the SIT (Specific ion Interaction theory) approach.

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ANA-O68

Surface chemical properties of methyltriphenylphosphonium polyoxometalates

G. De Tommaso[a], *M. Iuliano*[a], *M. Mozzillo*[a]

a Dipartimento di Scienze Chimiche, Università di Napoli "FEDERICO II", Via Cinthia 4, 80126, Napoli, Italia

gaetano.detommaso@unina.it

Polyoxometalates (POM) represent a class of oxygenated compounds, formed from first transition series metals. They find application in the fields of catalysis in the medical field, by their anti-cancer, antiviral and antibacterial properties. Recently POM, containing organic groups such as derivatives of pyridine, of tetraalkylammonium and tetraalkylphosphonium [1] were prepared. In the present work the surface chemical properties of the methyltriphenylphosphonium esamolibdate and the methyltriphenylphosphonium decatugstate, were investigated in order to verify their applicability for the removal of metals as cadmium and lead from waste waters. The measurements were carried out at 25° C in suspensions containing NaCl and $NaClO_4$ 0.1 and 1.0 moldm^{-3} as ionic medium. The acid-base behavior of the two solids was studied through potentiometric titrations. The interaction solid–metal ion was monitored by determining the amount of analyte adsorbed per gram of solid (Γ, mmol/g), as a function of time, until equilibrium was reached. The experimental data are in agreement with a kinetic of pseudo second order. The equilibrium adsorption were studied in the range of pH between 2.0 and 6.0 for the Cd (II) and between 2.0 and 8.0 for the Pb (II). From the analysis of equilibrium data it was established that the adsorption of Cd (II) and Pb (II) can be interpreted with a model of speciation surface that involves two types of different sites.

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ANA-O69

Sequestering ability of amino acids towards bioavailable metal cations

Emilia Furia[a], *Donatella Aiello*[a], *Anna Napoli*[a], *Carlo Siciliano*[b], *Giovanni Sindona*[a]

a Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Via P. Bucci, 87036, Arcavacata di Rende, Italia

b Dipartimento di Farmacia e Scienze della Salute e della Nutrizione, Università della Calabria, Edificio Polifunzionale, 87036, Arcavacata di Rende, Italia

emilia.furia@unical.it

In our on-going investigation of metals with biological ligands, we were interested in the sequestering ability of the amino acids, tyrosine, ortho-tyrosine, proline and *trans*-hydroxyproline, towards two metal ions, Al (III) and Fe (III). These cations were chosen on the basis of their importance in biological systems. Their interaction with amino acids, proteins, nucleic acids or metabolites in biological systems may cause undesirable side effects due to the thermodynamics of the metal complexes thus formed in that particular setting. The equilibria were evaluated by potentiometry at the physiological conditions (*i.e.* 0.16 M NaCl and 37° C), in order to determine the complex species that are formed in an aqueous environment, and the relative formation constants. The adoption of the constant ionic medium method was necessary in order to minimize activity coefficient variation in spite of the change of the reagent concentrations. By this approach, it was possible to replace in the calculations activities with concentrations and to minimize the liquid junction potential due to the hydrogen ion concentration.

The present study involved, at first, the determination of the solubility of the ligands under the selected experimental conditions. Solubility studies are of both theoretical and practical interest and they allow the determination of activity coefficients for nonelectrolyte solutes in aqueous solutions containing a large excess of salts. The knowledge of the activity coefficients of neutral species is necessary when modeling the dependence of equilibrium constants on ionic strength. To be able to establish the complexing power, and hence the competition between the proton and the metal ions towards the ligands, it was also necessary to determine the values of the protolysis constants of the amino groups and the protonation constants of the carboxylic groups.

The equilibrium behaviour and the speciation model were verified by high resolution mass spectrometry to define the possible structures of the complexes formed in aqueous solution in a wide pH range.

ANA-O70

Two kojic acid derivatives as promising ligands for Fe(III) and Al(III).

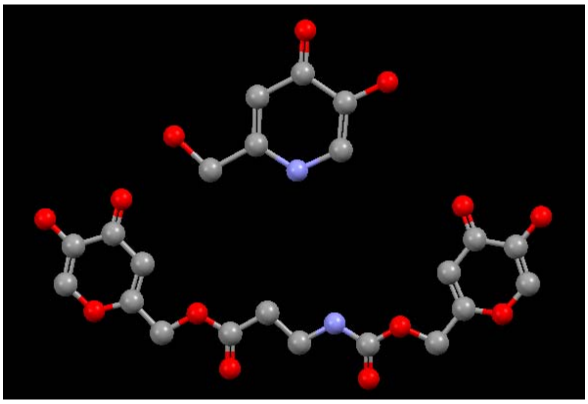
Joanna Izabela Lachowicz, Valeria Marina Nurchi

Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari, Cittadella Universitaria , 09042, Monserrato, Italia

lachowicz@unica.it

The importance of iron chelators in medicine has significantly increased in recent years. Iron, essential for life, is potentially more toxic than other trace elements when in excess, because humans lack effective means to screen cells against iron overload. In order to protect patients from the consequences of iron toxicity, chelating agents have been introduced in clinical practice. Unfortunately, the ideal chelator for treating iron overload in humans has not been identified yet [1].

In the framework of our research, we have recently synthesized two new ligands, the bidentate 5-hydroxy-2-(hydroxymethyl)pyridin-4(1H)-one, which combines properties of both kojic acid and deferiprone, and the tetradentate (5-hydroxy-4-oxo-4*H*-pyran-2-yl) methyl3-({[(5-hydroxy-4-oxo-4*H*-pyran-2-yl) methoxy]carbonyl}amino)propanoate. Complex formation of these ligands with Fe(III), Al(III), Zn(II) and Cu(II) has been studied by means of potentiometry, spectrophotometry and NMR.



The speciation has been confirmed by electrospray ionization-mass spectrometry (ESI-MS), and quantum chemical calculations. We obtained intriguing results that give new regard on complex formation of pyridinone complexes.

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ANA-O71

Thermodynamic parameters and binding ability towards Ca^{2+}, Mg^{2+} and Zn^{2+} of some polyelectrolytes

Clemente Bretti, Rosalia Maria Cigala, Concetta De Stefano, Anna Irto,
Gabriele Lando

Dipartimento di Scienze Chimiche - Università di Messina, Viale Ferdinando Stagno d'Alcontres, 31, I-98166 Messina (Vill. S. Agata), Italy.
glando@unime.it

This contribution reports a study on the thermodynamic parameters - ΔG, ΔH and $T\Delta S$ - of the poly methyl vinyl ether-co-maleic acid or Gantrez™ (GTZ). GTZ AN169 (2000 kDa, anhydride form), GTZ S95 (220 kDa, acid form) and GTZ S97 (1200 kDa, acid form) were studied in $NaCl_{(aq)}$ ($0 < I$ / mol dm$^{-3} \leq 1.7$), $KCl_{(aq)}$ ($0 < I$ / mol dm$^{-3} \leq 1.0$) and $(C_2H_5)_4NI_{(aq)}$ ($0 < I$ / mol dm$^{-3} \leq 1.0$) at three temperatures, namely T = 291.15, 298.15 and 318.15 K. Considering the nature of ligands, it was necessary to determine the critical micelle concentration (CMC) to define the concentration limit in the potentiometric experiments. This important parameter was determined by means two experimental techniques: light scattering and conductivity. In the data analysis of GTZs we considered other two poly-acrylic co-maleic acids, PCA, 3kDa and 70 kDa, whose protonation data were already reported in ref [1]. The best model for the protonation of the three GTZs was obtained assuming that a monomeric unit consisted of two methyl vinyl ether-co-maleic acid residues, therefore four carboxylate groups were considered and four protonation constants were determined. The protonation constants of polyelectrolytes follow the trend $(C_2H_5)_4N^+ >> K^+ > Na^+$, indicating that the interaction of the polycarboxylate anion with Na^+ cation is stronger than that with K^+. The protonation constants of GTZ AN169 are slightly higher than the corresponding values for GTZ S97 and GTZ S95. At the same time, for the PCA polymers the protonation constants of the 70 kDa are higher than the values of the 3 kDa, indicating that the molecular weight influences the acid base properties of the polymer. The dependence of the protonation constants on ionic strength was interpreted in terms of variation of the activity coefficients (by means of the Debye-Hückel and Specific ion Interaction Theory (SIT) approaches) and of formation of weak alkali metal ion pairs. In general the proton association process is slightly endothermic and it is entropic in nature. The binding ability of GTZ AN169 towards Ca^{2+}, Mg^{2+} and Zn^{2+} was measured in NaCl at different ionic strengths and temperatures. The most important species was the neutral M_2L one.

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ANA-O72

Towards ultrasensitive simple miniaturized devices based on chemical luminescence detection

Mirasoli M.[a,b]*, M. Di Fusco*[a,b]*, M. Zangheri*[a]*, F. Di Nardo*[c]*, L. Anfossi*[c]*, M. Guardigli*[a]*, Roda A.*[a]

a Dipartimento di Chimica "G. Ciamician", Università di Bologna, Via Selmi 2 , 40126, Bologna, Italia
b Centro Interdipartimentale per la Ricerca Industriale Meccanica Avanzata e Materiali, Università di Bologna
c Dipartimento di Chimica, Università di Torino, Via P. Giuria 7, 10125, Torino, Italia

mara.mirasoli@unibo.it

Microfluidic chips are being increasingly proposed for out-laboratory analyses, transferring traditional bench-top analytical procedures into portable and self-operating analytical devices. Chemical luminescence detection techniques (bio-, chemi-, electrochemi-, and thermochemi-luminescence), in which light is generated by a chemical reaction, are particularly attractive for lab-on-chip applications, combining high detectability with the requirement of simple instrumentation.

A versatile portable device for chemical luminescence-based multiplex assays was developed, in which different supports for bioanalytical assays (such as plastic microfluidic, microarray or paper-based) are coupled with the detection unit in a lensless "contact imaging" configuration, employing an ultrasensitive cooled CCD camera. Alternatively, full detector integration was reached exploiting on-chip amorphous silicon photosensors deposited on glass.

Silica nanoparticles for thermochemiluminescence detection were developed for implementing a reagentless chemical luminescence detection principle, thus further simplifying the microfluidic network. In addition, different types of assays, such as enzyme-based assays, immunoassays, nucleic acid amplification and hybridization assays, were implemented to enable specific detection of multiple analytes in a broad range of concentrations, down to pmol/L levels.

The newly developed device can simultaneously perform different assays exploiting the microarray configuration and/or using different luminescence chemistries and labels, thus providing multiplexing capability.

ANA-O73

Un biosensore SPR per lo studio di interazioni tra Liposomi e Steroidi Androgeni Anabolizzanti (SAA)

Paolo Bollella[a,c], *Marta Letizia Antonelli*[a] , *Francesco Botré*[c,d],
Gabriele Favero[b], *Franco Mazzei*[b], *Cristina Tortolini*[a,b]

a Dipartimento di Chimica, Università Sapienza, P.le A. Moro 5, 00185, Roma, Italia
b Dipartimento di Chimica e Tecnologie del Farmaco, Università Sapienza,
c Laboratorio Antidoping, Largo G. Onesti 1, 00197, Roma, Italia
d Dipartimento di Medicina Sperimentale, Università Sapienza, Viale Regina Elena 324, 00161, Roma, Italia

bollella1989@hotmail.it

La tecnologia SPR (Surface Plasmon Resonance) è stata utilizzata per mettere a punto un metodo analitico di "screening", sensibile e maneggevole da utilizzarsi nell'ambito del controllo/prevenzione "*antidoping"*[1]. Lo scopo della ricerca è quello di creare un "biosensore" [2], basato sulla trasduzione SPR con superficie attiva modificata, che consenta di indagare sulle interazioni liposomi/ormoni ed anche sulla loro cinetica.

La superficie in oro usata nella strumentazione SPR [3] è stata modificata realizzando un SAM misto, a sua volta funzionalizzato con la Fitosfingosina: biorecettore specifico per i liposomi. Mediante questa configurazione la misura SPR ha permesso di collegare le risposte strumentali all'affinità dei liposomi considerati (cationici, anionici e non ionici, oltre a 2 preparati farmaceutici) con la superficie attiva dell'SPR. Sono state poi studiate le interazioni tra detti liposomi e gli SAA (Testosterone e 19-Nortestosterone), nonché quelle dei liposomi caricati con i relativi metaboliti glucuronati. Per le interazioni Liposomi/SAA è stata indagata la cinetica di rilascio e/o di aggregazione.

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ANA-O74

Premio di Laurea

Nature-inspired DNA switching probes for antibodies detection

Simona Ranallo[a], Alexis Valleè-Belisle[b], Kevin W. Plaxco[c], Giuseppe Palleschi[a], Francesco Ricci[a]

a Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Via della ricerca Scientifica 1,00133 Roma, Italia
b Laboratory of Biosensors and Nanomachines, Département de Chimie, Université de Montréal, Québec, Canada
c Center for Bioengineering & Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106, United States

simona.ranallo@uniroma2.it

Recent years have seen an explosion in the number of well-characterized disease markers, molecules present in blood or at the surface of cells that are diagnostic of specific diseases such as HIV, cancer, or Alzheimer's. Unfortunately, current methods for the detection of such molecules are either multistep, wash- and reagent-intensive processes requiring sophisticated measurement protocols or simply do not display sufficient sensitivity. In response to the above argument we have developed a novel, DNA switching-based method for antibody detection that, in contrast to current methods, is rapid, single-step, and inexpensive**.** The inspiration behind our approach is derived from nature's sensing systems, which employ nanometer-scale protein and nucleic-acid-based "switches" to detect thousands of distinct molecules (including disease markers) in real time within complex physiological environments. More specifically, we exploit the "designability" of DNA to fabricate molecular nanoswitches that supports the one-step fluorescent detection of specific antibodies. The DNA probe acts as a versatile scaffold and is modified with signalling labels and with a pair of antigens (recognition elements). The nanoswitch is designed to adopt a stem-loop conformation (non-binding state) in the absence of the target antibody. The antibody binding will shift the conformational equilibrium of the probe towards the open signalling binding state allowing a rapid and sensitive detection of the target antibody. We show here the results obtained with our DNA-switching probe used for the quantitative detection of different antibodies (IgG) including clinically relevant HIV antibodies, even in serum sample.

ANA-O75

Using triplex DNA to achieve pH-control over reactions

Alessandro Porchetta,[a] *Alessia Amodio,*[a] *Andrea Idili,*[a] *Matteo Castronovo*[b]*,*
Chunhai Fan[c]*, Giuseppe Palleschi*[a] *and Francesco Ricci*[a]

a Dipartimento di Scienze e Tecnologie Chimiche, University of Rome, Tor Vergata, Via della Ricerca Scientifica, 00133, Rome, Italy
b Department of Medical and Biological Science and Engineering, University of Udine, Piazzale Kolbe 4, 3310, Udine, Italy;
c Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China.

alessandro.porchetta@uniroma2.it

By taking advantage of the pH-dependence of parallel Hoogsteen interactions here we have rationally designed a general strategy to re-engineer molecular beacons and a model aptamer (cocaine aptamer) with pH-dependent nucleotide motifs (i.e. triplex DNA) so that their binding activity/function can be finely regulated by changes of pH. More specifically, we have re-engineered these DNA-based receptors so that their sequence contains a triplex-forming portion that can allosterically activate or inhibit the target binding.

Moreover, we have developed two triplex-based DNA strand displacement strategies that can be triggered at both basic and acidic pHs. In the first strategy (OH^--activated) we have designed a clamp-like DNA sequence that can trap the strand to be released into a very stable DNA triplex complex thus inhibiting strand displacement under conditions at which such triplex structure is favored (acidic pHs). In the second strategy (H^+-activated), we have instead designed a clamp-like invading strand that can bind the preformed complex through the formation of both Watson-Crick and Hoogsteen interactions. At acidic pHs this leads to an improvement of the strand-displacement process compared to a reaction where only Watson-Crick base pairings take place. The possibility to activate/inhibit and finely regulate the toehold-mediated DNA strand displacement process through a simple change of the solution's pH appears particularly suitable as an additional control over the formation and functionality of DNA-based nanoarchitectures and nanomachines.

ANA-O76

Analytical characterization of Ag-fluoropolymer nanocoatings deposited by ion beam co-sputtering

M.C. Sportelli[a], M.A. Nitti[b], M. Valentini[b], R.A. Picca[a], D. Melisi[b], E. Bonerba[c], L. Sabbatini[a], G. Tantillo[c], A. Valentini[b], N. Cioffi[a]

a Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro", Via Orabona 4, 70126, Bari, Italia
b Dipartimento Interateneo di Fisica "M. Merlin", Università degli Studi di Bari "Aldo Moro", Via Amendola 173, 70126, Bari, Italia
c Dipartimento di Medicina Veterinaria, Università degli Studi di Bari "Aldo Moro", St.da P.le per Casamassima Km 3, 70010, Bari, Italia

nicola.cioffi@uniba.it

Fluoropolymers and polytetrafluoroethylene (PTFE) in particular, are useful anti-stain/hydrophobic materials often employed in the development of engineered textiles/surfaces [1, 2]. Although plasma-based methods are widely employed, Ion Beam Sputtering (IBS) of a PTFE target may represent a valid low-cost alternative for the direct deposition of Teflon-like thin films [3]. Moreover, this approach allows the single-step preparation of metal/fluoropolymer nanocomposites by simultaneously co-sputtering the inorganic and PTFE targets [4]. In this work, we report on the IBS preparation of Ag-fluoropolymer nanocoatings, consisting in Ag nanoclusters (Ag NCs) finely dispersed in the Teflon-like matrix, as promising antimicrobial materials. Different loadings (φ) of Ag NCs may be achieved by tuning the material deposition conditions, thus combining the well-known silver bioactivity with the waterproof properties of the polymer matrix. Transmission Electron Microscopy (TEM) and X-ray Photoelectron Spectroscopy (XPS) were used to investigate the as-deposited nano-coatings in terms of morphology and surface composition, as a function of φ.

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ANA-O77

Solution processed ZnO field-effect transistors for sensing applications

Mandeep Singh, Kyriaki Manoli, Maria Magliulo, Mohammad Yusuf Mulla, Gerardo Palazzo, Luisa Torsi

Department of Chemistry, University of Bari, Via Orabona, 4, I-70126 Bari, Italy

kyriaki.manoli@uniba.it

Over the years, metal oxide based thin film transistors (TFTs) have attracted a great deal of attention due to their high charge-carrier mobility and excellent chemical/mechanical stability. In particular, zinc oxide (ZnO) has potential in transparent TFT owing to its high optical transparency and high conductivity [1]. We are presenting a solution processable ZnO based TFT in bottom and top gate configurations. ZnO thin films were prepared with the sol-gel spin coating method. The ZnO structure has been assessed by XPS and UV/VIS spectroscopy. For the bottom gate configuration, the ZnO thin film were calcined at different temperatures and time. The devices calcinated at 450 °C temperature for 5 hrs shows higher mobility and Ion/Ioff ratio as compared with the devices processed at lower temperatures. The gating of the transistor has been performed with water and Posphate Baffer solution. Till now only one report is available on the water gated ZnO based TFT [2] and no report is found on the PBS gated. We have fabricated a water and PBS gated ZnO based thin film transistor without doing any further treatment of the ZnO surface. The devices so produced shows excellent characteristics with mobility as high as 0.168 cm^2/Vs and Ion/Ioff ratio in the order of 104. These devices have the potential to be used for biosensing applications.

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ANA-O78

Determination of the limit of detection of XPS surface analysis for As, Zn and Pb

Davide Atzei, Fabio Brundu, Bernhard Elsener, Marzia Fantauzzi, Antonella Rossi

Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari, Complesso Universitario di Monserrato, S.S. 554 Bivio per Sestu, I – 09042 Monserrato (Cagliari)

datzei@unica.it

In this work the detection limits of arsenic, zinc and lead by x-ray photoelectron spectroscopy were evaluated. The pure oxides and mixtures of As (III), Zn (II) and Pb (II) oxides at different concentrations with silica obtained by ball milling were analyzed by XPS using an ESCALAB200 spectrometer (Vacuum Generator Ltd). The surface composition was determined by quantitative XPS analysis according to the first-principle model using Scofield's photoionization cross section [1] modified for taking into account the matrix and the geometry of the instrument. All mixtures were analysed also by ICP to ascertain their concentration with an independent analytical technique. The response of XPS (at%) *vs* weight (at%) and vs ICP (at%) was checked and good linearity was observed. Samples containing these three elements in a silica matrix, allowed assessing the quality of the procedures for calculating the areas of photoelectron peaks and the atomic concentrations.

Two different approaches [2,3] were used to estimate the limit of detection of arsenic, zinc and lead and the results obtained were in good agreement. Under our experimental conditions the calculated LODs of arsenic, zinc and lead in oxides and in a silica matrix were found to be 0.16 (atoms %), 0.07 (atoms %) and 0.07 (atoms %) respectively if an Alk$\alpha_{1,2}$ X-ray source was used. Zn LOD was also calculated for the Mgk$\alpha_{1,2}$ source and it was found to be 0.15 atoms %.

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ANA-O79

Hydrofobizing coatings for stone protection

P. Fermo[a], *G. Cappelletti*[a], *G. Padeletti*[b], *S. Kaciulis*[b]

[a]*Dipartimento di Chimica, Università di Milano, Via Golgi 19, Milano*

[b]*Istituto per lo Studio dei Materiali Nanostrutturati – CNR. cp 10. 00016 Monterotondo Staz., Roma, Italy*

paola.fermo@unimi.it

Conservation of historical buildings is an important issue and the environmental conditions seriously affect the monumental stones. The protection of cultural heritage buildings and monuments by surface treatment with polymers is a common practice due to their ability to form a protective layer on the monumental surface as well as to control the transport of different fluids from the surface to monument interior.

In this study we have treated stones commonly employed during centuries (Carrara, Candoglia, Botticino and Angera) with both commercial water-repellent protective agents (siloxanes) and new formulated coatings obtained by mixings resins with TiO_2 nanparticles. The surface properties of the coating and the relative interaction with the adopted stones were studied using different techniques such as contact angle measurements, electron microscope coupled with an energy dispersive spectrometer (SEM-EDS), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and CIE-Lab colorimetric analyses.

In order to investigate the stability of the coatings both accelerated aging tests by UV irradiation (500W, 250-315 nm) and prolonged exposure in a typical urban polluted environment were carried out. Not significant color variations (i.e. $\Delta E^* < 5$) were registered.
The effectiveness of the different tested coatings in reducing water absorption and salts formation has been also demonstrated.

ANA-O80

Characterization of anodically growth films by electrochemical and surface analytical methods

Antonella Rossi [a], *Veronica Bueno*[b], *Bernhard Elsener*[a,b]

[a] *Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Cagliari Campus Universitario di Monserrato – S.S. 554 bivio per Sestu – 09142 Cagliari, Italia*
[b] *ETH Zurich, Institut of Building Materials, 8093 Zurich Switzerland*
[c] *Chemistry of Materials and Chemical Engineering Department, Politecnico di Milano, 20131 Milano, Italy..*

rossi@unica.it

X-ray photoelectron spectroscopy (XPS) is considered one the most useful techniques for the characterization of anodic oxide films especially for corrosion studies. It was already applied to carry out a research on the anodic corrosion films formed on Fe-Mo alloys in alkaline solutions [1] and for investigating mild steel surface in alkaline media [2]. The present research combined electrochemical and surface analytical methods, in order to fill the knowledge gap still existing in the chemistry/electrochemistry of mild steel in alkaline media in the presence of stray currents. Alternating currents (ac) may cause serious corrosion damages on metallic structures, even when they are under cathodic protection (cp) [3]. Aim of this work was to obtain an insight into the nature and the mechanism of the electrode reactions during ac-corrosion processes. Mild steel samples were exposed to 1M NaOH solutions in order to reproduce the high pH levels that can be locally reached at the metal surface when cathodic protection with and without AC currents is applied. "AC-voltammetry" (ACV), by means of which the samples are disturbed with a sinusoidal potential that is superimposed to the steps of a direct potential, was used here. Optical microscopy, scanning electron microscopy (SEM), focused ion beam (FIB) and X-ray photoelectron spectroscopy (XPS) were used for characterizing the surface films before and after electrochemical tests. The combination of XPS and ACV has shown that after an ACV scan to positive potentials $Fe(OH)_3$ was formed, after a backward scan mainly Fe^{2+} was detected. This oxidation / reduction cycle with the formation of non-protective iron hydroxides containing-layers on the mild steel surface might explain the high corrosion rates found in the presence of AC stray currents.

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ANA-O81

XPS and AFM investigation on thin, insulating poly o-aminophenol, PoAP and on its potential ability to recognize "amyloids" suspended in water.

Maria E. Carbone, Rosanna Ciriello, Antonio Guerrieri, Anna M. Salvi

Dipartimento di Scienze, Università di Basilicata, Viale Ateneo Lucano10, 85100,PZ(1)

maria.carbone@unibas.it

In continuation to previous studies[1,2], we report complementary investigation on PoAP formed by electrochemical oxidation of o-aminophenol on Pt substrates, at neutral pH. Here, guided by current profiles on the cyclic voltammograms, XPS and AFM analyses were carried out at various stages of PoAP growth for a better insight on the mechanism of polymerization initiating at the electrode surface. The outcome shows a self-similar propagation of PoAP chains at any growth stage, the terminal groups, indicated by XPS as carbonyls, resulting from further post-synthesis oxidation[1,2]. Once completed the characterization of the entire PoAP, this study has been augmented by assessing the binding propensity of the outermost carbonyls towards elastin-like peptides (ELPs), made of VGGVG sequence whose propensity, as *n*-repeats, to form amyloid- like fibrils, when suspended in water, was already demonstrated[3]. To this am, we have compared XPS analyses and optical and topographic AFM images of PoAP films before and after immersion in $(VGGVG)_n$ suspensions (n=0, n=3, n=5) for 6 hours at 37°C, at various concentrations. The promising results and implications will be discussed, in view of developing a methodology for PoAP bio-sensing amyloids, using EQCM[4].

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ANA-O82

Improving Surface Plasmon Resonance imaging DNA sensing with gold nanostars

S.Mariani [a], *S. Scarano* [a], *J. Spadavecchia* [b], *M. Minunni* [a]

a Dipartimento di Chimica "Ugo Schiff", Università di Firenze, via della Lastruccia 3-13, 50019 Sesto Fiorentino (FI), Italy

b Laboratoire de Réactivité de Surfaces, UMR CNRS 7197, Université Pierre & Marie Curie − Paris VI, Site d'Ivry − Le Raphaël, 94200 Ivry-sur-Seine, France

maria.minunni@unifi.it

DNA based Surface Plasmon Resonance imaging (SPRi) sensing is often coupled to metal noble nanoparticles (NPs) for the enhancing of sensitivity [1], being a priority goal mostly for clinical diagnostics applications [2].

In this research the effect of optical coupling between Surface Plasmons (SPs) and electric field of Localized Surface Plasmons (LSPs) of gold nanostars (NSs) [3] was studied for the increase of SPR signal both in surface nanostructuring and in molecular architectures approaches since NSs show a strong plasmon excitation and a strongly enhanced electromagnetic field localized at the sharp tips that could entail in improved analytical performances [4].

The gold surface nanostructuring was optimized and covalently performed via dithiols binding while molecular architectures approach consisted in a sandwich assay where NSs were linked to thiolated DNA as signal enhancer.

As results nanostructured surface provided a higher biosensor sensitivity in hybridization signal (about 50%) than gold flat surface while the employment of NSs labeled molecular architectures lowered the detection limits of three order of magnitude (from 10 nM to 10 pM). Moreover both biosensors were well-regenerable by the simple injection of chaotropic agents. In future other NSs based nanostructuring approaches (e.g. based on affinity DNA interaction) will be tested while the NSs labeled molecular architectures strategy will be applied for the PCR-free selective detection of DNA sample extracted from real samples.

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ANA-O83

Surface Plasmon Resonance Imaging genosensors to detect pathogens in food

Angela M. Aura[a], Roberta D'Agata[a], Cristina Valenti[b], Giuseppe Spoto[a,b]

a Dipartimento di Scienze Chimiche, Università di Catania, Viale Andrea Doria 6 , 95125, Catania, Italy
b Consorzio I.N.B.B., Viale delle Medaglie d'Oro 305, 00136, Roma, Italy

amaura@unict.it

The detection of pathogens in food represents an important topic in modern analytical chemistry. Traditional methods often operate with poor sensitivity and selectivity and require time-consuming sample treatments and prolonged analysis time [1]. Optical biosensors based on Surface Plasmon Resonance Imaging (SPRI) [2] allow detecting pathogens in real-time with good selectivity and specificity, at relatively low cost, without the use of molecular labels [3]. An enhancement in SPRI sensitivity can be achieved using gold nanoparticles (AuNPs) [4]. In this communication, we describe the development of SPRI genosensors for the detection of Staphylococcus Aureus (S. Aureus) pathogen in food, through in situ DNA hybridization to synthetic and specific probes immobilized on SPRI gold surfaces according the most appropriate surface chemistry. For this purpose, we combined a sandwich hybridation approach of the target sequence of S. Aureus and the use of properly functionalized gold nanoparticles conjugated to an biotinylated oligonucleotide probe complementary to target sequence that is not involved in hybridization with the oligonucleotide probe on SPRI gold surface. In this respect, AuNPs are able to amplify the signal SPRI and enhance the method sensitivity.

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ANA-O84

Rapid Aflatoxin B_1 and Ochratoxin A analysis by an optical portable instrument

Fabiana Arduini[a], *Daniela Neagu*[a], *Danila Moscone*[a], *Giuseppe Palleschi*[a]

[a]*Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Via della Ricerca Scientifica, 00133 Rome, Italy*

fabiana.arduini@uniroma2.it

In this work, we report a fast analytical method for both aflatoxin B_1 (AFB_1) and ochratoxin A (OTA) detection using a fiber optic system coupled to a portable and miniaturised spectrophotometer/fluorimeter. Until now, multiclass mycotoxins were analyzed by means of GC-MS or LC-MS/MS, however these analytical systems require laboratory set-up, skilled personnel and expensive instrumentation.

In the case of OTA, the analysis was based on the intrinsic OTA fluorescence. The detection of OTA was carried out using an OceanOptics USB2000-FL Spectrometer obtaining a detection limit of 0.1 ppb. For cleanup and extraction of OTA in real samples, two types of immunoaffinity columns (OchraTest from Vicam™ and NeoColumn from NEOGEN Europe Ltd) were tested successfully with wine and soluble coffee with recovery values between 96.5% and 110%. Using the same instrument, but changing the position of the fibres, the AFB_1 was detected at ppb level using a spectrophotometric method, based on acetylcholinesterase (AChE) inhibition by the mycotoxin. The AChE residual activity was determined using the spectrophotometric Ellman's method [1].

The detection of both OTA and AFB_1 in millet fortified at legal limit values was performed using Afla-Ochra HPLC™ from VICAM and AflaOta-Clean from Lc-Tech immunoaffinity columns with satisfactory results, demonstrating the suitability of this procedure as screening method for these mycotoxins.

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ANA-O85

Thickness determination of nanosized films by XPS

Marzia Fantauzzi[a], *Bernhard Elsener*[a], *Manuela Pisu*[a], *Antonella Rossi*[a]

[a] *Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari, SS 554 – bivio per Sestu , 09042, Monserrato (CA), Italia*

fantauzzi@unica.it

Various analytical techniques are applied for measuring film thickness and in many analytical problems a requisite is that the method is non-destructive.

Within the many methods reported in the literature very popular are ellipsometry, multiple beam interferometry and more recently FIB – SEM. The first two might be considered non-destructive or quasi non-destructive techniques while the last one requires obtaining a section of the material under investigation. In the case of ellipsometric measurements the knowledge of the optical parameters of the layers is necessary while the applicability of the second technique is limited to thicknesses higher than 10 nm. In many cases naturally grown layers or protective layers applied on a substrate to hinder oxidation reactions and to avoid degradation of the surface have thicknesses within 0.5nm and 10 nm.

In this research X-ray photoelectron spectroscopy was applied for determining the thickness of surface films formed on a nickel-free stainless steel (DIN 1.4456) used for biomedical applications. The thickness of the surface film was calculated using three different approaches: the three-layer model [1], angle-resolved XP-spectra and argon ion etching. Being the last one a method that is still very widely applied for investigating thin surface film despite it is a destructive and sputtering might be not uniform in the analysed area.

When using the three-layer model, thickness of surface layers was found to range from 3.3 (0.1) nm to 4.3 (0.2) nm depending on the oxy-hydroxide growth conditions. Similar results have been obtained by ARXPS; Argon ion concentration depth profiles also indicated the interface substrate/oxide film at values lower than 5nm.

A critical comparison of the different methods will be presented and discussed.

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Chimica Analitica

Poster

ANA-P1

Development of a dual cyclodextrin system-capillary electrophoresis method for the determination of the enantiomeric purity of levosulpiride

Serena Orlandini, Benedetta Pasquini, Massimo Del Bubba, Sergio Pinzauti, Sandra Furlanetto

Department of Chemistry "U. Schiff", University of Florence, Via U. Schiff 6-Via della Lastruccia 3-13, 50019 Sesto Fiorentino, Italy

benedetta.pasquini@unifi.it

In levosulpiride (L-SUL) pharmaceutical formulations, R-SUL should be considered as an enantiomeric impurity, and it is essential to have at disposal a rapid analytical method to control the chiral purity of the product. Quality by Design (QbD) [1] has been recently introduced into the pharmaceutical industry with the objective of achieving a desired state for pharmaceutical manufacturing and product quality [2]. In this study, for the first time in the literature, QbD was applied in the field of capillary electrophoresis (CE) chiral separations, in order to develop a rapid and reliable CE method suitable for the analysis of L-SUL and its chiral impurity. A dual cyclodextrin (CD) system made by sulfated-β-CD and methyl-β-CD was identified as the separation system leading to the best results in terms of selectivity. The effects of selected critical process parameters, both qualitative and quantitative, on enantioresolution and analysis time were deeply studied by a multivariate strategy involving a screening phase and response surface methodology. The application of QbD strategy made it possible to define a multivariate zone where the quality of analytical data was assured with a selected degree of probability.

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ANA-P2

Fast analysis of glibenclamide and its related substances by capillary electrophoresis

Serena Orlandini, Benedetta Pasquini, Massimo Del Bubba, Sergio Pinzauti, Sandra Furlanetto

Department of Chemistry "U. Schiff", University of Florence, Via U. Schiff 6-Via della Lastruccia 3-13, 50019 Sesto Fiorentino, Italy

benedetta.pasquini@unifi.it

A fast and reliable capillary zone electrophoresis method was set up for the simultaneous determination of glibenclamide (GLI), an antidiabetic drug belonging to the class of sulfonylureas, and its main impurities reported in European Pharmacopeia. The method was developed following QbD principles according to ICH guideline Q8 [1], implementing each step of QbD workflow for separation methods as recently reported [2]. The analytical target profile was defined by the baseline separation and the accurate determination of GLI and its impurities in the pharmaceutical dosage form, with LOQ values for the impurities equal or lower to 0.1% with respect to the main compound. In the screening phase different critical process parameters, each studied at three levels by a symmetric screening matrix, were taken into consideration: voltage, temperature, background electrolyte concentration and pH, injection time. The subsequent response surface study was carried out by using a Box-Behnken design and allowed the design space to be identified. By applying the selected working conditions, a complete separation of the analytes was obtained in less than 2 min. The developed method was validated according to ICH guideline Q2(R1) [3] and then applied to the analysis of real samples of glibenclamide tablets.

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ANA-P3

Evaluation of the inclusion complex formation of levosulpiride and cyclodextrins by capillary electrophoresis, molecular modeling and NMR

Benedetta Pasquini[a], *Fabrizio Melani*[b], *Serena Orlandini*[a], *Sergio Pinzauti*[a], *Sandra Furlanetto*[a]

[a]*Department of Chemistry "U. Schiff", University of Florence, Via U. Schiff 6, 50019 Sesto Fiorentino, Italy*
[b]*NEUROFARBA, University of Florence,Via U. Schiff 6, 50019 Sesto Fiorentino, Italy*

benedetta.pasquini@unifi.it

The complexation system between levosulpiride (L-SUL) and different cyclodextrins (CDs) was investigated with the aim of evaluating the intermolecular interactions involved in enantioseparation by capillary electrophoresis (CE). A molecular modeling study made it possible to explain the different affinities of L-SUL for several cyclodextrins tested during CE method scouting. The calculated binding energies showed the most stable complexes, obtained with sulfated-β-CD and methyl-β-CD. A correlation between CE migration time and stability complex of analyte–CDs complexes was postulated. Furthermore, rotating-frame Overhauser effect spectroscopy NMR (ROESY) experiments were carried out to confirm the mechanism of separation, providing valuable and complementary information. 2-D NMR ROESY spectra clearly indicated the formation of complexes, highlighting the presence of the benzene sulfonamides moiety of L-SUL inside the hydrophobic cavity of the CDs.

ANA-P4

Frazionamento solubile/insolubile di Cd, Pb e Cu nella neve dell'Antartide e relazione con l'aerosol

G. Libani, C. Truzzi, A. Annibaldi, S. Illuminati, C. Finale, G. Scarponi

Dipartimento di Scienze della Vita e dell'Ambiente, Università Politecnica delle Marche, Via Brecce Bianche, 60131, Ancona, Italia

g.libani@univpm.it

È stata messa a punto una metodologia di frazionamento chimico per la determinazione delle frazioni solubile (in acqua) e insolubile (estraibile con HCl diluito) di Cd, Pb e Cu in campioni di neve dell'Antartide. I campioni scongelati sono stati filtrati e la frazione insolubile in acqua è stata estratta con HCl ultrapuro diluito (pH ~1.5). La determinazione dei metalli è stata effettuata mediante voltammetria di ridissoluzione anodica ad onda quadra (SWASV) [1-5]. È stata verificata l'additività delle due frazioni rilevate per la determinazione del totale estraibile. Le concentrazioni totali dei metalli in campioni raccolti in un'area pulita nei pressi della Base Mario Zucchelli sono dell'ordine di 10-20 pg/g per il Cd, 20-40 pg/g per il Pb e 60-120 pg/g per il Cu con una sostanziale equidistribuzione tra frazione solubile e insolubile. Questi frazionamenti sono confrontabili (e mostrano lo stesso trend temporale) con quelli dell'aerosol raccolto nella stessa area e nello stesso periodo, confermando la stretta relazione esistente tra la distribuzione dei metalli nella neve e nell'aerosol. Le concentrazioni rilevate in prossimità della Base aumentano a causa del contributo antropico e la distribuzione cambia, con il Cd presente in maniera predominante nella frazione solubile (~80%), mentre Pb e Cu sono maggiormente concentrati nella frazione insolubile (rispettivamente 70-80% e 70%).

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ANA-P5

Contributo Ritirato

ANA-P6

A new flow-through system for the calibration of Polar Organic Chemical Integrative Samplers (POCIS)

Emanuele Magi, Shivani Tanwar, Marina Di Carro

Dipartimento di Chimica e Chimica Industriale, Università di Genova,
Via Dodecaneso 31, 16146, Genoa, Italy

emanuele.magi@unige.it

The use of passive sampling for the monitoring of micropollutants in different water matrices is rapidly increasing [1], expecially of the Polar Organic Chemical Integrative Sampler (POCIS). This sampler, designed to sample and concentrate hydrophilic contaminants, consists in a sorbent phase sandwiched between two microporous polyethersulfone membranes: chemicals diffuse from the water through the membrane and adsorb into the sorbent. POCIS can provide Time-Weighted Average (TWA) concentration of contaminants in water if the sampling rates (R_S), specific for each compound and representing the quantity of water cleared by the sampler per time unit, are known [2]. In our laboratories POCIS samplers were employed for various studies[3-5]; recently a homemade flow-through calibration system has been developed and used to calculate the sampling rates of eight analytes belonging to three different classes of pollutants: pesticides, non-steroidal anti-inflammatory drugs (NSAIDs) and perfluorinated compounds. Different water flow rates, resembling the typical range of a river, and two analyte concentrations were tested to evaluate their possible influence on R_s. POCIS extracts were analyzed by LC–MS/MS, using multiple reaction monitoring to maximize sensitivity. Results highlight that the calculated sampling rates are rather constant at the considered concentrations and flow rates. The average sampling rates obtained with the calibration have been employed to assess the TWA concentration of the analytes in river and drinking waters. Results are in good agreement with the concentration levels usually detected in the considered real waters.

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ANA-P7

In vitro permeability of silver nanoparticles through oral mucosa

M. Crosera[a], C. Bianco[a], E. Baracchini[a], M. Mauro[b], F. Filon Larese[b], M. Bovenzi[b], P. Barbieri[a], G. Adami[a]

a Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Trieste,
Via Giorgieri 1, 34127, Trieste, Italia
b Dipartimento Clinico di Scienze mediche, chirurgiche e della salute, Università di Trieste,
Strada di Fiume 447 - Ospedale di Cattinara, 34149 - Trieste, Italia

gadami@units.it

AgNPs can come in contact with human oral mucosa because of their wide use as antiseptical agents in many products, mouthwash, teeth brush, food packaging and as main ingredient in water purification devices.

In vitro permeation experiment was performed using Franz diffusion cells with porcine buccal mucosa adapting the method used for skin permeation studies[1]. Two different donor phases were applied separately to the outer surface of the mucosa of two groups of cells. The first was a suspension of AgNPs at a concentration of 500 mg/L, while the second one was a solution obtained from ultrafiltration of the first one and containing only Ag ions. Both donor phases were diluted with 1 ml of physiological solution and applied for 4 h. AgNPs were as small as 19 ± 5 nm (mean and S.D.). Analyses of Ag concentrations were performed by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS).

Ag permeation was demonstrated through oral mucosa, with similar flux permeation values in receiving solutions of AgNPs exposed cells and in Ag-ions exposed ones (6.76 ± 4.49 ng cm^{-2} h^{-1} and 5.18 ± 4.29 ng cm^{-2} h^{-1}, respectively). Ag content evaluated inside the mucosa demonstrated similar values in both series too (1.60 ± 2.02 μg/cm^2 for AgNPs and 1.17 ± 0.78 μg/cm^2 for Ag ions).

In conclusion, when Ag is applied as NPs solution, the mucosal content and the permeation profile of the metal are similar to those obtained when a solution containing only Ag ions is used. Results may suggest that the permeation flux through oral mucosa and the mucosa content of the metal are mainly due to the absorption of the ions released by the AgNPs.

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ANA-P8

Skin penetration of cobalt oxide nanoparticles

M. Crosera[a], *C. Bianco*[a], *E. Baracchini*[a], *M. Mauro*[b], *F. Filon Larese*[b], *M. Bovenzi*[b], *T. Montini*[a], *G. Adami*[a]

a Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Trieste,
Via Giorgieri 1, 34127, Trieste, Italia
b Dipartimento Clinico di Scienze mediche, chirurgiche e della salute, Università di Trieste,
Strada di Fiume 447 - Ospedale di Cattinara, 34149 - Trieste, Italia

gadami@units.it

In-vitro experiments were performed using Franz diffusion cells with human skin, obtained from surgical waste, to evaluate skin penetration and permeation of cobalt oxide (II-III) nanoparticles (Co_3O_4NPs).

Three different experiments were conducted using intact (exp. 1 and 2) and damaged skin (exp 3): in exp. 1 a suspension of Co_3O_4NPs at a concentration of 1000 mg/L in physiological solution was used as donor phase; in exp. 2 a solution obtained from an ultrafiltration (Amicon 10kD) of the suspension used in the previous experiment has been used; in exp. 3 a damaged skin protocol has been used. Six cells were treated only with physiological solution (blank cells). The experiments were run for 24 h. A physiological solution was used as receiving phase. Cobalt concentrations in the receptor fluid samples have been evaluated by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS).

Co_3O_4NPs were smaller than 50 nm with a surface area ranging between 40 and 70 m^2/g. Cobalt into receiving phases after 24 hours was significantly higher using the damaged skin protocol (47.2±41.1 ng/cm^2) while no significant differences were shown between blank cells (2.18±0.10 ng/cm^2), those with intact skin exposed to Co_3O_4NPs (2.34±0.23 ng/cm^2) and those with intact skin exposed to the ultrafiltrated solution (2.64±0.56 ng/cm^2).

These data suggest that Co_3O_4NPs can permeate the skin only using a damaged skin protocol while no absorption has been found in intact skin. Co_3O_4NPs can't release ions in physiological condition so the permeation of cobalt is lower than that measured when cobalt NPs have been tested[1].

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ANA-P9

Monitoring of hexachlorocyclohexane isomers in the Sacco's River Valley

Roberta Bernini, Isabella Carastro, Pietro Carai, Pier Paolo Danieli, Bruno Ronchi

Dipartimento di Scienze e Tecnologie per l'Agricoltura, le Foreste e l'Energia (DAFNE),
Università della Tuscia di Viterbo,
Via San Camillo De Lellis, 01100, Viterbo, Italia

i.carastro@unitus.it

The Sacco's River Valley is a wide area located in the central Italy mostly devoted to agriculture but also comprising several industrial sites. Since 2005 this area is undergoing an environmental crisis due to the contamination by hexachlorocyclohexane isomers (HCHs), organochlorine pesticides widely used in the past for crop protection. Chemically, the HCHs are isomers (namely: α, β, γ, δ, ε, η and θ) which differ for the physical-chemical properties and persistence in the environment related to the axial-equatorial substitution pattern of chlorine atoms around the six carbons ring [1]. A peak of contamination by HCHs was revealed in March 2005 when high levels of the β-isomer (β-HCH, 20 times higher than the legal limits) were detected in milk produced from a dairy farm located within the Sacco's River Valley.

The present study was focused on the investigation of the occurrence and distribution of HCHs isomers in different samples (soil, water, milk, feed and vegetables) collected in nine dairy farms located in the Sacco's River Valley. The samples were collected in June-September 2013 and January-April 2014. After the appropriate preparation, all samples were analyzed by GC-ECD and GC-MS. At several years from the onset of the agro-environmental crisis, our analytical data confirmed a high degree of pollution in the investigated area, which deserves continuous environmental monitoring due to the strong impact of persistent organic pesticides on rural environment and human food chain.

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ANA-P10

Detection of MCs in natural and culture samples with an optimized colorimetric PP2A inhibition method

K. Petropoulos[a] ,G. Volpe[a], L. Micheli[a], , L. Lvova[a], C. Guanais Branchini[a], E.Viaggiu[b], R.Congestri[b], L. Guzzella[c], F. Pozzoni[c], C. Di Natale[d], G. Palleschi[a], and R.Paolesse[a]

a Department of Chemical Science and Technologies,
b Department of Biology,
c Department of Electronics Engineering,
University of Rome Tor Vergata, via della ricerca scientifica 1, 00133, Rome, Italy
d IRSA-CNR, via del mulino 19, 20861, Brugherio, Italy

Konstantinos.Petropoulos@uniroma2.it

We present a colorimetric protein phosphatase (PP2A) inhibition method for the detection of microcystins (MCs) in water and culture samples without a preconcentration step. We have optimized the sensitivity of the assay by increasing the concentration of the cofactor $MnCl_2$ and adjusting the testing sample volume into the well. In these conditions a typical sigmoid calibration curve was obtained with a detection limit of 0.08 µg/l, a working range between 0.2 and 0.8 µg/l and an IC_{50} value of 0.33 ± 0.06 µg/l.

Tap water and river water samples were investigated in terms of recovery with good results. Moreover, two *Microcystis aeruginosa* strains, one toxic and the other non-toxic, were cultured in Bold's Basal Medium, at standard light and temperature conditions and monitored for MCs' release in the medium over a four-week growth period. The results obtained with our assay were both compared with a standard chromatographic technique (UHPLC-DAD) and a potentiometric E-tongue system. Using PLS regression, the prediction of MCs' release by the toxic strain was possible with satisfactory correlation coefficients and mean relative errors of validation equal to 0.0089 (*vs* HPLC-DAD) and 0.373 µg/l (*vs* E-tongue system).

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ANA-P11

Potential Ecological Risk Assessment posed by TBT to costal water of Apulia (IT) and Albania

P Massanisso[a], *S. Manzo*[b], *C.Cremisini*[a], *L.Parrella*[c]

a ENEA,UTPRA-GEOC, CR Casaccia, Via Anguillarese 301, 00123, Rome, Italy
b ENEA, UTTP-CHIA, CR Portici. P. le E. Fermi, 1, 80055 - Portici, Naples, Italy,
c Università degli Studi di Napoli "Federico II"-CRIAcq, Naples, Italy

paolo.massanisso@enea.it

Tributyltin (TBT) has been used worldwide as additives in antifouling paints, in order to protect the ship's hull or submerged static structures from the colonization of aquatic organisms (bio-fouling). Due to the high toxic effects posed to various non-target aquatic species, the International Maritime Organization (IMO) banned the use of TBT, starting from 2008. However, several studies [1] showed that TBT may remain in the sediment for years, sediment acting as a source for water column exposures.

Under the frame of CARISMA project, funded by the Italian Ministry of Foreign Affairs, the following specific studies have been conducted on TBT in Apulia (IT) and Albania coastlines: (i) determination of TBT concentration in ports and marinas in different season, in summer and after the nautical season in winter, (ii) the ecotoxicological assessment of sampled seawater and (iii) an evaluation of the probabilistic ecological risk assessment (ERA) of TBT for the marine environment.

In the present study, the ERA procedure developed by US-EPA has been applied [2]. The numerical hazard quotients (HQs) have been obtained as the ratio of the measured exposure concentrations to the 5th percentile of species sensitivity distributions, used as toxicity benchmarks. The estimated 5th percentile from literature toxicity data is 3 ng/L for TBT. If the exposure concentration is equal or exceeds the effect concentration, the HQ value is equal or greater than one, and an ecological risk is suspected.

Preliminary results have shown HQ values >1 in summer whereas the results on winter seems to be less significant.

Consequently, based on summer data, the ban of TBT is not yet sufficient to cancel any deleterious effects on aquatic exposed organisms and further investigation on the presence, the source and the impact of TBT in the marine environment are necessary in order to evaluate the associated risk.

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ANA-P12

Implementazione di un modello di migrazione di contaminanti in ambito marino costiero

P. Massanisso, *L.Monte, M. Angeluzzi, G.Armiento*

ENEA, UTPRA/GEOC, CR Casaccia, Via Anguillarese, 301 – 00123 Roma.

paolo.massanisso@enea.it

Il modello di migrazione studiato ha utilizzato le potenzialità del DSS (Decision Support System) MOIRA, messo a punto da ENEA in collaborazione con varie Istituzioni di ricerca Europee.

Per le applicazioni di MOIRA in ambiente marino [1] è stata introdotta la possibilità di considerare movimenti bidirezionali dei flussi d'acqua tra i vari comparti per simulare gli effetti della circolazione delle acque e dei processi di stratificazione e destratificazione verticale.

Il modello è stato ottimizzato alle condizioni specifiche del sito studiato e dei contaminanti considerati (metalli pesanti). Lo studio, effettuato nell'ambito del progetto bandiera RITMARE finanziato dal MIUR, è stato eseguito mediante l'integrazione del modello di migrazione e di misure sperimentali in situ, allo scopo di valutare la dinamica temporale del comportamento di tali sostanze inquinanti nel sistema ambientale rappresentato dal bacino idrografico del fiume Sarno e dal golfo di Castellammare.

I campionamenti di acque e sedimenti sono stati effettuati lungo l'asta fluviale del Sarno e nel golfo e le relative analisi dei metalli mediante ICP-MS.

In particolare, sono stati presi in considerazione il Cr e l'As quali esempi di due elementi caratterizzati da comportamenti ambientali significativamente differenti dovuti alla diversità delle loro caratteristiche chimico-fisiche e della loro origine prevalentemente antropica per il Cr e geogenica per l'As.

I risultati preliminari suggeriscono, tra l'altro, che i contributi di metalli provenienti dal fiume non sono sufficienti a giustificare le concentrazioni misurate nell'ambiente marino. Risulta pertanto importante determinare i flussi di queste sostanze trasportate dalle correnti che attraversano il golfo di Napoli per un'analisi affidabile del loro bilancio.

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ANA-P13

Ultra high performance liquid chromatography-tandem mass spectrometry determination of UV filters in environmental surface waters

Patrizia Foglia[a], *Anna Laura Capriotti*[a], *Roberto Samperi*[a], *Serena Stampachiacchiere*[a], *Salvatore Ventura*[a], *Aldo Laganà*[a]

a Dipartimento di Chimica, Università degli Studi di Roma "La Sapienza", P.le Aldo Moro 5, 00185, Rome, Italy

patrizia.foglia@uniroma1.it

UV filters include various and heterogeneous chemical classes present as ingredients in personal care products, such as sunscreen products, cosmetics, hair sprays, etc., to protect skin and hair from the negative effects of sunlight. Furthermore, they are also present in several plastic products and packaging, paints, glasses, textiles, to prevent yellowing and degradation of polymers and pigments [1]. As a consequence of their widespread employment, UV filters are continuously released in the environment [2], so causing a serious thread. Currently, the EU Regulation permits the employment of 26 compounds, within certain limits, in cosmetic (sun-screen) products.

The aim of this work was to develop and validate a highly sensitive multiresidue method based on solid phase extraction, employing graphitized carbon black as sorbent material, followed by UPLC/ESI-MS/MS for the analysis of sixteen UV filters and environmental degradation products with a wide range of physicochemical properties. Recoveries above 70% were obtained for all the analytes from lake water samples. A survey on few water samples from three lakes in the area of Rome showed that some of these UV filters are present in small amount.

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ANA-P14

Metal baseline in lacustrine systems of Terra Nova Bay and concentration evolution in surface waters.

Zelani I[a], *Malandrino M.*[a], *Giacomino A.*[a], *Buoso S.*[a], *Sivry Y.*[b], *Benedetti M.*[b],*Abollino.O.*[a]

a Dipartimento di Chimica, Università di Torino, Via Verdi 8,10124,Torino, Italia
b Université. Paris Diderot, Sorbonne Paris Cité, IPGP, UMR 7154, CNRS, Paris, France

isabella.zelano@unito.it

Major, minor and trace elements were determined in freshwater, algae and mosses of lacustrine systems in Terra Nova Bay (Antarctica) to determine a background level of such elements in the most pristine environment on Earth and to monitor a potential local and/or global anthropogenic contamination. Samples were collected during the field works of 2009-2010-2011 within the framework of the Italian National Program of Research in Antarctica (PNRA). Correlation between variables were obtained by processing results with Principal Component Analysis (PCA). Hierarchical Cluster Analysis (HCA) was used to highlight differences and similarities among the investigated lakes. Data show that in all matrices potentially anthropogenic pollutants (e.g. Cd, Pb, Zn, Cu and Ni) have a strong correlation with the lithogenic elements (e.g. Al, Si, Fe). Comparing algae and mosses, metals were found to be generally less concentrated in the latter than in algae because of the considerable bioaccumulation factors typical of algae[1], while mosses reflect the presence or absence of pollution due to atmospheric transport. Content of potentially anthropogenic pollutants in waters was compared with older results (since the early '90s[2, 3]) to present a historical overview of metal evolution. No clear trend was identified for any of the investigated elements, suggesting that their concentration evolution is hardly correlated to a permanent anthropic contribution.

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ANA-P15

Surface chemical species in size-fractionated airborne particulate matter of Antarctica

Simona Rella[a], *Cosimino Malitesta*[a]

a Dipartimento di Scienze e Tecnologie Biologiche e Ambientali, Di.S.Te.B.A.,
Università del Salento, via Monteroni, 73100 Lecce, Italy

simona.rella@unisalento.it

Surface characterization of airborne particulate matter (PM) is of paramount importance in understanding its transport and environmental impact. In this respect, XPS continues to be applied as a tool for unravelling its surface chemical speciation (see e.g. ref. 1).
Within the framework of PNRA 2009 (Project PROGDEF 09_153), we have already reported [2] first results relevant to PM collected in Antarctic site of Faraglioni (74°42.968’ S, 164°06.895’ E) on cellulose filters with dimensional fractionation (5 stages, 1 back) in the period 2010/2011. The present communication completes illustration of XPS data recorded..
Measurements have been performed using an AXIS Ultra DLD XP spectrometer (Kratos Analytical, UK) with an Al monochromatic source (1486.6 eV). Blank filters have been analyzed as well. C 1s, O 1s, N 1s, Na 1s, Ca 2p, Cl 2p, S 2p, Si 2p, Fe 2p, F 1s, P 2p, Zn 2p, Mg 1s, Al 2p region have been recorded on each sample. In addition, Mo, Sr, Mn, Cr, Ti e Cu resulted below LODs, while detected by ICP-MS data [3].
Apart Fe and Zn concentrated in a single size class, the other elements appears generally distributed overall size classes. The median size class shows often higher concentration for each element. Speciation has been performed on the basis of binding energies. N-C, N^+ and NO_3^- species have been detected with peculiar size distribution.

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[3] M. Grotti, personal communication

ANA-P16

Persistent Organic Pollutants in Antarctica: occurrence and trends

Martellini T.[a], *Cincinelli A.*[a], *Corsolini S.*[b], *Pozo K.*[b], *Giannarelli S.*[c],

Francesconi S.[c], *Muscatello B.*[c],*Fuoco R.*[c]

a a Dipartimento di Chimica, Università di Firenze, Via della Lastruccia, 3, 50019 Sesto Fiorentino, Firenze

b Dipartimento di Scienze fisiche, della terra e dell'Ambiente, Università di Siena,Via Mattioli 4, Siena

c Dipartimento di chimica e chimica industriale, via Risorgimento, Pisa

tania.martellini@unifi.it

Persistent Organic Pollutants (POPs) are chemical substances that persist in the environment, bioaccumulate through the food web, and pose a risk of causing adverse effects to human health and the environment. The Polar Regions are considered a final sink for many POPs. They have been detected in the region since the 1960's, and various studies have been conducted to study the contamination of POPs in the environment and wildlife of the Arctic and Antarctic regions. Their occurrence in these pristine areas has been explained by the global distillation process and long-range atmospheric transport (LRAT) is considered to be the main pathway for POPs to reach the Polar Regions. In the framework of the Italian National Program for Antarctic Research (PNRA), the research projects "Flows of POPs between poLar Abiotic and Biotic compartments" (PdR 2009/A1.04) and "Environmental contamination in Antarctica: levels and trends of legacy persistent organic pollutants (POPs)" (PdR 2009/A2.10) aimed to determine the occurrence, levels and fate of legacy and emerging POPs including polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated naphthalenes (PCNs), organochlorine pesticides (OCPs) and polybrominated diphenylethers (PBDEs) in abiotic and biotic samples. In particular, passive air samples were collected at six sites in the coastal area of Terra Nova Bay and analysed in order to assess levels and spatial distribution of POPs. Sea water samples were collected at different depths from seven oceanographic stations located in the Ross sea and close to the Circumpolar Convergence to evaluate their possible sources and relationship with physical and biological processes taking place in the water column. *Trematomus bernacchi* were also collected in the Ross sea to evaluate the POPs (bio)accumulation in marine organisms.

ANA-P17

Solid-phase extraction and HPLC-FD determination of Fluoroquinolone antibiotics from waters on silica-grafted monolayer reduced graphene oxide

Andrea Speltini, Michela Sturini, Federica Maraschi, Luana Consoli, Alberto Zeffiro, Antonella Profumo

Dipartimento di Chimica, Università di Pavia, Via Taramelli 12 , 27100, Pavia, Italia

andrea.speltini@unipv.it

Fluoroquinolones (FQs) are emerging contaminants of great environmental relevance whose determination requires accurate analytical methods [1]. Since graphene has attracted great interest as a new solid-phase extraction (SPE) sorbent, due to the huge surface area and possibility of multiple chemical interactions with a wide range of molecules [2], in this work we have synthesized a hybrid material consisting of monolayer graphene oxide (GO) flakes covalently-bonded onto aminopropyl silica microparticles. Chemical reduction in aqueous hydrazine allowed to obtain the reduced GO (RGO). The final materials (silica-RGO 5-18wt%) were tested as reversed-phase sorbent for the SPE of FQs from natural waters, followed by HPLC-FD. Recovery and precision were evaluated on tap water samples (500 ng L^{-1}, n=3). Elution with alkaline aqueous solutions gave absolute recovery in the range 71-110% (RSD<8%). Sample volumes up to 250 mL provided enrichment factors up to 100, achieving method detection limits of few ng L^{-1}. The reusability of the silica-RGO cartridge was also evaluated. The proposed analytical procedure will be applied to the determination of these emerging contaminants at the low nanograms per litre levels in actual water samples.

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ANA-P18

Determination of pesticides in wheat with micro-solid phase extraction (µSPE) followed by UHPLC-MS/MS

Flavio Della Pelle[a,b], *Manuel Sergi*[a*] *Rossana Scarpone*[c], *Camilla Montesano*[d], *Roberta Curini*[d], *Dario Compagnone*[a], *Alberto Escarpa*[b]

[a] *Faculty of Bioscience and Technology for Food, Agriculture and Environment, University of Teramo, 64023, Teramo, Italy*
[b] *Departamento de Química Analítica, Química-Física e Ingeniería Química. Facultad de Química. Universidad de Alcalá, 28871 Alcalá de Henares, Madrid, España*
[c] *Istituto Zooprofilattico dell'Abruzzo e del Molise "G. Caporale", 64100 Teramo, Italy*
[d] *Department of Chemistry, Sapienza University of Rome, P.le A. Moro 5, 00185 Rome, Italy*

flaviod.p.86@hotmail.it

The challenge in the analysis of pesticides in food and feed is the development of simple, rapid, cost-effective and reliable analytical multi-residual methods. A common problem in the use of pesticides is the erroneous application regarding the dose, timing and frequency of application. The wheat derived products are the basis of the Mediterranean diet (pasta, bread, etc.); the analysis of target pesticides at low concentrations in grains products requires the elimination of matrix interferences in order to make possible a chromatographic analysis followed by mass spectrometry. The purpose of this work is the development of a rapid and effective method of extraction and analysis of pesticides in wheat and derivatives. In this work µSPE with modified tips was employed for the clean-up step; these tips are made of fiberglass functionalized with apolar chains of octadecylsilane into monolithic structure. The analyses were focused on the most widely used pesticides found in the wheat matrix [1]: *pirimiphos-methyl* ,chlorpyrifos-ethyl, chlorpyrifos-methyl , malathion. The determination was carried out using a UHPLC-MS/MS. The optimized method allows to obtain, with a few simple steps (loading, washing, elution), an effective cleanup of the matrix wheat, exploiting the µ-SPE extraction procedure, coupled with LC-MS/MS analysis.

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ANA-P19

Combined derivatization and HPLC-FL-DAD for simultaneous analysis of Octreotide and Gabexate Mesylate metabolite in human pancreatic juice samples

G. Carlucci[a], *F. Selvaggi*[b], *S. Sulpizio*[b], *C. Bassi*[c], *R. Cotellese*[b], *V. Ferrone*[a], *P. Innocenti*[b], *M. Locatelli*[a]

[a] *Dipartimento di Farmacia,* [b] *Dipartimento di Scienze Cliniche e Sperimentali -Università degli Studi "G. d'Annunzio" di Chieti-Pescara , Via dei Vestini , 66100 Chieti;* [c]*Dipartimento di Chirurgia - Ospedale "G.B. Rossi" Verona, Italia*

gcarlucci@unich.it

Ocreotide, is a synthetic long-acting cyclic octapeptide, which is a somatostatin analog that has a longer half life and more selectivity in inhibiting hormone secretion than somatostatin. It is used for the clinical management of endocrine disorders where it acts by inhibiting the release of growth, insulin, glucagon, and some other hormones [1]. Gabexate mesylate, is a nonantigenic synthetic inhibitor of plasmatic and pancreatic serine proteinases, that is used therapeutically in the treatment of pancreatitis and disseminated intravascular coagulation and as a regional anticoagulant for hemodialysis [2]. Proteases are widely distributed in the human body and may be involved in several diseases, especially acute pancreatitis.

A HPLC method with DAD and FLD detection was developed and validated fro the simultaneous quantification of these drugs in human pancreatic juice samples. Octreotide and gabexate mesylate metabolite after derivatization with NBD-F were separated on a Luna C_{18} column using gradient mode. Biphalin and methy-*p*-hydroxybenzoate were used as internal standards.

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ANA-P20

Conservative Quantification of Amino Functionalities Chemically Bonded on Porous Solids

Marco Pierini[a], *Alessia Ciogli*[a], *Antonella Fontana*[b], *Francesco Gasparrini*[a], *Giuliana Manzi*[a], *Gabriella Siani*[b], *Claudio Villani*[a]

a Dip. di Chimica e Tecnologie del Farmaco, Università di Roma "La Sapienza", P.le Aldo Moro 5, 00185, Rome, Italy
b Dip.di Scienze del Farmaco, Università "G. D'Annunzio", 66013, Chieti, Italy

marco.pierini@uniroma1.it

Amino-functionalized solid materials, involving basic groups, such as $-NH_2$, $-NHR$, $-NR_2$, are widely employed in a variety of applications, especially in the field of CO_2 capture and storage technologies, focused on environmental and industrial purposes, as well as in that of the separations technology, which finds very large enforcement within both academic and pharmaceutical context. In particular, in the role of stationary phases for chromatographic techniques, amino groups are commonly linked to solid matrices of silica through alkyl chains, which, for example, can be successfully employed in HILIC applications and, in general, in the effective resolution of restricted but important classes of compounds (e.g. mixtures of mono- or oligo-saccharides). In this communication we are going to present an original, really effective and operatively simple procedure, developed with the aim to quantify the density of amino groups chemically bonded to the surface of porous solids and to ensure a full recovery of the material (i.e. "*conservative*" method). The approach is based on the salification of the amino-functionalities through a species (**HA**$^{\mathbf{UV}}$) of suitable acidity and UV absorptivity. The quantification is then performed either by retro-titrating, via UV spectrophotometry, the **HA**$^{\mathbf{UV}}$ displaced from the salt by addition of a stronger acid, or directly, by analyzing the characteristic vibrational bands of the salified material by IR spectrometry in presence or in the absence of suitable external standards.

ANA-P21

Study for the speciation and rapid measurement of copper content in contaminated insulating oils

R.M. De Carlo[a], *C. Sarzanini*[a], *M.C. Bruzzoniti*[a]

[a] *Dipartimento di Chimica, Università di Torino, Via Pietro Giuria 5, 10125, Torino (Italy)*

rosa.decarlo@unito.it

Many recent studies highlighted that damages into power transformers can be originated by degradation phenomena of their liquid insulator (mineral oil) and by the release of copper-based compounds, deriving from core and conductors, into the insulator itself. Consequently, the knowledge of the forms in which copper contaminants are present in the mineral oil is of crucial importance, as well as the prompt determination of copper species in the oil, and the identification of possible procedures to reduce the risk damage. At this purpose, the study here presented is focused on the development of liquid-liquid and liquid-solid (LLE/SPE) extractions, to identify the forms in which copper is present in mineral oil to reduce the metal content. Additionally, the development of strategies for the on-site measurement of copper in oil is presented. For the extraction studies, 16 insulating oils sampled from in-service transformers were selected. The residual copper concentration after extraction was measured by inductively coupled plasma optical emission spectrometry (ICP-OES). LLE were performed comparing the extraction efficiency of acids (HCl and HNO_3) and ligands at different complexation capacities (sodium ethylenediaminetetraacetate, ammonium pyrrolidinedithiocarbamate, pyridinedicarboxylic acid and sodium diethyldithio-carbamate). For SPE studies, the performances of substrates at different physico-chemical characteristics were evaluated. In detail an hydrophobic (Amberlite XAD-16), a chelating (Chelex 100), an anion-exchange (A-200) and a cation-exchange (Dowex Marathon C) resin were selected. Both the studies showed that, in the samples studied, the percentage of copper present in the cationic form was included between 4% and 42%. The SPE study showed that in the samples considered, the percentage of copper present as non-polar complexes was included between 12% and 53%. The results obtained by the characterization study posed the basis for the on-site determination of copper, through metal-selective colorimetric reactions. Since, as evidenced by the SPE study, copper can be present in oil mainly as cationic and non-polar compounds, a sample pretreatment was necessary to remove the matrix and to solubilize copper before the colorimetric reactions. The analytical performances of colorimetric reactions with different ligands are shown.

ANA-P22

Development of innovative multidimensional protein identification approach combining organic monolithic and reversed phase pre-columns.

Susy Piovesana[a], *Anna Laura Capriotti*[a], *Chiara Cavaliere*[a], *Patrizia Foglia*[a], *Francesco Gasparrini*[b], *Riccardo Zenezini Chiozzi*[a], *Aldo Laganà*[a]

a Dipartimento di Chimica, Università degli Studi di Roma La Sapienza, P.le Aldo Moro 5, 00185 Roma (Italia)
b Dipartimento di Chimica e Tecnologie del Farmaco, Università degli Studi di Roma La Sapienza, P.le Aldo Moro 5, 00185 Roma (Italia)

susy.piovesana@uniroma1.it

Bottom-up proteomics is the most mature and most widely used approach for protein identification and characterization. On-line nano/capillary-scale reversed phase LC–ESI–MS^n provides high-resolution separations of peptide digests. Practical limitations occur when protein identification starts from very complex peptide mixtures or from low-abundance peptides. In order to improve the throughput of bottom up approach, we developed a new on-line capillary multidimensional system using two chemically different pre-columns: one polymeric methacrylate-based monolithic support and the other C18 stationary phase packed with silica microparticles. The peptides were resolved on reversed phase stationary phase in capillary column format. In detail, the trapping step involves both pre-columns connected in series and the low to high molecular weight peptides were fractionated in two portions: the monolithic pre-column keeps peptides with medium-high molecular weights while the RP packed pre-column holds peptides with low masses. In elution step, the capillary C18 packed column will be coupled alternately with the two pre-column to resolve the on-line split samples. This innovative system ensures a protein score gain up to 40 % compared with a conventional pre-column/column approach.

ANA-P23

Activated carbons for the removal of organic micropollutants from groundwater

Valentina Pifferi[a], *Luigi Falciola*[a], *Mattia Villella*[a], *Manuela Antonelli*[b], *Nicoletta Promontorio*[b]

a Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133, Milano, Italy
b Dipartimento di Ingegneria Civile e Ambientale, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133, Milano, Italy

valentina.pifferi@unimi.it

According to US-EPA (United States-Environmental Protection Agency) adsorption on Granular Activated Carbons (GAC) constitute the best available Technology for the removal of Volatile Organic Compounds (VOC), Natural Organic Matter (NOM) and pesticides from drinking water. In this presentation, we compare the adsorption capacity of two commercially available GACs: a coal-based carbon (GAC-M; Cecarbon Gac 1240, Arkema) and a coconut-shell carbon (GAC-V; Acticarbone NCL 1240, Arkema). The study was conducted on real samples from the Integrated Water System of the City of Milano.

Considering the variability of the groundwater contamination, a preliminarily statistical analysis of the monitoring data was carried out to identify water-treatment plants that are characterized by a specific contamination profile and that can be considered as representative of Milano groundwater pollution as a whole. Five water treatment plants were identified and thus studied.

A standard methodology for the determination of adsorption capacity of the activated carbons by a micro-isotherm technique for adsorbates at ppb concentrations was used (ASTM D5919-96). 5 carbon concentrations were studied: 1, 8, 12, 20 and 30 mg/L for GAC-M and 1, 3, 5, 8 and 12 mg/L for GAC-V. Isotherm data were collected from experimental samples. 53 analytes were determined using EPA Methods for VOCs (524.3 version 1.0, 2009; 5030C version 3.0, 2003) and APAT-IRSA method for pesticides (5060, 2003). In addition, chemico-physical characterization of the two GC types were performed, to correlate specific surface and porosity volume to adsorption properties.

The coconut-shell carbon presents better adsorption performances towards all the tested pollutants and adsorption capacity that is greater even in adverse conditions. For these reasons it can be considered the most suitable adsorbent.

ANA-P24

Amperometric sniffer for volatile amines based on paper-supported room temperature ionic liquids enabling rapid assessment of fish spoilage

R. Toniolo[a]*, N. Dossi*[a]*, R. Svigelj*[a]*, G. Bontempelli*[a]*, S. Susmel*[a]

[a] *Department of Food Science,*

University of Udine, via Cotonificio 108, I-33100 Udine, Italy

Rosanna.Toniolo@uniud.it

Detection and quantitative determination of volatile amines (VAs) has a great relevance in environmental monitoring and in food analysis, in view of their importance as both ubiquitous air pollutants and indicators of fish spoilage[1]. In fish, the main species responsible for the typical flavor of spoiled fish are VAs and, in particular, trimethylamine (TMA) and ammonia that are the predominant nitrogen compounds in the headspace during fish storage. They are accompanied by small amounts of dimethylamine (DMA) and methylamine (MA), while other VAs are only present at trace levels. These compounds are naturally present also in fresh fish, even though at low levels (below 20-30 ppm, depending upon fish species), and their concentration remains constant enough for about 8-10 days under iced storage. After this time, a progressive enhancement of their concentration occurs which is particularly rapid for TMA.

In this communication we propose a sensitive amperometric sniffer consisting of a gas sensors based on a room temperature ionic liquid (RTIL) supported on paper, recently developed by us [2] for the rapid assessment of fish spoilage. It involves its use as a detector for a simple flow analysis apparatus where amines from the head-space in equilibrium with fish samples are injected. The method presented appears particularly attractive for disposable-portable devices for decentralized control operations with short analysis time, minimal reagent consumption and low detection limits.

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ANA-P25

Caratterizzazione di ossidi di rodio disperso su nanotubi (MWCNT) per la riduzione catalitica di nitrato e nitriti in mezzo acido

Michela Contursi, Innocenzo G. Casella

Dipartimento di Scienze, Università degli Studi della Basilicata, Via dell'Ateneo Lucano 10,
85100 Potenza, Italy.

innocenzo.casella@unibas.it

Molti settori dell'industria e dell'agricoltura intensiva sono causa di ingenti produzioni di nitriti, nitrati ed NO_x, generando importanti problematiche di ordine ambientale e quindi di smaltimento e controllo degli stessi.
La rimozione elettrochimica massiva di questi inquinanti presenta importanti punti di forza in termini di efficienza, selettività ed economicità di processo [1,2]. Risulta chiaro tuttavia, che un ruolo significativo circa le cinetiche elettrodiche ed il grado di selettività viene svolto dal particolare materiale elettrodico utilizzato e la sua specifica morfologia superficiale.
In questa comunicazione è presentato uno studio riguardante la preparazione e caratterizzazione elettrochimica oltre che morfologica di elettrodi a base di rodio polidisperso su nanotubi di carbonio (MWCNTs). Il film di rodio è stato elettrodepositato su grafite precedentemente modificata con MWCNTs attraverso procedura di scansione ciclica del potenziale tra 0.4 V e – 0.3 V vs. SCE in soluzione 50 mM H_2SO_4 contenente 4.0 mM $RhCl_3$. Una particolare attenzione è stata rivolta al meccanismo di riduzione degli analiti nella zona di scarica dell'idrogeno, dove il rodio esplica una importante attività di elettrocatalisi.
Gli elettrodi a base di nanotubi superficialmente modificati con particelle di rodio, sono stati caratterizzati tramite indagine AFM, al fine di poter esplicitare una potenziale correlazione tra attività di elettrocatalisi e morfologia superficiale del catodo. Inoltre è studiata con particolare attenzione la possibilità di elettroriduzione massiva di NO_2^-, NO_3^- sia in condizioni di amperometria a potenziale costante (DC) che utilizzando tecniche a potenziale pulsato.

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ANA-P26

Applicazione dei liquidi ionici di IV generazione per lo sviluppo di un biosensore enzimatico elettrochimico

P. Bollella, M.L.Antonelli, R.Caminiti, C.Sadun, L.Gontrani, O.Russina

Dipartimento di Chimica, Università La Sapienza, P.le A. Moro 5, 00185, Roma, Italia

bollella1989@hotmail.it

I liquidi ionici a temperatura ambiente (RTILs) sono sali stabili in acqua e aria, composti da cationi organici e anioni sia inorganici che organici. Hanno proprietà insolite tra cui bassa volatilità, bassa infiammabilità, elevata conducibilità ionica e un'elevata stabilità sia chimica che elettrochimica [1].

I composti RTILs sono di grande interesse, soprattutto in campo elettrochimico, perché permettono di aumentare notevolmente la finestra di potenziali (V) di lavoro, consentendo, in voltammetria ciclica (CV), la rilevazione di picchi catodici/anodici prima non visibili. In questo lavoro viene presentata la realizzazione di un biosensore elettrochimico che utilizza RTILs di IV generazione, a base di Colina e amminoacidi [2], per l'immobilizzazione di enzimi sulla superficie dell'elettrodo di lavoro [3]. Gli RTILs di IV generazione, a differenza dei precedenti, non sono tossici e in alcuni casi hanno una maggiore conducibilità ionica, che di conseguenza permette un ampliamento della finestra di potenziale. Le misure vengono condotte con una cella elettrochimica contenente un elettrodo di lavoro Glassy Carbon (GC), modificato con MultiWalled Carbon NanoTubes (MWCNTs) e un liquido ionico di IV generazione, un contro elettrodo di Pt e un elettrodo di riferimento a calomelano saturo (SCE). La superficie dell'elettrodo così modificata facilita l'immobilizzazione degli enzimi. Una possibile applicazione del biosensore così preparato, in corso di studio, è la determinazione degli acidi grassi, ad esempio negli olii e/o nel latte, sfruttando la reazione di idrolisi enzimatica catalizzata dall'enzima lipasi [4].

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ANA-P27

Electrochemical study of human Hepcidin-25: new approaches for detection of the key biomarker in iron metabolism

*Scarano S**, *Mariani S.*, *Minunni M.*

Dipartimento di Chimica 'Ugo Schiff', Università di Firenze, Via della Lastruccia 3, 50019,
Sesto Fiorentino (FI), Italy

simona.scarano@unifi.it

Hepcidin-25 (hepc25) is considered the key biomarker in iron metabolism, since its binding to the iron transporter ferroportin causes its degradation and, in turn, the regulation of iron efflux in blood [1]. Several pathways are involved in the regulation of this peptide hormone, including inflammation, infection, erythropoietic demand, hypoxia and, thus, body iron status. Therefore, efforts for specific, accurate and precise methods for the quantification of hepcidin-25 in biological fluids are dramatically increasing. Up to now, mass spectrometry and immunochemical methods have been developed and applied to hepc25 detection and quantification, despite their elevated costs and limits. Immunological methods display also difficulties related to the intrinsic characteristics of the peptide, i.e. low immunogenicity, aggregation and adsorption tendency, and conformational changes with temperature and environmental conditions. In this work we explored for the first time the electrochemical behavior of human hepc-25 on disposable and cheap screen-printed carbon electrodes (SPCE) by voltammetric techniques. The ATCUN (Amino-Terminal Cu-Ni) binding motif of the peptide, recently characterized [2,3] was exploited by probing the copper-hepc25 complex formation in solution. First very encouraging results indicate that a new route in hepc25 detection via electrochemical detection can be pursued, with dramatic advantages in terms of saving time and cost analysis.

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ANA-P28

Electrochemical determination of sulfamethoxazole using different kinds of electrodes

Abdellatif Ait Lahcen and Aziz Amine

Laboratoire Génie des Procédés et Environnement, Faculté de Sciences et Techniques,
Université Hassan II - Mohammedia, B.P.146, Mohammadia, Morocco

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azizamine@yahoo.fr

Pharmaceuticals and other micropollutants have been the focus of recent research due to their occurrence in different environmental compartments worldwide. Among of these micropolluants: sulfonamides are a class of widely used human and veterinary antibiotics but pose a risk as environmental pollutants. Several methods have been reported for the determination of sulfonamides in pharmaceuticals, food products, water and soil, including high-performance liquid chromatography (HPLC) , capillary electrophoresis, gas chromatography and spectrophotometric method. Electrochemical investigations are particularly appropriate approaches for some electroactive drugs such as sulfonamide antibiotics.

Several types of electrodes were tested in order to choose the most sensitive for the determination of sulfamethoxazole (SMX). The electrooxidative behavior and determination of sulfamethoxazole (SMX) on a variety of electrodes such as platinum, gold, glassy carbon and carbon paste electrodes based on carbon black nanoparticles of CB N110, N220, N375, N772, Carbon Nanopowder and acetylene black were investigated using linear sweep, differential pulse voltammetry (DPV) and square wave voltammetry (SWV). DPV and SWV were used to generate peak currents which were plotted versus concentration of SMX. A linear response was obtained in the range comprised between 10^{-6} M and 10^{-4} M. The limits of detection obtained with these electrodes were around 10^{-6} M for the carbon paste electrodes and screen printed electrode and 5 $x10^{-6}$ M for the glassy carbon electrode. However the Platinum and Gold electrodes showed the linear response in the range comprised between 10^{-5} M and 10^{-4} M and the limit of detection were around 7 $x10^{-6}$ M.

ANA-P29

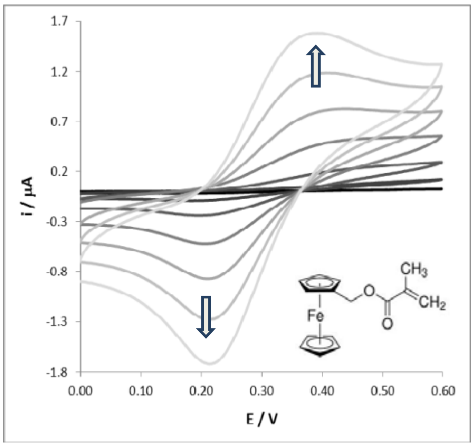
Development of novel electrode coatings based on poly(hydroxyethyl-methacrylate)

Giulio Maccaferri[a], Micaela Degli Esposti[b], Paola Fabbri[b], Erika Ferrari[a], Laura Pigani[a], Monica Saladini[a], Renato Seeber[a], Chiara Zanardi[a]

a Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia, Via G. Campi 183, 41125 Modena, Italia
b Dipartimento di Ingegneria Enzo Ferrari, Università di Modena e Reggio Emilia, Strada Vignolese 905, 41125 Modena, Italia

chiara.zanardi@unimore.it

A very critical point in the development of efficient electrode coatings to use in amperometric sensing is represented by the poor stability of the redox mediators on the electrode surface. In this communication we discuss the performance of a novel electrode coating based on a poly(2-hydroxyethyl-methacrylate) film, stably including different redox mediators through photo-induced copolymerization. Thanks to the characteristics of this polymer to swell by incorporation of large amounts of water, redox active species covalently bound to the polymer are in intimate contact with the electrolytic solution. As reported in the figure, when ferrocene is present inside the electrode coating, the progressive incorporation of the solvent medium within the film induces the increase of the cathodic-anodic current signal. The voltammogram finally shows the typical shape of a diffusion-controlled redox reversible charge transfer. The properties of the material, as a function of the synthetic parameters, have been studied by IR, thermal and electrochemical analyses.
First attempts to covalently bind different redox mediators, namely caffeic acid and curcumin derivatives, are also reported.



Ten subsequent voltammetric scans on a poly(2-hydroxyethylmethacrylate-co-ferrocenylmethylmethacrylate) modified electrode, 0.1M phosphate buffer solution - v = 0.02 Vs^{-1}

ANA-P30

Electrochemical Affinity Biosensors for the Detection of Tumor Necrosis Factor alpha

F. Bettazzi, D. Voccia, I. Palchetti

Dipartimento di Chimica, Università degli Studi di Firenze,via della Lastruccia 3, 50019
Sesto Fiorentino, Italy

ilaria.palchetti@unifi.it

Tumor necrosis factor-alpha (TNF-α) is involved in abroad range of physiological and pathological responses and is a key marker of inflammation. Serum TNF- α level is elevated in some pathological state including atherosclerosis, rheumatoid arthritis, psoriasis, Alzheimer's disease, septic shock, graft rejection, HIV infection, severe meningococcemia and others. Therefore, measuring TNF-a is important for the understanding of inflammation and discovering drugs that alleviate it.

A number of traditional immunoassays have been widely employed for the detection of this key biomarker, including colorimetric enzyme-linked immunosorbent assay (ELISA). These methods rely on antibody pairs for creation of sandwich immunoassays. Herein, two innovative affinity molecules, produced by evolutionary approaches, have been tested as detection ligands. These molecules, namely a nucleic acid aptamer and a combinatorial non-immunoglobulin protein, are known to interact with TNF-α selectively. These ligands were tested in different assay formats both using gold electrodes or magnetic beads as support for bioreceptor immobilization and differential pulse as electroanalytical technique.

Preliminary results of serum samples analysis were also reported.

ANA-P31

PEDOT modified electrodes for the determination of polyphenolic content in wine and must samples

L. Pigani[a], *R. Seeber* [a], *B. Zanfrognini*[a], *C. Zanardi*[a], *A. Ulrici*[b], *G. Foca*[b]

a Department of Chemical and Geological Sciences, University of Modena and Reggio Emilia, via G. Campi 183, 41125 Modena, Italy
b Department of Life Sciences, University of Modena and Reggio Emilia, via Amendola 2, 42100 Reggio Emilia, Italy

laura.pigani@unimore.it

The setup of new devices and methods meeting the requirement of rapid response, low cost, and even portability for reliable analysis of taste and of food characteristic parameters represents an emerging topic in food chemistry. Electrochemistry can give important contributions with this respect, offering both specific sensors for the direct determination of analytes of interest, and sensor arrays for blind analysis, in the frame of the so-called electronic tongues. In this context, we have focused our attention on poly(3,4-ethylenedioxythiophene) (PEDOT) modified electrodes to be used in both analytical approaches [1,2].

We report here our most recent results obtained using such modified electrodes for the estimation of natural antioxidants in model wine solutions and in wine and must authentic samples. In particular, our attention is focused on polyphenols, one of the most important classes of natural antioxidants. We have checked that PEDOT modified electrodes used in model wine solutions and diluted wine samples with different amount of added anthocyanins give rise to repeatable signals in which a well-defined current peak related to the polyphenolic content is detectable. The voltammetric signals will be employed also in multivariate regression analyses devoted to quantitative determination of parameters of interest, polyphenol content included.

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ANA-P32

Amperometric, screen-printed and surface plasmon resonance immunosensors for triazinic pesticide determination in bovine milk

Mauro Tomassetti[a], Elisabetta Martini[a], Luigi Campanella[a], Gabriele Favero[b], Gabriella Sanzò[b], Franco Mazzei[b]

a Dipartimento di Chimica, Università di Roma "La Sapienza", P.le Aldo Moro 5, 00185, Rome, Italy.
b Dipartimento di Chimica e Tecnologie del Farmaco, Università di Roma "La Sapienza", P.le Aldo Moro 5, 00185, Rome, Italy.

mauro.tomasetti@uniroma1.it

Immunosensors for triazinic pesticides determination have been studied by our research group using different construction techniques and measurement patterns. For classic amperometric and screen-printed devices "competitive" assays were used; conversely, the SPR transduction technique allowed a "direct" measurement format to be used. In the latter case, a calibration curve for Atrazine displayed a linearity range from 1.0×10^{-7} to 1.5×10^{-6} µM and an LOD value of about 5×10^{-8} µM. A detailed comparison was made of the analytical features of new SPR devices with those of two other developed immunosensors and the advantages and disadvantages of the new SPR methods investigated: the linear range of the screen-printed and classical devices were about three and five decades, respectively with LOD values of about 10^{-8} M and 5×10^{-11} M, respectively, although the measurement time using the SPR device was found to be about half that required in the case of the two competitive methods. Lastly some applications and recovery tests were carried out on real samples, checking triazinic pesticides in bovine milk samples. Satisfactory results were obtained.

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ANA-P33

Cholesterol bioassay by-means of a microfluidic device based on a prussian blue nanoparticle modified screen-printed electrode

Stefano Cinti [a], *Fabiana Arduini* [a], *Danila Moscone* [a], *Giuseppe Palleschi* [a],
Tony Killard [b]

a Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Via della Ricerca Scientifica, 00133 Rome, Italy.
b Department of Applied Sciences, University of the West of the Engand, Coldharbour Lane, BS16 1QY Bristol, UK.

Stefano.Cinti@Uniroma2.it

Despite considerable improvements in medical care over the past 25 years, cardiovascular disease remains a major public health challenge: it is now well established that the formation of the cardiovascular plaques is closely related to the level of cholesterol. Currently, assays for cholesterol involve initially collecting a blood sample from a patient and then sending it to a clinical laboratory for analysis: it is very important to develop rapid, cost-effective and easy-to-use analytical devices to measure cholesterol concentration directly from patients. Electrochemical sensors represent an alternative approach compared to optical methods for the rapid determination of cholesterol in the biological fluids, furthermore the integration of an electrochemical sensor in a microfluidic platform permits to detect the analyte of interest directly in a very low-volume sample, i.e. in a blood drop. In this work an amperometric cholesterol bioassay has been developed using a screen-printed electrode (SPE) modified with inkjet-printed Prussian Blue Nanoparticles (PBNPs) and using microfluidics for SPE encapsulation. Modified SPEs have been electrochemical characterized using cyclic voltammetry , then a microfluidic platform has been used to indirectly detect cholesterol in just 4 μL of serum obtaining satisfactory results in terms of sensitivity and linearity range (50-400 mg/dL). Preliminary studies have shown good results regarding the possibility of producing a point-of-care device for the measurement of blood cholesterol.

ANA-P34

MALDI mass spectrometry study of Glycated species

Donatella Aiello, Anna Napoli, Fabio Mazzotti, Leonardo Di Donna, Emilia Furia, Giovanni Sindona

Department of Chemistry and Chemical Technologies, University of Calabria, Via P. Bucci, Cubo 12/D, 87036 Arcavacata di Rende (CS), Italy

amc.napoli@unical.it

Glycation is the spontaneous reaction of biomolecules' nucleophilic groups with different reactive carbonyl compounds, including glucose and ribose.[1] Glycation affects nucleic acids[2], lipids[3] and most importantly proteins[4]. Within proteins, glycation occurs most frequently at the N-terminal amino group and at the side chains of Arg and Lys residues, but it may also occurs on Cys, His and Trp side chains. The initial reaction between a carbonyl and, for example, a lysine side chain leads to the reversible formation of a Schiff base. The Schiff base may undergo Amadori rearrangement, leading to Maillard reaction products.[5] The reaction endproducts of this multistep pathway are diverse and are collectively referred to as advanced glycation endproducts (AGEs). Glycation and AGEs formation are not enzyme catalyzed and the process is driven by the chemical reactivity of the molecules involved. The chemical transformations are generally slow and, depending on the reactivity of the carbonyl compound, progress over days and, sometimes, weeks.
MALDI mass spectrometry-based approach is proposed to study the formation of glycated species by coupling of reducing sugars carbonyl aldehydes and model molecule nucleophilic groups under strong oxidation experimental conditions.

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ANA-P35

Caratterizzazione del profilo lipidico di membrana di *Rhodobacter sphaeroides* sottoposto a stress da metalli mediante spettrometria di massa MALDI-TOF

Cosima Damiana Calvano[a], *Francesco Cardellicchio*[a], *Francesca Italiano*[b], *Francesco Palmisano*[a], *Massimo Trotta*[b]

[a]*Dipartimento di Chimica, Università di Bari, Via Orabona 4,70124, Bari, Italia*
[b]*CNR – Istituto per i Processi Chimico – Fisici, Via Orabona 4, 70124, Bari, Italia*

f.cardelicchio@gmail.com

Il batterio *Rhodobacter* (*R.*) *sphaeroides* ha capacità di resistenza allo stress da metalli tossici e potenzialità di "biosorption" verso metalli pesanti, tra cui cobalto e cromo[1]. Infatti, il batterio può modulare la propria attività metabolica in vari comparti cellulari tra cui la membrana cellulare, la cui struttura è influenzata dallo "stress" ambientale. Il presente lavoro si propone la caratterizzazione, mediante spettrometria di massa MALDI-TOF, del profilo lipidico di membrana del batterio *R. sphaeroides* esposto a cobalto (Co^{2+}) e cromato (CrO_4^{2-}) e il confronto con il profilo lipidico di membrana di batteri controllo, attraverso l'analisi delle varie classi fosfolipidiche. In particolare, l'interesse si è incentrato sulle classi dei sulfolipidi SQDG (sulfochinovosildiacilgliceroli), dei fosfatidilgliceroli (PG) e delle cardiolipine (CL)[2]. Dall'analisi degli spettri riguardanti i profili lipidici di *R. sphaeroides* controllo e stressato, è stato possibile osservare che l'esposizione al cobalto ha portato ad un aumento relativo al contenuto di CL e SQDG, molto probabilmente per compensare la diminuzione del contenuto di PG, mentre l'esposizione al cromato ha determinato una diminuzione sia dei PG che degli SQDG, lasciando inalterate le CL[3]. Questo risultato rappresenta certamente un importante passo in avanti per comprendere meglio le risposte allo stress ambientale da parte di microorganismi fotosintetici, potenzialmente impiegabili nel campo della bioremediation.

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ANA-P36

Tenori di metalli pesanti in campioni di latte e uova prelevati in un Sito di Interesse Nazionale (SIN) piemontese

Gabriella Monaco[a], *Paola Brizio*[a], *Stefania Squadrone*[a] , *Marco Vincenti*[b], *Maria Cesarina Abete*[a]

a S.S. Contaminanti Ambientali, Istituto Zooprofilattico Sperimentale del Piemonte, Liguria e Valle d'Aosta, Via Bologna 148 , 10154, Torino, Italia
b Dipartimento di chimica, Università degli Studi di Torino, Via Pietro Giuria 7 , 10125, Torino, Italia

contaminanti.ambientali@izsto.it

I siti d'interesse nazionale (SIN) sono aree individuate dal Ministero dell'Ambiente e della Tutela del territorio e del Mare sul territorio nazionale; esse sono state definite (legge n°426 del 9/12/1998 e s.m.i.) in relazione alle caratteristiche del sito, alle quantità e pericolosità degli inquinanti presenti e all'impatto sull'ambiente circostante. L'IZSPLV è responsabile del monitoraggio di 8 su 57 SIN, identificati per l'elevato inquinamento dovuto ad attività antropiche. Lo studio è stato condotto su campioni di latte e uova prelevati in uno dei suddetti siti; sono stati determinati Be, Cd, Cr, Ni, Tl e Pb. La quantificazione di quest'ultimo nei campioni di latte è stata condotta mediante GF-AAS, al fine di garantire l'osservanza dei limiti stabiliti dalla normativa. Per quanto concerne gli altri metalli, entrambe le matrici oggetto dello studio sono state sottoposte a mineralizzazione in forno a microonde, previa aggiunta di acido nitrico e perossido di idrogeno. I campioni sono stati opportunamente diluiti ed analizzati in ICP-MS; per abbattere le interferenze per la determinazione di Cr e Ni si è utilizzata la cella di collisione/reazione. La concentrazione di tutti i metalli analizzati è risultata inferiore al LOQ del metodo (0.004 mg/kg per Pb nel latte e 0.020 mg/Kg per tutti gli altri elementi); tali risultati rassicurano in merito al livello di contaminazione dovuto a tali specie nel territorio oggetto dell'indagine e sul loro impatto nella filiera alimentare.

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ANA-P37

The study of wood by Direct Exposure Mass Spectrometry (DE-MS): comparison between electronic and chemical ionisation

Diego Tamburini [a], *Erika Ribechini* [a], *Jeannette J. Łucejko* [b],

Maria P. Colombini [a,b]

a Department of Chemistry and Industrial Chemistry, University of Pisa, via Risorgimento 35, Pisa, Italy
b Institute for the Conservation and Valorization of Cultural Heritage, CNR, Via Madonna del Piano 10, Sesto Fiorentino, FI, Italy

maria.perla.colombini@unipi.it

From a chemical point of view, wood is a complex material. It mainly consists of three interlinked biopolymers, representing almost 95% of the wood: cellulose, hemicelluloses and lignin.

DE-MS is a fast fingerprint technique that allows us to obtain an overall mass spectrum of organic materials, without any or negligible sample pre-treatment. The main advantage of coupling pyrolysis directly to mass spectrometry is the short analysis time and the possibility of extending the range of detectable pyrolysis fragments to structures too large to be analysed by gas chromatography. However, a complex mass spectrum is obtained as a result of the overlapping of the mass spectra of many pyrolysis products and this is particularly true for a complex material such as wood.

This work presents the application of DE-MS to the study of wood, with the principal aim to compare the results obtained using different ionisation methods: electronic impact (EI) and chemical ionisation (CI) using methane (CH_4) as reagent gas.

To achieve a proper picture of the mass spectra obtained from wood analysis, the study of several lignin pyrolysis products, such as vanillin, syringaldehyde, coniferyl and sinapyl alcohols, vanillic and syringic acids, cellulose and holocellulose used as reference compounds was performed. All these substances were analysed by DE-MS (both EI and CI) in order to study their mass spectra.

Different species of wood belonging to softwood (fir, pine) and hardwood (oak, maple, poplar, alnut, etc.) were successively analysed and the results compared. In addition, Principal Component Analysis (PCA) was applied to the hardwood dataset, highlighting differences between the mass spectra obtained from chemical and electronic ionisation.

Concluding, the results indicated that it was possible to identify some m/z ratios which are characteristic of CI and that these m/z values correspond to ionization fragments that are emphasised using CI ionization in comparison with EI.

ANA-P38

A shotgun proteomics approach to investigate the protein corona effect for targeted delivery

V. Colapicchioni[a] *, G. Caracciolo*[b]*, C. Cavaliere*[a]*, G. La Barbera*[a]*, S. Piovesana*[a]*, D.Pozzi*[b]*, A. Laganà*[a]

a Dipartimento di Chimica, Università di Roma "La Sapienza", P.le A. Moro 5, 00185 Roma, Italia
b Dipartimento di Medicina Molecolare, Università di Roma "La Sapienza",Viale Regina Elena 291, 00161, Roma, Italia

valentina.colapicchioni@uniroma1.it

Over the past few years, there has been extensive interest in developing nanoparticles (NPs) for drug and gene delivery. Among NPs, cationic liposomes are particularly attracting. When liposomes, and more broadly NPs, enter a physiological environment, medium components compete for binding to the NP surface leading to formation of a rich protein shell known as the "protein corona" [1]. The "protein corona effect for targeted drug delivery" is an innovative targeting strategy based on the exploitation of the "protein corona". In this study we introduce a shotgun proteomic approach to validate such effect in cancer cells. As a first step, the protein corona composition is characterized by nanoLC/MS-MS. Then, differential proteomic analysis is executed in order to compare the protein profile of the target cells before and after the interaction with the protein corona-nanoparticles systems. In this work we validated the methotology treating human prostate cancer PC3cells with PEGylated multicomponent cationic liposomes, which have recently emerged as successufull nanocarries [2]. By comparing differentially expressed proteins, it is evident that the "protein corona" induces a switch from a not specific to a receptor mediated uptake mechanism in PC3 cells. This methodology will be employed to validate the protein corana effect for targeted drug delivey. Furthmore, it could be a useful method to study the cellular internalization mechanism of liposomes in biological environment.

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ANA-P39

TAGs speciation of "Soppressata" from "Suino Nero di Calabria" by MALDI-MS and MS/MS.

Aiello Donatella[a], Aiello Gilda [a], Mazzotti Fabio[a], Di Donna Leonardo, Napoli Anna[a], Carlo Siciliano[b], Sindona Giovanni[a]

a Department of Chemistry and Chemical Technologies, University of Calabria, Via P. Bucci, Cubo 12/D, 87036 Arcavacata di Rende (CS), Italy
b Department of Department of Pharmacy, Health and Nutritional Sciences, University of Calabria, Edificio Polifunzionale, 87036 Arcavacata di Rende (CS), Italy

amc.napoli@unical.it

Animal fats comprise complex mixtures of mono- (MAGs), di- (DAGs) and triacylglycerols (TAGs). Traditional characterisation of these mixtures requires time-consuming and complex methods, including stereospecific enzymatic hydrolysis and partial hydrolysis of the molecules by derivatization and analysis by chiral chromatography. The most efficient separations of TAGs have been achieved using reversed phase HPLC combined with APCI mass spectrometry, allowing an unambiguous identification of compounds.[1] MALDI-TOF mass spectrometry is achieving greater importance in lipids speciation since sample preparation is extremely fast and easy to perform, and the method is highly specific, accurate and sensible.[2,3] Lipids profile, containing MAGs, DAGs and TAGs could be useful for the determination of authenticity of local sausages production, leading to a certification of the authenticity of local landraces essential when fake exotic varieties can be used to replace authentic local varieties. The salami "soppressata" from "suino nero di Calabria" was selected as case of study to determine the lipids profile and to identify and characterize specific TAGs without any previous chromatographic separation. MALDI MS and MS/MS analysis have yielded to consistent results, related to a fingerprint of "suino nero" meat suggesting some additional quality parameters closely associated with TAG composition and integrity.

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ANA-P40

Evaluation of coffee powder aroma release through piezoelectric gas sensors array

Daniel Pizzoni[a], Delvana Mutarutwa[a] ,Paola Pittia[a], Luciano Navarini[b], Dario Compagnone[a]

a Faculty of Bioscience and Technology for Food, Agriculture and Environment,
b Illycaffè spa, 34147 Trieste, Italy

dcompagnone@unite.it

Food aroma is dependent on the original volatile molecules composition and product matrix, but other factors intrinsic and extrinsic as well as the modification occurring during food processing and storage may affect it. A main role is also plaid by the interactions between the aroma molecules and the food matrix that have been studied in many works (e.g.[1]). These could enhance or decrease the volatile compounds retention and affect the aroma perception. Therefore the study of the aroma release from food and drinks is an important task in food science and technology. In last years, electronic noses have been proved to be a very useful tool for food and aromas analysis [2].

In this work an application of a quartz crystal microbalance (QCM) gas sensors array for the study of coffee powder aroma release is presented.

Coffee powders with different geographical origins (and their mix) have been analysed with two QCM sensors array (a porphyrin based one and Gold-nanoparticles-peptide based one). Data have been processed with principal component analysis and PLS-DA techniques, showing interesting results in term of discrimination.

In further analysis the effect of the decaffeination process has also been evaluated.

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ANA-P41

Determination of YLOID in soil and olive tree system (*Olea europea*) by ICP-MS technique: a hopeful proxy for the geographical characterization of food products? A case study. (II)

L. Tutone and F. Saiano

Dipartimento di Scienze Agrarie e Forestali, Università di Palermo, Viale delle Scienze 13,
90128 Palermo, Italia.

filippo.saiano@unipa.it

The rising importance given from legislators and consumers to provenance of food purchased and/or eaten, in last years motivated several researches to identification of the geographical origin of food. The olive oil play a fundamental role in the Mediterranean diet. Traceability of olive oils is relevant not only in assessing their origin, but also in protecting against frauds. The knowledge of a chemistry relationship between the soil and the agricultural products is an important tool for the quality assessment of food. YLOID (Y, La and Lanthanoid) have recognized as very useful tracers due to their generally coherent and predictable behavior. This behavior can also be applied to explain the mechanisms of element intake by plants. Current knowledge suggest no preferential sorption of any element in overall root samples as well as in epigeal samples of several plants. Taking into account of our previous works carried out on grapevine – soil system [1, 2], we applied the same technique to evaluate and trace the YLOID distribution in *Olea europea* olive – soil system. We carried out the soil and olives sampling in the experimental farm "Campo Carboj" located in Menfi (AG, Sicily) where are present several *Olea* cultivars of different Mediterranean countries on an identical soil with the aim to observe if different olive cultivar could reproduce the same soil YLOID distribution. In this study, the YLOID amounts and distribution in olive-soil system were determined and relationship Yb vs La and/or the pattern of distribution of YLOID were calculated. The obtained results in terms of lanthanides were critically discussed based on the different amount found.

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ANA-P42

Determination of biogenic amines in Sicilian DOP cheeses with DAD-HPLC

M. Barbera, L. Settanni, F. Saiano

Dipartimento di Scienze Agrarie e Forestali, Università di Palermo, Viale delle Scienze 13, 90128 Palermo, Italia.

filippo.saiano@unipa.it

The importance of observing biogenic amines content lies in potential toxicity to humans, since the consumption of food containing high concentration of biogenic amines may cause toxic reaction in susceptible individuals, such as nausea, hot flushes, sweating, headache, heart palpitation, whose intensity is dependent on quantitative and qualitative differences. Not all amines are equally toxic: histamine, tyramine and 2-phenylethylamine are a major concern thus the presence of biogenic amines significantly influence the food quality and safety. Biogenic amines are compounds formed by amino acid decarboxylation in fermented food and considerable research has in recent years been undertaken to evaluate the presence of these compounds in various fermented foods including cheese. Many factors have been found to effect the production of biogenic amines in cheeses, in particular the presence of microorganisms capable to decarboxylating free amino acid. The presence of amines depends on cheese variety, seasoning and microflora, so each product has a typical profile and a different concentration of these compounds. For these reasons aims of this research were to validate the method used to determine the biogenic amines and successively to study their presence in different Sicilian DOP cheeses.

The method was validate in terms of linearity, sensitivity, precision, and recovery while the accuracy was tested by the standard addition procedure.

Determination of biogenic amines (tryptamine, 2-phenylethylamine, putrescine, cadaverine, histamine, tyramine, spermidine and spermine) from cheese samples was performed by acid extraction and derivatization by modifying reported methods. The analyses and quantification of dansylated biogenic amines were carried out by reverse phase high performance liquid chromatographic method. The method provides a satisfactory linearity and sensitivity.

The content of biogenic amines has been found depending on to the kind of cheese and the seasoning with the lowest concentration values detected in unripened cheeses.

ANA-P43

Sviluppo di metodi innovativi per verificare la presenza di *Salmonella* nei vegetali di I e IV gamma

L. Fabiani[a], *G. Volpe*[a], *E. Delibato*[b], *S. Piermarini*[a], *E. Pucci*[b], *F. Capuano*[c], *G. Palleschi*[a]

a Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma "Tor Vergata", Via della Ricerca Scientifica 1, 00133 Roma, b Dipartimento di Sanità Pubblica Veterinaria e Sicurezza Alimentare, Istituto Superiore di Sanità, V.le Regina Elena 299, 00161 Roma, c Dipartimento Ispezione Alimenti, Istituto Zooprofilattico Sperimentale del Mezzogiorno, Portici (NA)

giulia.volpe@uniroma2.it

Il consumo di vegetali freschi di I e IV gamma, contaminati da microrganismi patogeni, ha recentemente causato diversi focolai epidemici. A tal proposito, in questi ultimi anni, il RASFF ha più volte richiamato l'attenzione dei paesi membri riguardo al pericolo di *Salmonella*, attribuibile principalmente alle pratiche di coltivazione, manipolazione e trasformazione. Lo scopo del presente studio è lo sviluppo e la valutazione di due differenti approcci analitici, una Real-Time PCR ed un saggio ELIME, per verificare la presenza di *Salmonella* nei vegetali di I e IV gamma. Poiché il metodo di riferimento per la ricerca di *Salmonella* (EN/ISO 6579) richiede tempi lunghi, la necessità di sviluppare metodologie rapide e efficienti rappresenta una priorità per le autorità competenti ed i produttori. La Real-Time PCR proposta, utilizza una coppia di primer e una sonda fluorescente in grado di amplificare una regione del locus *ttr*, altamente conservata in tutti i sierotipi di *Salmonella*. La curva standard ottenuta tracciando il Ct medio contro il log delle concentrazioni di *S.* Napoli ha mostrato una buona linearità 10-10^8 UFC/ml, con un LOD pari a 10 UFC/mL. La metodica è stata validata analizzando, dopo 24 h di prearricchimento, campioni di I e IV gamma ed i risultati ottenuti sono stati confermati dal metodo EN/ISO 6579. Esperimenti, per valutare il tempo minimo di prearricchimento, sono stati condotti e verranno presentati. Il saggio ELIME proposto, di tipo sandwich, si basa sull'uso di particelle immunomagnetiche accoppiate ad una striscia di 8 elettrodi stampati, magnetizzati, quali trasduttori elettrochimici del segnale. Per ottimizzare il metodo sono stati analizzati differenti sierotipi di *Salmonella* (recentemente isolati da vegetali prodotti in Italia) cambiando tipo e quantità di particelle magnetiche, testando anticorpi monoclonali e policlonali anti-salmonella sia con cellule intere che bollite (nell'intervallo 10^4-10^7 UFC/mL), variando la concentrazione del PAb-HRP, i tempi e gli "steps" di incubazione. Particolare attenzione è stata rivolta alle prove di specificità.

Si ringrazia il progetto, RF-2009-1538880, "Development of innovative methods for the detection of pathogenic bacteria in fresh vegetables and in irrigation and washing water of crops"

ANA-P44

Applicazione della chemiometria all'analisi quantitativa delle cere d'api mediante GC e micro FT-Raman

Nobili Lara[a], *Dora Melucci*[a], *Chiara Ceci*[a], *Francesca Corvucci*[b], *Roberto Colombo*[b], *Giorgia Serra*[b], *Michela Boi*[b]

[a] *Dipartimento di Chimica "Ciamician", Università di Bologna, Via Selmi 2, 40126, Bologna, Italia.*
[b] *CRA-API, Consiglio per la ricerca e la sperimentazione in agricoltura – Unità di ricerca di apicoltura e bachicoltura, Via di Saliceto 80, 40128 Bologna, Italia*

lara.nobili2@studio.unibo.it, *dora.melucci@unibo.it*

La cera d'api è considerata il principale prodotto dell'alveare, dopo il miele, ed è da sempre impiegata in molteplici campi. Essa, tuttavia, viene spesso messa in commercio in forma adulterata con paraffina (cera minerale), cera microcristallina, spermaceti (cera animale) ed altre sostanze liposolubili più economiche che si fissano facilmente in questa matrice grassa [3]. Il problema relativo alla sofisticazione e all'autenticità di questo prodotto diventa centrale soprattutto per il suo utilizzo in campo alimentare, farmaceutico e cosmetico.

Per ottenere una descrizione quantitativa delle cere d'api si è deciso di applicare un'analisi combinata micro FT-Raman [2] con la tecnica chemiometrica PLS-DA. La spettroscopia Raman sta acquisendo sempre più importanza in campo analitico per le qualità di cui dispone: è un metodo che non necessita di preparazione del campione, rapido e non distruttivo. L'elaborazione chemiometrica dei dati ottenuti permette inoltre di migliorare la qualità del segnale Raman acquisito ed incrementare l'affidabilità del metodo sviluppato.

L'applicazione di questa nuova tecnica è stata confrontata con l'approccio classico di analisi delle cere d'api che viene attualmente effettuata in gas cromatografia [1].

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ANA-P45

Development and validation of an HPLC/DAD method for the determination of 13 Sulphonamides in eggs

Simona Summa , Sonia Lo Magro , Antonio Armentano , Marilena Muscarella

Istituto Zooprofilattico Sperimentale della Puglia e della Basilicata, Via Manfredonia 20, 71121 Foggia, Italy

m.muscarella@izsfg.it

Sulphonamides (SAs) are synthetic compounds derived from sulfanilamide widely used in veterinary medicine to treat or prevent infectious diseases. SAs antimicrobial activity arises from their ability to inhibit parts of the microbe's folic acid pathway, which interferes with DNA synthesis [1]. The presence of sulphonamide residues in food for human consumption represents a serious issue because of their potential allergenic and carcinogenic character and the possible development of antibiotic resistance [2].

A sensitive and selective multiresidue HPLC/DAD method for determination of 13 sulphonamides (Sas) in eggs was developed and validated. A good matrix clean-up coupled to a careful optimization of chromatographic separation allowed to obtain a good specificity and sensitivities comparable to those reached by using LC/MS/MS methods.

The necessary requirements for precision (RDS_R% below 23%) and trueness (recovery ranging from 45.2% - 87.5%) were fulfilled. Decision limit (CC_α) values below 18.5 $\mu g\ kg^{-1}$, comparable to those reported in MS detection, demonstrated the suitability of the method in residues surveillance plans for the SAs analysis in eggs without the use of sophisticated and expensive systems.

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ANA-P46

Multiresidue mycotoxins determination in biscuits by high performance liquid chromatography-tandem mass spectrometry

Serena Stampachiacchiere[a], *Chiara Cavaliere*[a], *Susy Piovesana*[a], *Roberto Samperi*[a], *Salvatore Ventura*[a], *Aldo Laganà*[a]

a Dipartimento di Chimica, Università degli Studi di Roma "La Sapienza", P.le Aldo Moro 5, 00185, Roma, Italy

serena.stampachiacchiere@uniroma1.it

Mycotoxins are a group of naturally occurring toxic compounds produced by the secondary metabolism of many filamentous fungi. Most of mycotoxins are moderately stable in the majority of food processing systems therefore they can be found even in finished products. A sensitive and simple method has been developed for the simultaneous determination of 19 mycotoxins in biscuits using high performance liquid chromatography coupled to tandem mass spectrometry [1]. Due to the matrix complexity and the high amount of contaminants, a solid phase extraction method using graphitized carbon black was employed for an effective clean-up step. Accuracy was carried out in the selected matrix using blank samples spiked at three analyte concentrations. Recoveries between 63 and 107% and relative standard deviations lower than 12% were obtained. The method was validated in terms of linearity, recovery, matrix effect, precision, limits of detection and quantification for all considered mycotoxins. Matrix-matched calibration was used for quantification purposes, in order to compensate for matrix effect. The coefficients of determination obtained were in the range of 0.9927-1. Limits of quantification, ranging from 0.04 µg/kg for enniatin B1 to 80.2 µg/kg for nivalenol, were always lower than maximum permitted levels for every regulated mycotoxin by the current European legislation.

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ANA-P47

Lyso-Phosphatidylcholines: New Seafood Quality Biomarkers?

S. Granafei[a], *I. Losito*[a,b], *L. Facchini*[a],
F. Palmisano[a,b], *T.R.I. Cataldi*[a,b]

[a]*Dipartimento di Chimica,* [b]*Centro Interdipartimentale SMART, Università degli Studi di Bari Aldo Moro, Via E.Orabona, 4 - 70126 Bari, Italia*

sara.granafei@uniba.it

Fish is an important source of vital macronutrients like proteins and lipids and micronutrients such as vitamins and minerals. However, the nutraceutical properties of wild and farmed fishes deserve a tight control of safety and quality, which encompasses growth conditions, proper conservation and handling. Most often "quality" and "safety" of fish corresponds to aesthetic appearance and freshness or degree of spoilage, respectively, along with the absence of harmful bacteria, parasites or toxic compounds [1]. Currently, there are acclaimed methods to evaluate seafood quality: (i) sensorial methods, which analyze and interpret food features as perceived through sight, smell, taste and touch, and (ii) biochemical and chemical methods, such as the most popular "total volatile basic amines" determination [1]. Lipidomics can be very useful in the research on foods, including seafoods [2]. Indeed, change in the composition of phospholipids (PLs) during storage is one of the most important *post mortem* modifications affecting the freshness of fish, with oxidation and hydrolysis of PLs as the main reasons of quality deterioration [1]. At the best of our knowledge, a possible role of lyso-phosphatidylcholines (LPCs), namely the main by-products of PL hydrolysis, as biomarkers of fish quality and safety has not yet been claimed but, in our opinion, it cannot be ruled out. LPCs are important intermediates in the synthesis and metabolism of PCs, which are major components of the cellular lipid bilayer. LPCs are produced from PCs as a result of phospholipases activity, leading to hydrolysis of fatty acyl groups from the *sn*-1 or *sn*-2 positions of the PC glycerol backbone. Here, a LC-MS investigation on the LPCs of different samples of farmed *Sparus aurata*, complemented by tandem MS analysis to establish the chemical identity, including regioisomery, is described.

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ANA-P48

Analisi sperimentale e modellazione del processo di estrazione della Rutina da Grano Saraceno (*Fagopyrum tataricum*) con CO_2 supercritica

Giuseppe Di Sanzo [a], *Vincenza Calabrò* [b], *Gerardo Baviello* [a], *Oliviero Maccioni* [d], *Silvia Mazzuca* [e], *Giuseppe Oriolo* [a], *Valeria Gallo* [b], *Roberto Balducchi* [c].

c ENEA, C.R. TRISAIA, Unità Tecnica Tecnologie Trisaia, Rotondella (MT)
a ENEA, C.R. TRISAIA, Lab. di Sviluppo Sostenibile della Produzione Primaria, Rotondella (MT)
d ENEA, C.R. CASACCIA, Lab. di Radiazioni Biologia e Biomedicina, S.Maria di Galeria (RM)
b Dipartimento di Modellistica per l'Ingegneria, Università della Calabria, via P. Bucci, cubo 39/c, I-87030 Rende (CS)
e Dipartimento di Chimica e Tecnologie Chimiche - CTC, Università della Calabria, via P. Bucci, 87030 Rende (CS)
giuseppe.disanzo@enea.it

La propensione a nutrirsi in modo "sano", la maggiore aspettativa di vita e la ricerca di migliori standard di vita, hanno incoraggiato l'industria alimentare a sviluppare la sperimentazione e la commercializzazione di nuovi alimenti funzionali. L'ENEA ha individuato il Grano Saraceno (*Fagopyrum tataricum*) caratterizzato da una più elevata concentrazione di sostanze bioattive, in particolare emerge la Rutina con quantità fino a 200 volte superiore rispetto al Grano Saraceno comune. Il presente lavoro si propone come obiettivo lo studio di fattibilità ed il controllo del processo di estrazione con CO_2 supercritica della Rutina; nell'ambito del Progetto BUCKFOOD "Sviluppo di prodotti alimentari funzionali a base di grano saraceno" finanziato dal MiSE - Industria 2015, al fine di approfondire gli studi sul Grano Saraceno tartarico e valutare il suo impiego per la realizzazione di alimenti funzionali. Le estrazioni sono state condotte attraverso l'uso di un estrattore SPE-ED SFE 2 (Applied Separations). Un'altra tecnica estrattiva adoperata è la macerazione, usata come metodo di confronto. La caratterizzazione degli estratti sono state effettuate mediante HPLC. In particolare è stata analizzata la fattibilità dell'estrazione mediante il processo con CO_2 SFE (Supercritical Fluid Extraction) della Rutina dalla farina ottenuta dal *Fagopyrum tataricum* varietà Donan, effettuando delle prove sperimentali originali; la tecnica adottata è dunque risultata idonea, e si è successivamente cercato di mirare all'ottimizzazione del processo. Nel corso della sperimentazione si sono effettuate delle scelte rispetto ai parametri principali che caratterizzano la tecnica di processo adottata, ma dal confronto con la quantità di Rutina estratta mediante macerazione, si intuisce che si può migliorare la resa ottenuta dal processo con CO_2 SFE. Dal punto di vista teorico, l'analisi modellistica ha permesso l'interpretazione chimico-fisica del processo, anche se la mancanza di maggiori informazioni, derivanti dall'analisi della letteratura, non ha permesso di determinare con maggiore precisione i parametri caratteristici del modello.

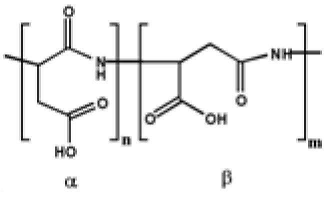
ANA-P49

Acid base properties and sequestering capacity of polyaspartic acid towards divalent metal cations

Clemente Bretti, Rosalia Maria Cigala, Gabriele Lando, Silvio Sammartano

[a] *Dipartimento di Scienze Chimiche - Università di Messina, Viale Ferdinando Stagno d'Alcontres, 31, I-98166 Messina (Vill. S. Agata), Italy.*

cbretti@unime.it


Poly-α,β-D,L-aspartate

In this contribution a study on the acid-base properties and on the complexing ability of the polyaspartic acid (Pasp) towards some metal cations, as Ca^{2+}, Mg^{2+}, Zn^{2+} and Sn^{2+} is reported. The study was performed in $NaNO_3$, KCl, $(CH_3)_4NCl$ and in $(C_2H_5)_4NI$, at different ionic strengths ($0 < I$/mol $L^{-1} \leq 3.0$) and temperatures ($278.15 \leq T$/K ≤ 318.15), using two analytical techniques, potentiometry and voltammetry. On the basis of a previous paper [1], the titration curves of the ligand were modeled assuming a monomeric unit consisting of four aspartyl residues (m = n = 2, so MW=548.28, as Na_4L), see Figure, giving four protonation constants. The dependence on the ionic strength and on temperature was modeled by different equations, such as the Debye-Hückel type equation and SIT approach (Specific ion Interaction Theory). From the analysis of the experimental data it was evidenced that, in $NaNO_3$, the protonation constants increase with increasing the temperature and decrease with increasing the ionic strength. The Ca^{2+}/Pasp, Mg^{2+}/Pasp and Zn^{2+}/Pasp systems were studied only by potentiometry, whereas in the case of the Sn^{2+}/Pasp, the formation of scarcely soluble species was evidenced and the use of voltammetry was necessary, for the use of low metal cation concentration (~ 10^{-7} mol L^{-1}). The general speciation scheme consists of two species, ML and MLH, for the Zn^{2+}/Pasp system we also have the mixed hydrolytic species MOHL, and for the Sn^{2+}/Pasp system four species were found: MLH_2, MLH, ML and MOHL. In all the experimental conditions the stability trend of the complex formation constants is: $Sn^{2+} >> Zn^{2+} > Ca^{2+} \approx Mg^{2+}$. The sequestering ability of this ligand towards the four metal cations was studied by means of an empirical parameter, $pL_{0.5}$, which allows us to evaluate this capacity cleaned by competitive reaction (*e. g.* protonation of the ligand, hydrolysis of the metal cation).

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ANA-P50

Acid - base properties of halloysite clay nanotubes in NaCl medium

S. Cataldo[a], *A. Gianguzza*[a], *A. Pettignano*[a], *S. Sammartano*[b] ...

[a] *Dipartimento di Fisica e Chimica, Università di Palermo, Viale delle Scienze, edificio 17 , Cap 90128, Palermo, Italia*
[b] *Dipartimento di Scienze Chimiche, Università degli Studi di Messina, Viale Ferdinando Stagno d'Alcontres, 31, Cap-98166 Messina (Vill. S. Agata), Italy*

alberto.pettignano@unipa.it

Halloysite clay nanotubes (HNTs) have a series of important properties that make this kind of material very useful for different purposes in several fields. Among the various applications, are worth mentioning: i) their use as additive for devices in the capture tumor cells in blood; ii) nanoparticles for the entrapment and controlled release of active molecules; ii) additive agents in wound and personal care; iv) sorbents for water contaminants etc [1,2]. In all these applications, the knowledge of acid-base properties of HNTs is very important and gives useful information on the behaviour of these natural clay nanotubes in different experimental conditions (ionic strength, medium, pH, etc.).

The acid-base properties of HNTs have been studied by ISE-H^+ potentiometric titrations in NaCl medium in the range $0.025 \leq I$ mol $L^{-1} \leq 0.500$, at T = 25°C. The analysis of experimental data gave evidence of two different functional groups in terms of protonation constants here indicated with HNT_1 (SiOH) and HNT_2 (AlOH). The experimental data were processed by using four different models successfully adopted with natural and synthetic polyelectrolytes in previous papers: Högfeldt, Linear, Henderson-Hasselbalch and diprotic like models [3]. The results obtained with the four models for the protonation constants of SiOH groups of HNTs were in good accordance, whilst the acid-base properties of AlOH groups were well defined by one protonation constant calculated by processing the potentiometric titration data with the computer programs STACO and BSTAC.

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ANA-P51

Experimental approach to the study of solution equilibria of surfactants

Clemente Bretti, Rosalia Maria Cigala, Concetta De Stefano, Gabriele Lando

[a] *Dipartimento di Scienze Chimiche - Università di Messina, Viale Ferdinando Stagno d'Alcontres, 31, I-98166 Messina (Vill. S. Agata), Italy.*

rmcigala@unime.it

In this contribution a study on the equilibria involved in a multicomponent solution as the soap formula is proposed. The soap is an "*emulsion solution*" rather complex, due to the presence of many components, involved in many different equilibria that are often neglected. In general the main components present are: glycerol (Glyc), a mixture of different surfactants (*e. g*. sodium dodecyl sulfate, SDS), NaCl and water. Other additives, which are characteristic of the soap formulation, are: the omadine® (2-Mercaptopyridine-N-Oxide zinc salt, ZPT, as fungistatic and bacteriostatic), carboxymethyl cellulose (E466 as viscosity modifier and emulsion stabilizer), xanthan gum (E 415) and carrageenan (as thickening agents and stabilizers). In this contribution the acid-base properties of glycerol, SDS and 2-Mercaptopyridine-N-Oxide (PT) were studied, together with the hydrolysis of the zinc, the solubility and the complex formation constants of the Zn^{2+}/2-Mercaptopyridine-N-Oxide system and Zn^{2+}/sodium dodecyl sulfate, in soap formulation and in NaCl aqueous solutions at T = 298.15 K, using potentiometry, voltammetry and UV-visible spectrophotometry. The experimental conditions of the soap formulation used are: glycerol 17%, SDS 2%, NaCl 12% (ionic strength contribution from NaCl is I = 2.3 mol L^{-1}), water (at a given amount, so that the sum respect to the percentages of the other components gives 100%). From an experimental point of view, the study of the surfactants is quite difficult because the solutions under stirring and $N_{2(g)}$ bubbling form a foam and another aspect to consider is the impossibility of the use of the voltammetry, due to the interferences on the electrode surface because the surfactants present in the mixture hamper the correct signal recording. Therefore potentiometry and UV-visible spectrophotometry were used for the study of the equilibria in presence of the surfactants. The potentiometric data were analyzed considering the presence in the soap formula of different components that can undergo a proton displacement. In the speciation model, the following species were taken into account: SDSH, PTH and $(Glyc)H_{-1}$, together with the Kw (autoprotolysis of water) whose value becomes significant for pH values higher than 10.5. In general, it was evinced that the equilibrium constants in soap formulation are higher than those in NaCl aqueous solution and this is consistent with the decrease of the dielectric constant of the solvent.

ANA-P52

Adsorption of policyclic aromatic hydrocarbons onto solids containing tetraphenylborate

G. De Tommaso[a], *M. Iuliano*[a], *A. Fusco*[a]

a Dipartimento di Scienze Chimiche, Università di Napoli "FEDERICO II", Via Cinthia 4, 80126, Napoli, Italia

gaetano.detommaso@unina.it

Polycyclic aromatic hydrocarbons (IPA), produced by industrial activities, traffic and domestic heating, are considered to be priority pollutants because they are toxic, mutagenic and carcinogenic. [1] The IPA contamination of surface waters is the first stage for their spread in different ecosystems. In the present work the chemical properties of the surface of solids such as the 1 -ethyl -3- methylimidazolium tetraphenylborate and hexadecyltrimethylammonium tetraphenylborate [2] have been investigated. Their adsorbent capacities were studied in respect of naphthalene and acenaphtene. The measurements were carried out at 25° C in suspensions containing NaCl, LiCl and $N(C_2H_5)_4ClO_4$ as ionic medium in the range 0.1–1.0 $moldm^{-3}$. The surface chemistry of the two solids was studied by potentiometric methods. Measuring the surface charge as a function of pH, it is highlighted the absence of surface charges and, therefore, no acid-base properties. The interaction solid–IPA was monitored by determining the amount of analyte adsorbed per gram of solid (Γ, mmol/g), as a function of time, until equilibrium was reached. The free concentration of IPA (C_e) was determined by spectrofluorimetric measures. The results obtained, for both solids, are described by the Langmuir model . The analysis of the adsorption properties in suspensions containing electrolytes of different nature (Li^+, Na^+ and $N(C_2H_5)_4{}^+$) showed no interaction of the solids with the ions of the medium.

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ANA-P53

Speciation studies on mercury(II)-phosphonic ligand systems

Concetta De Stefano, Claudia Foti, Ottavia Giuffrè, Demetrio Milea

Dipartimento di Scienze Chimiche, Università di Messina,
Viale F. Stagno d'Alcontres, 98166 Messina, Italy

cfoti@unime.it

Phosphonic chelating compounds are widely used in a broad variety of applications: in water treatment, in laundry detergents, as corrosion inhibitors, in industrial cleaning, as molecular tools in recognition and sensing of biologically relevant molecules, in drug delivery and treatment, or as linkers between the inorganic and organic parts of a bio-device [1,2]. Most of these applications derive from the coordination abilities of phosphonates towards metal ions. This requires the availability of reliable data on the stability constants of the complexes and the knowledge of the speciation of the corresponding systems.

In this light, in the last years we started a systematic study on the complexing ability of phosphonic acids towards many metal and organometal cations. Here we report the results obtained for ligands containing from mono to penta phoshonic groups towards Hg^{2+}. Ligands considered were: mono-, di-, tri- phosphonate derivatives of nitrilotriacetic acid [N-(phosphonomethyl) iminodiethanoic acid (*NTAP*), N,N-bis(phoshponomethyl)glycine (*NTA2P*), Nitrilo-tris(methylene-phosphonic acid) *NTA3P*], 1-Hydroxyethane-1,1-diphosphonic acid (etidronic acid, *HEDP*), diethylentriamine-penta(methylphoshponic) acid (*DTPMP*).

The complexing ability of the different ligands towards Hg^{2+} has been investigated and formation constants of species were determined, with the aim to obtain predictive equations having general validity for this ligand class.

On the light of the speciation models, the sequestering ability of various ligands toward Hg^{2+} has also been quantified.

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ANA-P54

Spectroscopic characterization of CT complexes of DDQ with amino molecules

Valentina Ribotta, Enrico Chiavazza[a], Pier Giuseppe Daniele[a], Silvia Berto[a], Mery Malandrino[a]

a Dipartimento di Chimica, Università di Torino, Via Pietro Giuria 7, 10125, Torino, Italy

mery.malandrino@unito.it

The interaction of the electron acceptor 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) with molecules containing nitrogen atoms was studied in acetonitrile and ethanol by spectroscopic techniques. The DDQ forms charge transfer (CT) complexes with electron donors and these complexes absorb radiations in the visible range with high molar absorptivity values. This reactions can be used for the quantification of the donors [1-6]. In this work the attention was focused on the study of the interaction of DDQ with two pharmaceutical products containing amino groups: atenolol and procaine. In order to obtain stable and coherent results, we evaluated preliminarily the stability of DDQ in the two polar solvents and the time necessary to obtain a stable and high response with the drugs at 298.15 ± 0.1 K. For both the systems, the stoichiometry of the complexes were defined with Job's plot method and the stability constants were calculated from spectrophotometric titration data using the software Hyspec [7]. The NMR spectra recorded at room temperature and at T = 233.15 K allowed us to define the portion of the donor molecule involved in the complex formation and to confirm the values of formation constants.

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ANA-P55

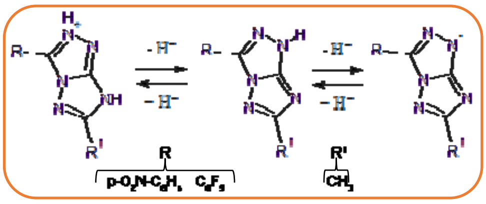
Acid base characterization of triazolo-triazole heterocyclic systems

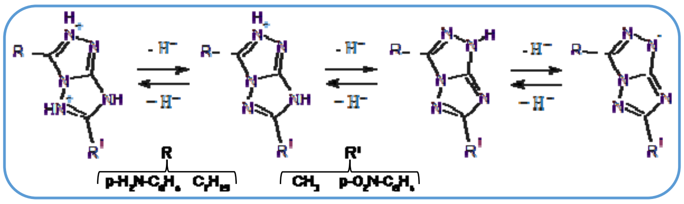
C. Manfredi[a], R. Centore[a], E. Vasca[b], C. Maglione[a], S. Volino[a], P. Scarano[a]

a Dipartimento di Scienze Chimiche, Università di Napoli, Via Cintia 46, 80126 Napoli, Italia
b Dipartimento di Chimica e Biologia, Università degli Studi di Salerno, Via Giovanni Paolo II 132, Cap 84084, Fisciano (SA), Italia

carla.manfredi@unina.it

Heterocycles are key compounds of synthetic chemistry. Besides their long standing and relevant application as drugs and bioactive compounds, aromatic heterocycles are playing a fundamental role in modern material chemistry as building blocks of conjugated active molecules in many emerging fields of organic electronics and optoelectronics: conducting polymers, organic field-effect transistors,[1] organic solar cells,[2] nonlinear optically active compounds.[3] In this work we propose a study of acid-base properties of four [1,2,4]triazolo[3,2-c][1,2,4]triazole systems[4]. The experimental method elected consists of potentiometric, spectrophotometric titrations, in constant ionic medium NaCl 0.5M at 25.00±0.02°C. Electronic absorption spectra have been interpreted with the following equilibria:





These results shown that the acid-base properties of [1,2,4]triazolo[3,2-c][1,2,4]triazole derivatives critically depends on the substituents at the heterobicycle.

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ANA-P56

Electrochemical immunosensor for hepatitis a virus (HAV) determination in food and clinical samples

A. De Stefano[a], *L. Micheli*[a], *M. De Santis*[a], *D. Donia*[b], *M. Divizia*[b], *G. Palleschi*[a]

a Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma "Tor Vergata" Via della Ricerca Scientifica, 00133, Roma, Italia
b Dipartimento di Medicina Sperimentale e Chirurgia, Università di Roma "Tor Vergata", Via Montpellier, 1, 00133, Roma, Italia

alessia.de.stefano@uniroma2.it

Hepatitis A is an acute infectious disease of the liver due to a *picornavirus*, Hepatitis A virus (HAV). Globally, the disease are believed to occur in around 1,4 million people a year eating or drinking contaminated food or water.

Current legislation for water, shellfish (EC 2073/2005 EC B53/2004) and plant (EC 2073/2005) does not provide for any limitation due to the presence of HAV and other enteric viruses in the irrigation and housing water. In addition, there will be no official method for the detection of these viruses. Currently, the environmental presence of HAV virus is only determined after the outbreak. The diagnosis is based on the patient's symptoms and more specifically through the search for anti-HAV IgG antibodies in blood.

In this work we show the development of a disposable electrochemical immunosensor for the detection of *HAV* antigens in food matrices and/or in the environment. This rapid and low-cost analysis method can involve the use of a portable instrument to perform measurements directly in the field.

This electrochemical immunosensor is based on competitive enzyme-linked immunosorbent assay (ELISA) format using screen printed electrodes. Results showed a working range between $1 \cdot 10^{-6} - 1 \cdot 10^{-2}$ IU/mL. The proposed system was applied to food and drinking water. The results obtained on real samples by the proposed immunosensor were compared with those of the qRT-PCR analysis, levels in different samples.

ANA-P57

HPLC analysis of elemental sulphur released in a bioprocess for the removal of H_2S in biogas

Aliboni A.[a], *Lona L.*[ab]*Felici C.*[c], *Izzo G* [a]*and De Luca E.*[a]

a ENEA, CRE Casaccia Dip UTRINN-BIO, Via Anguillarese 301 00123 Santa Maria di Galeria (RM) Italia, b Università della Tuscia, Dip. Dafne, Via de Lellis SNC, 01100 Viterbo, Italia, c ENEA, CRE Casaccia Dip UTRINN-STD, Via Anguillarese 301 00123 Santa Maria di Galeria (RM) Italia

andrea.aliboni@enea.it

Chlorobium limicola is an anaerobic photosynthetic bacterium that uses H_2S as a source of electrons. It transforms sulphide to elemental sulphur (S_8) that can be further oxidized to sulphate (SO_4^{2-}) [1]. The study of metabolic pathways requires the analysis of all sulphur species. Elemental sulphur is traditionally analysed by UV-VIS spectrophotometry following liquid-liquid extraction with chloroform [2]. This method suffers from long process times, chloroform toxicity and poor accuracy. HPLC methods reported in literature also require this extraction prior to analysis [3]. An HPLC method for the analysis of sulphur in *C. limicola* culture media has been here devised exploiting sulphur solubility in tetrahydrofuran. Briefly, 250 μL of aqueous culture medium are mixed with 750 μL of THF along with a known amount of phenylethyl salicylate, the internal standard. The mixture is sonicated and filtered, then analyzed over an Ascentis ® C18 column, 250 x4,6 mm 5 μm particles (Supelco, Bellefonte, PA, USA). The eluent was 75% THF and 25% 0,1% formic acid in water at 1 mL/min for 7 minutes, UV detection at 290 nm. Phenylethyl salicylate has a retention time of 3,6 ± 0,1 min, sulphur 5,6 ± 0,1 minutes. Limit of detection for sulphur in these conditions is 15 pg, RSD for sulphur determination is 2,5%. The proposed method is easy and fast to implement, lends itself to automation and totally eliminates the need to use chloroform.

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ANA-P58

Il Controllo di Qualità come strumento per la valutazione della incertezza di misurazione nella determinazione GC/MS dei composti organici volatili in campioni atmosferici

Graziano Bonacchi [a)], *Michele Fiore* [b)], *Vittoria Giudice* [b)], *Daniela Piazzese* [c)], *Rita Francesca Pomilla* [c)], *Roberto Zingales* [c)]

[a)] *Chimico libero professionista, Pistoia, Italy*
[b)] *Laboratorio della Struttura Territoriale ARPA Sicilia di Palermo, via Nairobi 4, I-90129 Palermo, Italy*
[c)] *Dipartimento di Fisica e Chimica, Università degli Studi di Palermo, Viale delle Scienze, I-90128 Palermo, Italy*

daniela.piazzese@unipa.it

In questa indagine sperimentale si riportano le incertezze di misurazione nella determinazione analitica di 12 composti organici volatili in campioni atmosferici (VOCs: *propene*, 1,3-*butadiene*, *trichlorofluoromethane*, *hexane*, *benzene*, *heptane*, *toluene*, *ethylbenzene*, *p*-*xilene*, *m*-*xilene*, 1,2,4-*trimethylbenzene*, 1,3,5-*trimethylbenzene*) utilizzando come i dati derivanti dal Controllo di Qualità Interno (ICQ), in accordo con la norma ISO 11352[1]. La metodologia adottata permette di stimare l'incertezza di misurazione nelle determinazioni analitiche come incertezza combinata $u_{c,rel}$ dello scarto tipo di ripetibilità intermedia ($u_{R_I,rel}$) e del "*bias*" associato al laboratorio ($u_{bias,rel}$). La norma di riferimento[1], applicata alle acque, in questa indagine per la prima volta è stata utilizzata nel controllo di qualità di composti organici volatili in atmosfera. La scelta dei dodici analiti è stata fatta considerando la loro elevata tendenza a favorire la formazione dell'ozono atmosferico. Le misure sperimentali sono state effettuate in GC-MS, previa criofocolizzazione del campione di aria prelevato mediante canister, applicando il metodo (EPA TO-15:1999). Le incertezze di misurazione stimate per tutti gli analiti soddisfano il criterio di accettabilità prescritto dalla legislazione europea[2], fissato per il benzene nel caso di misurazioni discontinue ad un valore del 30%.

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ANA-P59

Iron(III) sensing by kojic acid based-membrane

R. Colleoni, [a] *L. Allegri,* [a] *M. Urrutia Antia,*[b] *G. Alberti,* [a] *R. Biesuz,* [a]
A. Speltini, [a] *S. Vallejos,* [c] *F. C. García,* [c] *J. M. García,*[c]

[a] *Department of Chemistry, Università degli Studi di Pavia,*
via Taramelli 12 – 27100 Pavia (Italy);
[b]*Department of Chemistry; Universidad del Pais Vasco,*
Paseo Manuel de Lardizábal 3 – 20018 San Sebastián (Spain);
[c]*Faculty of Science; Universidad de Burgos,*
Plaza de Misael Bañuelos s/n – 09001 Burgos (Spain);

roberta.colleoni01@universitadipavia.it

We present a novel polymeric material for iron(III) sensing that features kojic acid as receptor moiety. The final material is transparent with good mechanical properties. In García's laboratory chromatic properties of the support are now being studied via spectrophotometric measurements. In our laboratory we have undertaken the characterization of the material performing kinetics, isotherms and sorption profiles in function of the pH. Kinetics profiles showed that the iron(III) uptake requires about one hour and a half, the behaviour makes this material not so different from other silica based solids for iron(III) sorption [1]. Preliminary sorption isotherms confirmed the expected amount of ligand copolymerized in the membrane. The sorption profiles in function of pH, also in presence of different competitors have been produced. The sorption exchange coefficient of iron(III) seems, so long, in pretty good agreement with the ones reported in literature for the complex in solution. [2,3]

Further investigations are in progress, but we are confident that such material could be employed for several feasible purposes.

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ANA-P60

Analytical characterization of magnetite nanoparticles prepared by microwave assisted hydrothermal synthesis

A. Rizzuti[a], *P. Mastrorilli*[a*], *M. Dassisti*[b]

M.C. Sportelli[c], *R.A. Picca*[c], *N. Cioffi*[c*]

a Dipartimento di Ingegneria Civile, Ambientale, del Territorio, Edile e di Chimica, Politecnico di Bari, Via Orabona 4, 70125, Bari, Italia
b Dipartimento di Meccanica Matematica e Management, Politecnico di Bari, Viale Japigia 182, 70126, Bari, Italia
c Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro", Via Orabona 4, 70126, Bari, Italia

nicola.cioffi@uniba.it

Magnetic nanoparticles (NPs) are receiving increasing attention due to their versatility in several fields ranging from biomedicine [1] to catalysis [2]. A careful control of size, morphology, and (aqueous/organic) solvent dispersibility is extremely important for the successful development of good quality Fe_3O_4 NPs, especially in terms of magnetic properties. Several approaches, including co-precipitation, sol-gel, hydro- and solvo-thermal methods, have been reported in literature leading to the preparation of magnetic NPs of different shape (e.g. rods, rings, wires, octahedra) [3]. Recently, microwave assisted hydrothermal methods have emerged as appealing strategies for the preparation of magnetic nanomaterials due to advantages, such as rapid heating, reduced reaction times and increased yield, if compared with conventional heating methods [4]. In this communication, we present the results of the analytical characterization of magnetite NPs obtained by the partial oxidation of $FeCl_2 \cdot 4H_2O$ by hydrazine in alkaline conditions, followed by microwave irradiation. Moreover, the influence of the added surfactant (e.g. oleic acid, polyvinylpyrrolidone, sodium citrate) on NP morphology and surface/bulk chemical composition is demonstrated through the analytical characterization of the as-prepared NPs by TEM, IR, TGA, and XPS.

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ANA-P61

SPRI detection and discrimination of a SNP in the K-ras oncogene

Cristina Valenti[a], *Roberta D'Agata*[b], *Angela M. Aura*[b], *Giuseppe Spoto*[a,b]

a Consorzio I.N.B.B., Viale delle Medaglie d'Oro 305, 00136, Roma, Italy
b Dipartimento di Scienze Chimiche, Università di Catania, Viale Andrea Doria 6 , 95125, Catania, Italy

cristy.valenti@gmail.com

Point mutations in the Kirsten rat sarcoma viral oncogene homologue (K-ras) gene are being recognized as an important diagnostic and prognostic markers in cancer. In particular, the specific G-G mismatch in K-ras codon 12, is present in 90% of all pancreatic cancer, so that it is an important task required for clinical usage [1]. Optical biosensors based on sequence-specific DNA hybridization have been widely used in clinical diagnostics, forensic sciences and biomedical research. Many studies on surface plasmon resonance imaging (SPRI) as an optical method for biosensing have been carried out because it allows to detect biomolecular interactions in real time and with high sensitivity [2]. In the present study, the SPRI biosensor has been used to develop a SNP detection assay for the detection of the K-ras G12D mismatch [3, 4]. A synthetic oligonucleotide probe were immobilized onto a gold surface sensor chip and the hybridization of the 95-mer single stranded DNA targets was monitored by the SPRI technique.

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ANA-P62

Determinazione di composti organostannici tramite campionamento passivo nel golfo di La Spezia

Paolo Massanisso, Caterina Marcoaldi, Sigfrido Cannarsa, Carlo Cremisini

ENEA,UTPRA, CR Casaccia, Via Anguillarese 301, 00123, Rome, Italy

kate-12@hotmail.it

Uno dei problemi rilevanti di contaminazione ambientale diffusa è rappresentato dalla presenza di composti organostannici nell'ambiente marino. Tali composti, in particolare il tributilstagno (TBT), sono stati largamente utilizzati come principi attivi nelle vernici antivegetative, impiegate soprattutto per la protezione degli scafi delle imbarcazioni. Una volta rilasciato in acqua l’elevata tossicità del TBT, l’elevata persistenza e la conseguente possibilità di essere accumulato in organismi di notevole importanza di mercato ha prodotto notevoli danni sia dal punto di vista ambientale che economico. Ad oggi, pur esistendo un bando internazionale che ne vieta l’utilizzo, la presenza del TBT è comunque diffusa in tutto il globo.

Il campionamento passivo mediante i dispositivi a membrana semipermeabile (SPMD) permette di concentrare all’interno di una fase (trioleina) l’analita in esame rendendo possibile la misura anche a concentrazioni estremamente basse. Tali sistemi passivi sono collocati in acqua per un fissato periodo di tempo e i risultati ottenuti rappresentano quindi un valore integrato nel tempo del composto cercato.

Lo scopo del lavoro è stato quello di effettuare una prima valutazione delle possibilità di utilizzo di tale dispositivo per la misura di composti organostannici in acqua di mare. Dopo dialisi in esano del campione SPMD, il metodo analitico utilizzato per la misura del TBT prevede la derivatizzazione mediante reattivo di Grignard e la determinazione analitica mediante GC-MS/SIM, utilizzando la diluizione isotopica come metodo di quantificazione.

Le prove effettuate provano che, il sistema passivo SPMD permette la quantificazione del TBT riuscendo a misurare concentrazioni ben al disotto di quelle ottenibili mediante campionamento attivo.

ANA-P63

Elemental analyses of woody biomass and solid byproducts from pyro-gasification

J. Tafur Marinos, M. Ginepro, V. Zelano

Dipartimento di Chimica, Università di Torino, Via P. Giuria, 10125, Torino, Italia

janethalicia.tafurmarinos@unito.it

Energy demand in the world is increasing continually in industrialised countries as well as in emerging countries, and it is satisfied for at least 70% from fossil fuels. The understanding of possible relationship that may exist between climate change, greenhouse gas and global warming requires research and development of alternative and renewable energy sources. Wood biomass is a source of renewable energy and now recognised as a potential alternative for sustainable energy production. Gasification is one of the most efficient technologies for biomass energy conversion, this process converts solid biomass into gaseous fuel by a partial oxidation at high temperatures. The gas obtained (syngas) then can be used for the cogeneration. However, in addition to the syngas, solid and liquid byproducts are obtained, and so the presence of these results in serious operational and environmental problems [1].

The aim of this research is to quantify the contents of major (Al, Ca, Fe, K, Mg, Na, P, Si, S) and minor elements (As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Zn) present in the solid residue of pyro-gasification. The methods of dissolution applied to the residue are the same used for the dissolution of the woody biomass, namely wet digestion, digestion dry, alkaline fusion and microwave digestion. Certified reference materials were used in order to verify the accuracy of the analytical methods.

The results obtained show that not all applied methods are suitable for the dissolution of the solid residue that, although it results from gasification of woody biomass, presents an increased difficulty of analysis. Moreover, the same problems observed in some biomass dissolution treatments, such as the incomplete dissolution of the matrix and the losses of some elements by volatilization, were observed.

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ANA-P64

A breath sampler prototype to collect end-tidal and dead space fractions

S. Ghimenti[a], *P. Salvo*[a], *T. Lomonaco*[a], *F. Detti*[a], *F. Bellagambi*[a],
C. Ferrari[b], *F. Di Francesco*[a, c], *R. Fuoco*[a]

a Department of Chemistry and Industrial Chemistry, University of Pisa, Via Risorgimento 35, 56126, Pisa, Italy
b National Institute of Optics – UOS Pisa, CNR, Via G. Moruzzi 1, 56124, Pisa, Italy
c Institute of Clinical Physiology, CNR, Via G. Moruzzi 1, 56124, Pisa, Italy

silvia.ghimenti@ifc.cnr.it

Breath analysis is a potential tool for modern medicine to obtain clinical information on the physiological processes in a non-invasive way. A typical respiratory cycle involves the exchange in the lungs of about 500 mL of air (mixed breath) which is formed by two fractions, namely dead space and end-tidal volume. The first portion of air (150 mL) is contained in the upper airways while the end-tidal air (350 mL) contains most of the chemical information on blood composition. End-tidal breath sample is the most representative and useful fraction to obtain physiological information due to rapid diffusion equilibrium between the compounds dissolved in the blood and air in the alveoli.

This work presents a breath sampler prototype which automatically collects end-tidal or dead space air over multiple breaths. This result was achieved by real time measurements of the CO_2 content and airflow value during the expiratory and inspiratory phases. Suitable algorithms, used to control a solenoid valve, guaranteed that a Nalophan bag was filled with the selected breath fraction even if the subject under test hyperventilates. The breath sampler showed low pressure drop (< 5 $cm{\cdot}H_2O$) and was made with inert or disposable components to avoid bacteriological risk for the patients and contamination of the samples.

The performance of the breath sampler was evaluated by comparing the expected and actual partial pressure values of CO_2 and the concentrations in dead space, end-tidal and mixed breath fractions of four volatile organic compounds (VOCs) (isoprene, acetone, toluene and ethanol). Results showed negligible deviations from the expected CO_2 values and a concentration ratio (end-tidal/mixed and dead space/mixed) of the selected VOCs in good agreement with those reported in literature.

ANA-P65

Kinetic and equilibrium studies for uranyl removal from aqueous solution by adsorption onto alginate gel beads. DPV and ICP measurements.

<u>Salvatore Cataldo</u>, Antonio Gianguzza, Nicola Muratore, Daniela Piazzese

Dipartimento di Fisica e Chimica, Università di Palermo,
Viale delle Scienze - Edificio 17, 90128, Palermo, Italia

salvatore.cataldo@unipa.it

The removal capacity of uranyl from aqueous solutions was investigated by sorption onto 2% alginate gel beads. DPV (Differential Pulse Voltammetry) and ICP-OES measurements were carried out in $NaNO_3$ aqueous solution for the kinetic and equilibrium studies. The kinetic results obtained by the two different techniques are in good accordance and confirm the possibility to carry out quantitative analysis of uranyl by DPV measurements. Direct measurements of uranyl by DPV were carried out without using complexing agent, as usually reported in the literature: this allowed us to know the UO_2^{2+} species formed in the ~ 2.3 to 5.0 pH range investigated. Different sorption equilibrium models were used to analyze the experimental data. The best fit was obtained by using a multiple equilibrium model (see Figure). A similar approach was recently used to study the lead(II) adsorption by AA gel beads.[1]

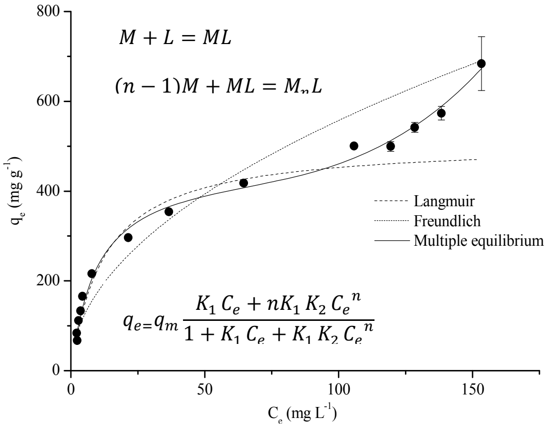

Figure. Adsorption isotherm of UO_2^{2+} by AA gel beads in 0.1M $NaNO_3$ at 25°C. Lines are according to three different models. M and L represent the adsorbate and adsorbent, respectively and q_m is the Langmuir adsorption parameter.

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ANA-P66

Identification of new Phenolic Compounds in Olive Leaves by Different Mass Spectrometry Scan Modes Application.

Anna Russo [a], *Attilio Parise* [a], *Gabriele Pacenza* [a], *Enzo Perri* [a], *Giovanni Sindona* [b]

a Consiglio per la Ricerca e la Sperimentazione in Agricoltura- CRA-OLI,
c/da Li Rocchi, Vermicelli, 87036 Rende (CS)
b Dipartimento di Chimica e Tecnologie Chimiche-CTC,
Università della Calabria, via P.Bucci, Arcavacata di Rende (CS)

anna.russo@entecra.it

Olive leaves consist of a residual food-processing material, rich in biologically functional compounds.

The recovery of these phytochemicals suffer serious shortcomings due to solvent toxicity.

The aim of the present study was the investigation on the extraction efficiency of ethanol/water mixtures in extracting phenolic compounds from fresh olive leaves.

These extracts were characterized by complementary use of chromatographic separation, UV and MS detectors (HPLC-UV and HPLC-MS).

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ANA-P67

On the Mechanism of Action of Cyanocobalamin in Acqueous Media: a Spin Trapper and Tandem Mass Spectrometry Investigation

Anna Russo [a], *Ilaria Santoro* [b],

Enzo Perri [a], *Giovanni Sindona*[b]

a Consiglio per la Ricerca e la Sperimentazione in Agricoltura- CRA-OLI,
c/da Li Rocchi, Vermicelli, 87036 Rende (CS)
b Dipartimento di Chimica e Tecnologie Chimiche-CTC,
Università della Calabria, via P.Bucci, Arcavacata di Rende (CS)

anna.russo@entecra.it

An innovative method based on the combination of mass spectrometry and spin trapper techniques is considered to study the mechanism of action of cyanocobalamin in acqueous media. It was considered a ternary system made of cyanocobalamin, 1,2-propanediol and a-(4-pyridyl 1-oxide)-N-tert butyl- *nitrone* (POBN). The formation of different type of compounds between the diol and the cofactor was observed. The results here reported are useful as (i) a simple procedure of chemical manipulation of cyanocobalamin and as (ii) an investigation on the cobalt chemistry in this particular organometallic complex.

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ANA-P68

Surface cleaning of brasses for musical instruments: an XPS study.

Federica Cocco[1]; Bernhard Elsener[1]; Marzia Fantauzzi[1]; Antonella Rossi[1]

1 Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari, ss 554 bivio per Sestu 09042 Monserrato Cagliari, rossi@unica.it

cocco.federica86@gmail.com

Brasses (Cu Zn alloys) are since centuries employed for manufacturing musical instruments due to their good acoustic properties. During their use, the surface of the instruments gets in contact with humid air, sweat and saliva. A contamination layer and a thin oxide film or a layer of corrosion product, called patina, is formed. As the acoustic properties of the instruments depend on the material composition the patina and corrosion products may compromise the quality of the sound. Thus the brass surface has to be cleaned without compromising the performance of the instruments.

The aim of this work is to compare different ways to remove the contamination layer and the patina at the surface of ancient brass musical instruments. The surfaces of a brass musical instrument of the XIX century and a series of model brass alloys have been characterized by X-ray photoelectron spectroscopy (XPS) and X-ray excited Auger electron spectroscopy (XAES) in the "as received" state, after ultrasonic cleaning in distilled water and in butanone, acetone and ethanol. Spectral features such a line-shape, peak energy and peak intensity for Cu2p, $CuL_3M_{45}M_{45}$, Zn2p, $ZnL_3M_{45}M_{45}$, C1s and O1s bands were examined. To characterize the chemical state of copper and zinc the Wagner plot [1] was used.

On the surface of as received samples as well after washing with distilled water no signals from metallic Cu and Zn were observed, thus the thickness of the oxide plus the organic layer was found to be larger than the XPS sampling depth. After cleaning with organic solvents the intensity of the C1s peak decreased and the metallic components of Cu and Zn signals were detected. The line shapes of Cu2p and Zn2p signals were similar to those found on mechanically polished brasses. Based on the assignment of the Wagner chemical state plot the compounds $Cu(OH)_2$, Cu_2O and $Zn(OH)_2$ (probably in the form of hydrozincite) were revealed. The composition of the oxide films was found to be ca. 70% copper oxide/hydroxide and 30% of zinc hydroxide. Cleaning with organic solvents did not affect the oxide composition.

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Chimica Farmaceutica

Keynote

FAR-K1

Covalent inhibitors of endocannabinoid metabolism: rational design and mechanistic studies

Marco Mor

Dipartimento di Farmacia, Università degli Studi di Parma, Viale Usberti 27/a, 43124 Parma, Italy

marco.mor@unipr.it

Arachidonoylethanolamide (AEA, anandamide) and 2-arachidonoylglycerol are the principal compounds that endogenously activate the two cannabinoid receptors, CB1 and CB2. Tissue levels of these endocannabinoids are regulated by their inactivating hydrolysis, catalyzed by Fatty Acid Amide Hydrolase (FAAH) and Monoglyceride lipase (MGL), respectively. Inhibition of FAAH produces different positive effects on anxiety, depression and post-traumatic stress, while MGL inhibition gives analgesic effects. Although reversible non-covalent inhibitors have been discovered for both enzymes, covalent active-site directed inhibitors still represent the mostly used pharmacological tools in animal studies, and continue to be developed. The design and optimization of covalent inhibitors requires careful consideration of compound reactivity and detailed elucidation of the mechanism of their reaction with the enzyme counterpart. On the other hand, the strategy of covalent targeting can offer interesting opportunities and the possibility to tune the pahrmacokinetics and pharmacodynamics of endocannabinoid modulators. The cases of carbamate-based FAAH inhibitors and cysteine-addressing MGL inhibitors will be illustrated in the talk.

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FAR-K2

Serotonin 5-HT$_7$ Receptor: a Novel Target for the Treatment of Neurodevelopmental Diseases

Marcello Leopoldo

Dipartimento di Farmacia - Scienze del Farmaco, Università degli Studi di Bari, Via Orabona 4, 70125, Bari, Italy

marcello.leopoldo@uniba.it

Serotonin 7 receptor (5-HT$_7$R) is part of a crucial neuro-transmission system with a proposed role in neurogenesis/neural plasticity [1] and in psycho-pathological processes like mood, cognitive or sleep disturbances [2]. LP-211 is a brain-penetrant selective 5 HT$_7$R agonist, developed in our laboratory, that is contributing to show that selective activation of 5-HT$_7$R may represent a novel strategy in the therapy of neurodevelopmental diseases such as Fragile-X syndrome [5] and Rett syndrome [6]. Moreover, the treatment of murine striatal and cortical neuronal cultures with LP-211 significantly enhances neurite outgrowth [7], suggesting the involvement of 5-HT$_7$R in modulation of neuronal morphology. Finally, magnetic resonance studies *in vivo* in the rats have evidenced that stimulation of 5-HT$_7$R by LP-211 during adolescent development may generate enduring changes in the morphology of the “cortical” loop (hippocampus, dorsal striatum, frontal cortex, hypothalamus) as well as in the strength of connectivity within the “limbic” loop (thalamus, nucleus accumbens, occipital frontal cortex) [8]. Altogether these findings suggest the involvement of 5-HT$_7$R in shaping central nervous system connectivity which may be intimately linked to psychiatric and neurodevelopmental disorders.

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FAR-K3

Design, Synthesis, Crystallographic Studies, and Biological Appraisals of New Tankyrase Inhibitors

Emidio Camaioni[a], *Paride Liscio*[ad], *Stefania Asciutti*[b], *Andrea Carotti*[a], *Antonio Macchiarulo*[a], *Martina Ferri*[a], *Tobias Karlberg*[c], *Herwig Schuler*[c], *Stuart A. Aaronson*[b], *Benedetto Natalini*[a], *Roberto Pellicciari*[d]

a Dipartimento di Scienze Farmaceutiche, Università di Perugia, Via Liceo, 1, 06123, Perugia, Italia
b Department of Oncological Sciences, Mount Sinai School of Medicine, 1425 Madison Ave, New York 10029, United States
c Department of Medical Biochemistry and Biophysics, Karolinska Institutet, S-17177 Stockholm, Sweden
d TES Pharma, via P. Togliatti 22bis, 06073 Località Terrioli, Corciano, Italy

emidio.camaioni@unipg.it

The human genome encodes two tankyrases, TNKS-1 and TNKS-2 which are members of the poly(ADP-ribose) polymerases (PARPs) family. By having an active role in telomere maintenance and Wnt pathway regulation, TNKSs take part in the complex arena of processes responsible of growth and progression of tumors. Inhibition of TNKSs activity appears therefore to be a promising strategy in the treatment of cancer. As an extension of our work in the field, we have recently reported the design, synthesis and biological appraisals of novel potent and selective TNKSs inhibitors [1]. Structure based optimization of the starting hit compound N-(4-chlorophenethyl)-6-methyl-[1,2,4]triazolo[4,3-b]pyridazin-8-amine (NNL) led us to disclose 4-(2-(6-methyl-[1,2,4]triazolo[4,3-b]pyridazin-8-ylamino)ethyl)phenol, a low nanomolar selective TNKSs inhibitor working as NAD isostere as ascertained by crystallographic analysis (PDB code 4M7B). Furthermore, cellular assays pinpoint [1,2,4]triazolo[4,3-b]pyridazine class of derivatives as powerful pharmacological tools for the unravelling of TNKS implications in physio-pathological conditions which imply Wnt pathway aberration.

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FAR-K4

AAI101, a new β-lactamase inhibitor combating emergent multidrug resistant pathogens

Stefano Biondi

CMC Director, Allecra therapeutics SAS, 13 rue du Village Neuf, 68300, Saint Louis, France.

sdb@allecra.com

There is an urgent need for new, well-tolerated antibiotics active against multidrug-resistant Gram-negative bacteria. Enterobacteriaceae (especially *E. coli* and *K. pneumoniae*) and non-fermentative rods (especially *Pseudomonas aeruginosa*) are very serious causes of nosocomial infections and infections associated with long-term healthcare facilities, where the causative pathogens increasingly are becoming resistant to most antibiotics currently used to treat them.

A scarcity of drugs capable of treating such infections led clinicians to reevaluate the therapeutic utility of polymyxins (polymyxin B, colistin), whose use was phased out during the 1970s due to nephrotoxicity. Allecra Therapeutics is actively involved in the attempt to solve this critical situation by developing new medicinal products able to cure severe infections caused by Gram-negative bacteria.

In particular, AAI101 is a novel extended spectrum β-lactamase inhibitor currently in clinical development in combination with β-lactam antibiotics.

This presentation will illustrate the pharmacological properties of AAI101 both *in vitro* and *in vivo* together with some clinical data obtained during phase I trials.

FAR-K5

Targeting DNA methylation: a medicinal chemistry approach

Antonello Mai

Sapienza University of Rome, P.le A. Moro 5, 00185 Rome, Italy

antonello.mai@uniroma1.it

DNA methyltransferases (DNMTs) are important enzymes involved in epigenetic control of gene expression and represent valuable targets in cancer chemotherapy. While a number of nucleoside DNMT inhibitors (DNMTi) have been studied in cancer including cancer stem cells, and two of them (azacitidine and decitabine) have been approved for treatment of myelodysplastic syndromes, only few non-nucleoside DNMTi have been identified so far, and much less validated in cancer. Through a process of hit-to-lead optimization, we describe here the discovery of some quinoline-based compounds related to SGI-1027 analogues as potent non-nucleoside DNMTi, and selective towards other AdoMet-dependent methyltransferases. Compound **5** was potent at single-digit μM against a panel of cancer cells, and less toxic in peripheral blood mononuclear cells. In mouse medulloblastoma stem cells **5** inhibited cell growth while the related compound **2** showed high cell differentiation. To the best of our knowledge, **5** is the first non-nucleoside DNMTi tested in a cancer stem cell line.

In a further experience, chemical manipulation performed on the H3K9 methyltransferases (G9a/GLP) inhibitor BIX-01294 afforded novel quinazoline derivatives with potent and selective inhibitory activity against DNA methyltransferase DNMT3A. The same compounds showed little (if any) inhibition of DNMT1 and failed in inhibiting GLP in opposite to BIX, used as reference drug. Tested in human lymphoma U-937 and RAJI cells, the new selective DNMT3A inhibitors displayed strong arrest of proliferation and cell death induction at 10 μM concentration.

FAR-K6

Developing novel polyamine conjugates for selective anticancer therapy

Anna Minarini

Dipartimento di Farmacia e Biotecnologie, Alma Mater Studiorum-Università di Bologna,
Via Belmeloro 6, 40126, Bologna, Italy

anna.minarini@unibo.it

The holy grail of anticancer therapy is to deliver the cytotoxic agent to the cancer cell selectively and minimise the exposure to normal cells. Today there are several methods of targeting drugs to the appropriate site but many, such as monoclonal antibodies, are expensive and time consuming to develop.

In recent years, extensive research has been devoted to the design of anticancer-polyamine conjugates since it was shown that rapidly proliferating and cancer cells display elevated intracellular polyamine content linked to increased activity of a specific polyamine transport system (PTS).[1] Although, there is limited molecular knowledge regarding the identity and protein components of the PTS found in animal cells, it is known that the PTS is able to transport large substituent groups attached to a polyamine backbone. A successful example of the application of this strategy is the design of F14512, an etoposide-spermine conjugate, currently undergoing phase I clinical trials.[2] The spermine moiety of F14512 functions both as a target vector for etoposide and as a subsidiary DNA anchor, leading to a reinforced inhibition of topoisomerase II.

Our concept was therefore to use endogenous transport pathways that are up-regulated naturally in cancer cells to deliver novel cytotoxic intercalating agents[3] more effectively to these cells and to assess the efficacy of these agents in terms of cytotoxicity and epigenetic changes. Different polyamine chains have been used to make hybrid drug molecules or conjugates in order to improve both the cellular import and the affinity for DNA. This study should help to better characterise the PTS and identify the optimal structural requirements for polyamine binding to the transporter.

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FAR-K7

Future therapeutic strategies to target HIV-1 integration and reverse transcription processes

Roberta Costi

Istituto Pasteur - Fondazione Cenci Bolognetti, Dipartimento di Chimica e Tecnologie del Farmaco, “Sapienza” University of Rome, P.le Aldo Moro 5, I-00185 Rome Italy

roberta.costi@uniroma1.it

Considerable success has been achieved in the treatment of HIV-1 infection, and many antiretroviral drugs are available targeting several distinct steps in the viral replication cycle. However, resistance to these compounds emerges readily, even in the context of combination therapy. Drug toxicity, adverse drug-drug interactions, and accompanying poor patient adherence can also lead to treatment failure. Finding new drugs, new drug targets and new therapeutic strategies may lead to redefining the goals of antiretroviral therapy, with an attempt to achieve the ultimate objective: the eradication of infection. One of such innovative approaches is the use of dual action drugs that combine two different pharmacological actions. RNase H activity of HIV-1 reverse transcriptase is an essential viral function that catalyzes highly specific hydrolytic events on the RNA strand of the RNA/DNA hybrid that are critical to the synthesis of double-strand proviral DNA from the RNA viral genome. Since its peculiar role, RNase H is a promising target for drug development although no RNase H inhibitor has been approved for treatment up to today. This is due to the difficulty to define a druggable pocket in the RNase H active site area since it presents a morphology more open if compared to that of integrase (IN), belonging to the same family of the enzymes. In the last decade we designed a number of IN inhibitors.[1,2] Among them we identified a series of diketo acids (DKA) as dual IN/ RnaseH inhibitors. Most of DKA ester derivatives were selective for HIV-1 RNase H versus IN, while the acid counterparts inhibited both activities being more potent on IN. Molecular modeling and site-directed mutagenesis studies on RNase H domain showed that ester and acid DKA derivatives have different orientation in the RNase H active site. Terefore in this study we provided important insights for rational lead optimization of RNase H inhibitors. Overall, we provide the first demonstration that RNase H inhibitor is able to block the reverse transcription process. A further innovative approach is the inhibition of association between IN and LEDGF/p75 in HIV-1 integration. The LEDGF/p75 is a protein that plays an important role in the integration process tethering IN to chromatin. Recently, we identify small molecules that disrupt the interaction between IN and LEDGF/p75

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Chimica Farmaceutica

Oral

FAR-O1

Design and synthesis of multi-target directed ligands with a potential CNS activity against neurodegeneration

Roberta Farina[a], *Leonardo Pisani*[a], *Marco Catto*[a], *Orazio Nicolotti*[a], *Ramon Soto-Otero*[b], *Angelo Carotti*[a]

[a] *Dipartimento di Farmacia-Scienze del Farmaco,*
Università degli Studi di Bari "Aldo Moro", Via Orabona 4, 70125, Bari, Italia
[b] *Department of Biochemistry and Molecular Biology, Universidad de Santiago de Compostela, San Francisco I, E-15782 Santiago de Compostela, Spagna*

roberta-farina@libero.it

The pharmacological treatment of age-related neurodegenerative disorders (NDs) represents an unmet medical need because of the low efficacy of current approved drugs, exerting mainly symptomatic effects, and the lack of effective disease-modifying therapeutics. The multifaceted nature of these pathologies calls for a new medicinal chemistry approach rooted on the design of agents addressing multiple biochemical alterations underlying the onset and progression of the neurotoxic cascade. Central Acetylcholinesterase (AChE) and Monoamine Oxidase-B (MAO-B) enzymatic activities have been largely proved to play a key role in NDs.[1] Herein we report the design and synthesis of dual AChE/MAO-B inhibitors[2] with a potential neuroprotective activity. The molecular framework was built *via* an hybridization approach, by connecting a coumarin skeleton (inspired by a in-house large library of MAO-B inhibitors)[3] to a donepezil-related basic moiety through spacers of different length and nature. Focused structural modifications were aimed at the improvement of pharmacokinetic properties, in order to modulate the lipophilic balance of the designed multi-target directed ligands and to obtain brain-permeating compounds with a potential in vivo activity in the CNS, as determined through PAMPA assays.

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FAR-O2

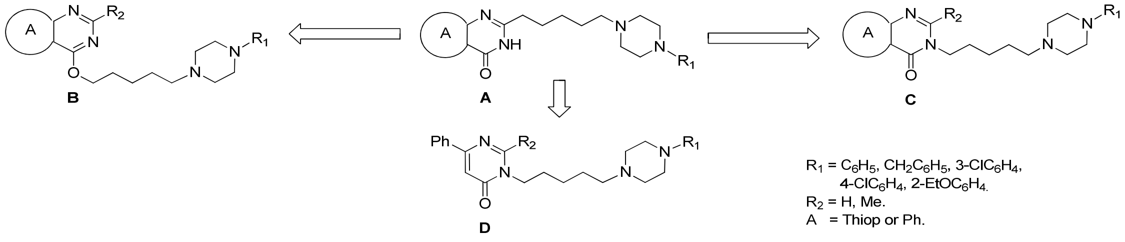
New alkylpiperazines as 5-HT$_7$R ligands

<u>Sebastiano Intagliata</u>[a], *Maria N. Modica*[a], *Giuseppe Romeo*[a], *Valeria Pittalà*[a], *Loredana Salerno*[a], *Maria A. Siracusa*[a], *Alfredo Cagnotto*[b].

[a]*Dipartimento di Scienze del Farmaco, Università degli Studi di Catania, viale A. Doria 6, 95125 Catania, Italy.*
[b]*IRCCS-Istituto di Ricerche Farmacologiche "Mario Negri", via La Masa 19, 20156 Milano, Italy.*

s.intagliata@hotmail

Since its identification, serotonin 5-HT$_7$ receptor (5-HT$_7$R) has been the subject of intense research efforts due to its presence in fuctionally relevant regions of the brain. For this reason it has been suggested to have a role in a wide range of physiological functions such as nociception, sleep, and locomotor activity regulation, learning and memory, and it is also involved in some pathologies like anxiety, depression, and epilepsy [1]. Given the potential utility of 5-HT$_7$R agents in CNS disorders, in the last years we have worked on the development of new selective 5-HT$_7$R ligands. Recently, we have reported the synthesis and the structure-affinity relationships (SAR) of a series of new thienopyrimidine and quinazoline alkylpiperazine derivatives (**A**), which were tested for their binding properties on cloned human 5-HT$_{1A}$R and 5-HT$_7$R [2]. The study presented herein describes further structural modifications on compounds of the previous series. In particular, to improve knowledges about SAR, we have: *i.* shifted the alkyl chain in other positions of the thienopyrimidine and quinazoline scaffold (**B** and **C**); *ii.* introduced a methyl group at the 2-position (**B** and **C**); *iii.* simplified the quinazoline to a pyrimidine scaffold (**D**). Synthetic pathways of new compounds along with preliminary binding data will be reported at the meeting.



$R_1 = C_6H_5, CH_2C_6H_5, 3\text{-}ClC_6H_4,$
$4\text{-}ClC_6H_4, 2\text{-}EtOC_6H_4.$
$R_2 =$ H, Me.
A = Thiop or Ph.

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FAR-O3

Identificazione di agenti selettivi per lo studio del potenziale terapeutico del recettore del Formil Peptide 2 (FPR2)

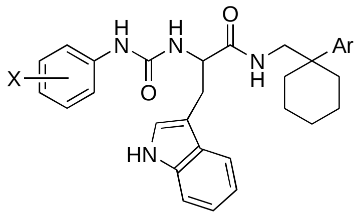
M. L. Stama[a], *E. Lacivita*[a], *I.A. Schepetkin*[b], *M. T. Quinn*[b], *R. Perrone*[a], *M. Leopoldo*[a]

[a]*Dipartimento di Farmacia - Scienze del Farmaco, Università degli Studi di Bari, via Orabona, 4, 70125 Bari, Italia*

[b]*Department of Immunology and Infectious Diseases, Montana State University, Bozeman, MT 59717, USA*

madiastama@alice.it

I recettori del Formil Peptide (Formyl Peptide Receptors, FPR) sono recettori chemioattrattanti accoppiati alle proteine G. Essi hanno un ruolo rilevante nella regolazione dei processi infiammatori e sono espressi nella maggior parte del leucociti, come i neutrofili, i monociti e le cellule dendritiche. L'attivazione dei FPRs è stata associata a malattie come danno da ischemia-riperfusione, malattie da prioni, amiloidosi, morbo di Alzheimer, cancro [1]. Poiché il potenziale di questi recettori come target terapeutico non è stato ancora esplorato, l'identificazione di agonisti o antagonisti potenti e selettivi è di grande importanza. Questo contributo illustrerà lo studio delle relazioni struttura-attività di derivati 3-(1H-indol-3-il)-2-fenilureido-propanamidici che possono attivare o bloccare FPR2 con spiccata enantiopreferenza [2]. Inoltre, verranno presentati dati di stabilità metabolica di alcuni degli agonisti, in vista di un possibile uso in studi in vivo.



X = NO_2, OCH_3, CH_3, Br
Ar = 2-Py, 4-Py, Ph

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FAR-O4

Benzofuran-based molecules as multi-target-directed ligands for Alzheimer's disease treatment

S. Montanari, F. Belluti, A. Bisi, S. Gobbi, M. Bartolini, A. De Simone, V. Andrisano, V. Di Marzo, A. Rampa

Department of Pharmacy and Biotechnologies, University of Bologna, Via Belmeloro 6, 40126, Bologna, Italy

serena.montanari5@unibo.it

Alzheimer's disease (AD) is the most common form of neurodegenerative disorder, characterized by an insidious onset and a chronic progression.[1] Several studies showed that this is a multifactorial disease and only palliative treatments are available to date. Recently, it has been demonstrated that the endocannabinoid system is involved in neuroprotective, anti-inflammatory and neurotrophic actions, which can be obtained by activating type 2 cannabinoid receptors (CB_2), either directly or by an endocannabinoid cellular reuptake inhibition.[2] In addition, CB_1 receptors activation or inhibition, depending on the timing of administration, was also suggested to be involved in AD.[2] Furthermore, the inhibition of the enzyme fatty acid amide hydrolase (FAAH), whose action would hydrolyze the endogenous ligands for CB_1 and CB_2 (e.g. anandamide), could be successfully considered as physiologic receptor activation. Taking into account these new elements, we tried to tackle AD's multifaceted nature with the multi-target-directed ligand paradigm, combining our long lasting experience on established AD targets with the attempt to hit these new biological structures. With this aim, considering our previous studies,[3,4] we designed and synthesized new potential antineurodegenerative and neuroprotective drug candidates, based on the benzofuran structure (general formula in fig. 1), which is the core moiety of LY320135, a high affinity antagonist/inverse agonist at CB_1 receptors.[5] The biological profile of the new compounds is now under evaluation, focusing on the inhibition of cholinesterases, Aß aggregation, BACE1 and FAAH, and on the interaction with CB_1 and CB_2 receptors.

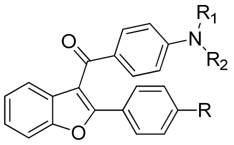

Fig. 1

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FAR-O5

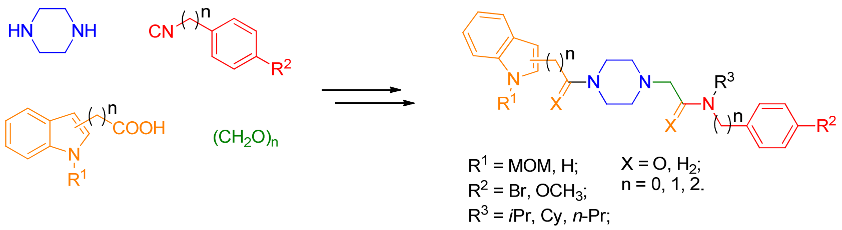
Multicomponent approach to the synthesis of a D2/D3 dopamine receptor ligands library and biological evaluation

Mattia Stucchi[a], *Giordano Lesma*[a], *Alessandra Silvani*[a],*Giulia Rainoldi*[a], *Alessandro Sacchetti*[b]

a Dipartimento di Chimica, Università di Milano, via Golgi 19, 20133, Milano, Italy
b Dipartimento di Chimica, Materiali ed Ing.Chimica 'Giulio Natta', Politecnico di Milano, p.zza Leonardo da Vinci 32, 20133, Milano, Italy

mattia.stucchi@unimi.it

The dopamine (DA) receptor system has been targeted in pharmacotherapeutic treatments of numerous disorders, including schizophrenia, abuse of drugs and Parkinson's disease. These receptors are divided in two classes: D1-like and D2-like. Among the D2-like, the D2 and D3 receptor subtypes possess 50% overall structural homology, and 75-80% in the agonist binding sites. Therefore the design of a selective ligand is a challenging task.[1] We focused our attention on the binding mode of two among the highest D3 selective agonists known to date,[2,3] and, relying also on docking studies, we carried out the design of a new family of piperazine-based compounds.
By means of a modified Ugi-four-component reaction,[4] we could obtain a large library of potential D2/D3 receptor ligands, in which functional groups and chains length are diversified, in order to investigate the influence on binding and selectivity. The biological evaluation is currently underway.[5]



R^1 = MOM, H;
R^2 = Br, OCH_3;
R^3 = *i*Pr, Cy, *n*-Pr;
X = O, H_2;
n = 0, 1, 2.

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[5]In collaboration with Dr. Harald Huebner, Friedrich Alexander University, Erlangen, Germany.

FAR-O6

Identification of new potent TRPV1 ligands showing analgesic properties

Francesca Aiello [a], Antonella Brizzi [b], Anna Artese [c], Giosuè Costa [c],
Alessia Ligresti [d], Mariateresa Badolato [a], Stefano Alcaro [c],
Federico Corelli [b], Luciano De Petrocellis [d], Fedora Grande [a] ,
Antonio Garofalo [a], Vincenzo Di Marzo [d]

a Dipartimento di Farmacia e Scienze della Salute e della Nutrizione, Università della Calabria, 87036, Arcavacata di Rende (Cs), Italy
b Dipartimento di Biotecnologie, Chimica e Farmacia, Università degli Studi di Siena, Via A. Moro 2, 53100, Siena, Italy
c Endocannabinoid Research Group, Istituto di Chimica Biomolecolare, Consiglio Nazionale delle Ricerche, 80078, Pozzuoli (Na), Italy
d Dipartimento Scienze della Salute, Università degli Studi "Magna Græcia", Viale Europa, 88100, Catanzaro, Italy

francesca.aiello@unical.it

Chronic pain is a widely recognized unmet medical target and the research for new analgesic agents is being intensively investigated by the pharmaceutical industry. Among the Transient Receptor Potential (TRP) channels, the TRPV1 (subfamily Vanilloid, Type-1) is considered as a highly validated pain target being abundantly expressed in sensory neurons and also in higher brain structures involved during pain processing and neurogenic inflammatory response.[1,2] Responsible for binding the natural pungent principle of capsicum, the capsaicin, and activated by endogenous arachidonic acid-derived lipids called "Endovanilloids", this receptor plays an important role in several human pathological conditions, such as inflammatory, visceral, cancer and neuropathic pain. Considering some common structural features inside the very extensive chemical diversity of known agonists and antagonists, we have identified a new class of TRPV1 effective ligands, derived from a 4-(thiophen-2-yl)butanoic acid amide moiety, endowed with a significant agonist activity.

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FAR-O7

Natural-product-inspired modulators of Alzheimer's disease: focus on amyloid and oxidative stress

M. Rosini[a], *E. Simoni*[a], *C. Lanni*[b], *M. Bartolini*[a], *A. Pinto*[b], *J. Fiori*[a], *V. Andrisano*[c], *M. Racchi*[b], *A. Minarini*[a]

a Dipartimento di Farmacia e Biotecnologie, Università di Bologna, Via Belmeloro 6, 40126 Bologna, Italia; b Dipartimento di Scienze del Farmaco, Università di Pavia, Viale Taramelli 12, 27100 Pavia, Italia; c Dipartimento di Scienze per la Qualità della Vita, Università di Bologna, Corso D'Augusto 237, 47921 Rimini, Italia

michela.rosini@unibo.it

Alzheimer's disease (AD) is a multifactorial syndrome, with a complex interplay of genetic and biochemical factors contributing to the pathological decline. Besides diffuse neuronal loss, AD brain exhibits evidence of protein folding defects. There is considerable evidence that amyloid-β peptide (Aβ) might trigger the disease process, and an increasing number of molecular targets, that may play an important role in the expression of its neurotoxicity, is emerging. In particular, the etiopathogenic loop generated by Aβ and oxidative stress indicates ROS overproduction as a crucial partner of Aβ toxicity [1].

Natural products offer a great structural diversity, and have already proven to be a rich source of therapeutics. Curcumin is a natural polyphenol that modulates several AD pathways, including oxidative injuries and Aβ aggregation. The active principle of garlic diallyl disulfide is able to counteract oxidative stress through antioxidant enzyme expression. These structures inspired us to design new chemical entities carrying the cinnamoyl function of the former and the allyl mercaptan moiety of the latter. Interestingly, most of the synthesized hybrids demonstrated to be less toxic than curcumin in different cell lines. In addition, modifications of the aryl substitution pattern allowed to modulate the antioxidant profile, and identify the derivative bearing the catechol moiety as an intriguing anti-aggregating agent. Thus, we obtained promising pharmacologic tools, which offer the chance to gain insight into the AD cross-talk between Aβ and radical species.

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FAR-O8

Low molecular weight heparins: have they to be considered biological or chemical drugs?

Paola Minghetti, *Francesco Cilurzo, Umberto Musazzi, Silvia Franzé*

Dipartimento di Scienze Farmaceutiche, Università degli Studi di Milano, Via G. Colombo 71, 20131, Milano, Italia

paola.minghetti@unimi.it

Low molecular weight heparins (LMWHs) represent a class of compounds widely used in the prophylaxis of thrombosis in patients undergoing to surgical interventions. They are manufactured by chemical or enzymatic degradation of heparin, which is obtained by extraction from porcine gut. According to the depolymerisation method, LMWHs differ for composition, average Mw polydispersity index and some other physico-chemical properties. The expiration of protection rights gives the opportunity to the development of copies of the innovator's product. FDA classifies LMWHs chemicals and the copies are referred as generics; while EMA considers them as biological medicines and the copies are referred as biosimilars. As a consequence, EMA requires appropriate powered clinical trials to establish comparable efficacy and safety between copies and innovator product, while FDA requires only in human pharmacodynamic studies. The quality, efficacy and safety of LMWHs represent a hot topic continuously debated and in evolution as demonstrated by the continuous revision of the existing guidelines. Conceivably, taking into account the intrinsic variability of LMWHs obtained also by using the same depolymerization method and the objective current impossibility to fully characterize such compounds, a conservative approach should be desired as it guarantees a higher level of safeness for the patient's health. Reasonably, a reduction of the amount of clinical studies required by EMA, supported by a more specific chemical and analytical characterization, is the best direction to be pursued in order to semplify the introduction on the market of the biosimilar products of LMWHs assuring at the same time the efficacy and safety of these drugs.

FAR-O9

Carbon Nanostructures as Drug Delivery Platform

Tatiana Da Ros

Dipartimento di Scienze Chimiche e Farmaceutiche, Università degli Studi di Trieste,
Piazzale Europa 1, 34127, Trieste, Italy

daros@units.it

Carbon nanostructures (CNSs), in particular carbon nanotubes (CNTs), play an important role in the "Room at the Bottom". They are among the more promising nanomaterials in many different fields as molecular electronics or field-effect transistors, due to their uncommonly combined mechanical and electrical properties, but they are also emerging building blocks in nanomedicine as innovative materials for neuroscience, drug delivery, cancer therapy, and biomaterials.

The chemical functionalization is a fundamental step in this direction as it renders these novel chemical structures easier to handle and compatible with physiological media and the conjugation to biological active molecules allows the creation of efficient drug delivery systems.

Within this contribution, we will explore the use of CNSs as efficient scaffold for the delivery of oligonucleotides and the effect of their conjugation to antitumor drugs as doxorubicin.

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FAR-O10

Dextran hydrogel containing ANXA1 N-terminal derived peptide Ac2-26 as wound dressing

Felicetta De Cicco, Valentina Bizzarro, Raffaella Belvedere, Antonello Petrella, Fabrizio Dal Piaz, Rita P. Aquino, Pasquale Del Gaudio

[1]*Department of Pharmacy, University of Salerno, via Giovanni Paolo II, 132 - 84084 Fisciano (SA), Italy*

pdelgaudio@unisa.it

Wound healing is a dynamic ordered process involving a variety of cellular and matrix components that, in some cases, fails in various pathological conditions. ANXA1 has been involved in a broad range of molecular and cellular processes, and its N-terminal derived peptide Ac2-26 is able to activate all three human formyl peptide receptors, promoting calcium fluxes and cell migration, stimulating healing process. A number of wound dressing devices loaded with active pharmaceutical ingredients have been developed using different polymeric materials. Dextran hydrogels may combine most of the required properties for an ideal topical formulation (good exudate absorbance, easy application and removal). In the present study, we propose an Ac2-26 loaded hydrogel based either on high mannuronic (M) alginate or low molecular weight chitosan as local controlled drug release formulation with enhanced wound healing activity. Rheological studies have been conducted to set polymer concentrations enabling to promote exudate absorption as well as easy administration and retention of Ac2-26 loaded gels into wound cavity (zero shear viscosity ranging between 4.1 and 9.5 KPas). Release behaviour, directly correlated to peptide and polymeric concentration, resulted in positive burst effect in the first hours of administration followed by a prolonged release between 48 and 72h for the most effective formulations. Furthermore, in vivo mice wound model, demonstrated that the combination of Ac2-26 peptide and high M alginate hydrogel (1μM) significantly decreased wound surface area compared with saline solution and unloaded alginate treatment, with its complete closure after 14 days, indicating that combination of Ac2-26 peptide with alginate hydrogel could effectively improve wound healing processes.

FAR-O11

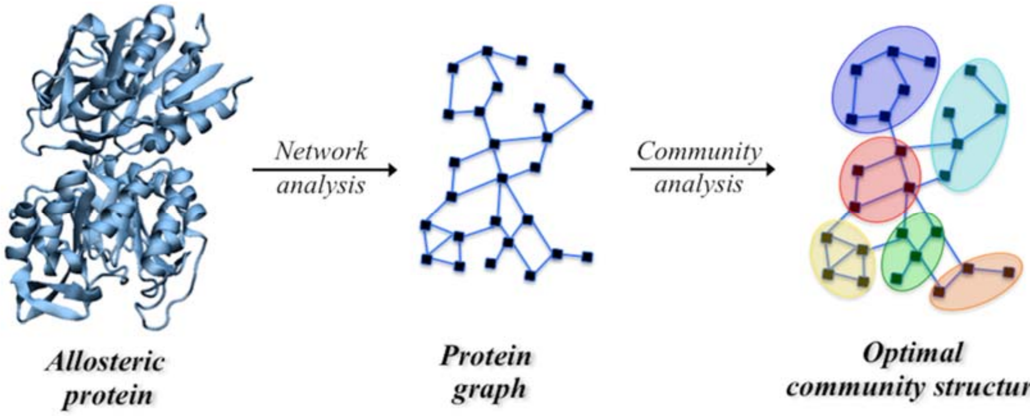
Community network analysis of protein dynamics: insights into allostery

Ivan Rivalta[a], Victor S. Batista[b]

a Laboratoire de Chimie, École Normale Supérieure de Lyon, Lyon, France.
b Department of Chemistry, Yale University, New Haven, USA

ivan.rivalta@ens-lyon.fr

Allosterism is an essential biological regulatory mechanism. In enzymes, allosteric regulation results in an activation or inhibition of catalytic turnover. The mechanisms by which this is accomplished are unclear and vary significantly depending on the enzyme. A metabolite binding to the enzyme at a site distant from the catalytic site is coupled with changes in structure, dynamics, or both at the active site. These interactions between the allosteric and active site involve complex conformational rearrangements of the protein secondary and tertiary structure. Interrogation of this complex biological phenomenon necessitates multiple experimental and theoretical approaches. In this talk, a computational approach based on molecular dynamics simulations and network models in combination with solution NMR spectroscopic is presented.[1, 2] The results uncover mechanistic aspects of allosteric signal propagation in the imidazole glycerol phosphate synthase (IGPS), a V-type allosteric enzyme.[3] The proposed allosteric pathway provides useful information for the design of new molecules that might hamper glutaminase activity in plant or human pathogens by interrupting the allosteric signal propagation of IGPS.



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FAR-O12

S-Trityl-(*R*)-cysteine, a Multipurpose Chiral Selector for Ligand-Exchange Liquid Chromatography Applications

Roccaldo Sardella, Federica Ianni, Antonella Lisanti, Stefania Scorzoni, Maura Marinozzi, and Benedetto Natalini

Dipartimento di Scienze Farmaceutiche, Università di Perugia, Via Fabretti 48, 06123 Perugia, Italy.

roccaldo.sardella@unipg.it

Several chelating species have been incorporated as chiral selectors in chiral ligand-exchange chromatography (CLEC) stationary phases. In this setting, we developed a coated chiral stationary phase (C-CSPs) with S-trityl-(*R*)-cysteine [(*R*)-STC] units adsorbed onto a conventional octadecylsilica (ODS) chain-based material. The stratification of 0.04-0.05 g of (*R*)-STC units onto the ODS chain carpet produces a very stable and effective C-CSP, with α and R_S values up to 5.71 and 12.09, respectively. Owing to its extraordinary performance, the (*R*)-STC-based CSP was successfully exploited also for preparative enantioisolations. As an example, up to 15.0 mg of racemic 1-aminoindane-1,5 dicarboxylic acid can be fully resolved into pure enantiomers with a single injection and in a quite limited run-time. With the use of the CLEC (*R*)-STC-based system and a Cu(II) nitrate containing eluent, the variation of the free (*R*)-Ala, (*R*)-Asp and (*R*)-Glu content in cheese samples of different ripening time was quantified, thus contributing to assess the impact of natural or artificial interventions on the product quality. An analogue method was used in the course of a multidisciplinary study focused on the assessment of the safety and efficacy of nitrogen organic fertilizers from animal-based protein hydrolysate, revealing that (*R*)-AAs are produced independently of the hydrolysis procedure employed.

Furthermore, molecular modelling-based classification analyses indicated that the electrotopological descriptor PPSA-1 is helpful to correctly rationalize the chromatographic process in the (*R*)-STC-based CLEC system.

FAR-O13

Multivariate curve resolution methodologies in stability drug studies

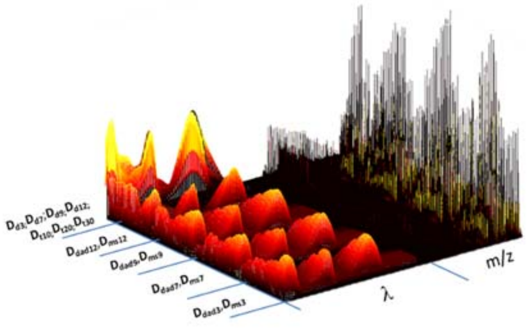
Michele De Luca[a], *Giuseppina Ioele*[a], *Romà Tauler*[b], *Gaetano Ragno*[a]

[a]*Department of Pharmacy, Health and Nutritional Sciences, University of Calabria, Rende (CS), Italy.*
[b]*Department of Environmental Chemistry, IDAEA-CSIC, Barcelona, Spain.*

michele.deluca@unical.it

In the last years, light has been recognized as one of the most important factors, together with heat and humidity, involved in drug degradation. The drug photostability studies are actually part of a general drug stability-monitoring program, which mostly consists of researching the causes of drug decomposition, determining the pathway of kinetic process and selecting the suitable tools able to reduce the degradation. The multivariate data analysis approach based on the use of the MCR–ALS methods, allowed the comprehensive study of the drug degradation processes [1-2]. The proposed strategy permitted the simultaneous analysis of multiple experimental data sets from different analytical techniques, including UV spectrophotometric and DAD/MS-chromatographic data sets, all together combined in hyper column- and row-wise augmented data sets.

Resolution of the wide data multiset was able to describe the kinetic drug photodegradation process of Amiloride, taking simultaneously in account the interaction of the light with others reaction systems, as acid-base equilibrium reactions [3]. This analytical procedure could be easily extended to the investigation of photodegradation and kinetic processes of several drugs and chemical compounds.



[1] M. De Luca, S. Mas, G. Ioele, F. Oliverio, G. Ragno, R. Tauler *Int. J. Pharm.* 2010, **386**, 99-10.
[2] M. De Luca, R. Tauler, F. Oliverio, G. Ragno *Drug Test Anal.* 2013, **5**, 96-102.
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FAR-O14

Contributo Ritirato

FAR-O15

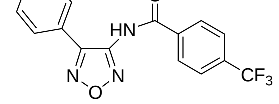
Sviluppo di MD77: nuovi derivati eterociclici inibenti STAT3

Arianna Gelain[a], *Federica Porta*[a], *Silvia Dell'Orto*[a], *Stefania Villa*[a], *Daniela Masciocchi*[a], *Daniela Barlocco*[a], *Fiorella Meneghetti*[a], *Nicola Ferri*[b], *Giulio Poli*[c], *Tiziano Tuccinardi*[c], *B-M Kwon*[d], *Akira Asai*[e]

a Dipartimento di Scienze Farmaceutiche, Università degli Studi di Milano, Via L. Mangiagalli 25, 20133 Milano, Italy
b Dipartimento di Scienze Farmacologiche e Biomolecolari, Università degli Studi di Milano, Via Balzaretti 9, 20133 Milano, Italy
c Dipartimento di Farmacia, Università di Pisa, Via Bonanno 6, 56126 Pisa, Italy
d Korea Research Institute of Bioscience & Biotechnology, Korea University of Science and Technology, Eoun-Dong, Yuseong-gu, Daejeon 305-860, Republic of Korea
e Center for Drug Discovery, Graduate School of Pharmaceutical Sciences, University of Shizuoka, 52-1 Yada, Suruga-ku, Shizuoka, 422-8526, Japan

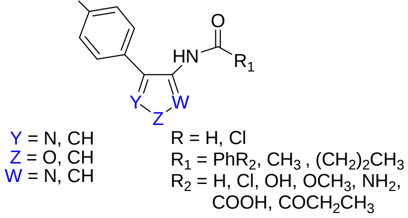
arianna.gelain@unimi.it

Le proteine STAT (Signal Transducers and Activators of Transcription) si trovano in forma latente nel citoplasma e vengono indirettamente attivate dall'interazione di citochine, fattori di crescita ed ormoni con la membrana cellulare. Mediano la traduzione dei segnali ed intervengono nella trascrizione genica, regolando diversi fenomeni tra cui la crescita e la sopravvivenza cellulare. In particolare poiché l'isoforma STAT3 risulta costitutivamente iperattivata in molte forme tumorali e la sua inibizione provoca l'apoptosi delle cellule malate ma ha effetti limitati sulle cellule sane, STAT3 rappresenta un promettente target per la terapia antitumorale. Durante le nostre ricerche [1,2], tuttora in corso, abbiamo sintetizzato il composto ossadiazolico **MD77** (**I**) dotato di una significativa attività inibente il dominio SH2 di STAT3 (IC_{50} =17,7 μM). Pertanto, al fine di determinare i requisiti strutturali essenziali per l'attività, abbiamo sviluppato una serie di nuovi composti correlabili a **MD77**. Le modifiche apportate hanno interessato sia l'anello ossadiazolico che le catene laterali presenti in posizione 3 e 4 di tale eterociclo (formula generale **II**). La sintesi, gli studi di molecular docking e la valutazione dell'attività inibente dei nuovi derivati verranno presentati.



MD77

(I)



(II)

[1] D-S Shin, D. Masciocchi, A. Gelain, S. Villa, D. Barlocco, F. Meneghetti, A. Pedretti, Y-M Han, D.C. Han, M.Y. Han, B-M Kwon, L. Legnani, L. Toma, *Med. Chem. Comm.,* 2010, **1**(2), 156-164.
[2] D. Masciocchi, S.Villa, F. Meneghetti, A. Pedretti, L. Legnani, L. Toma, B-M Kwon, S. Nakano, A. Asai, A. Gelain, *Med. Chem. Commun.*, 2012**,** **3**, 592-599**.**

FAR-O16

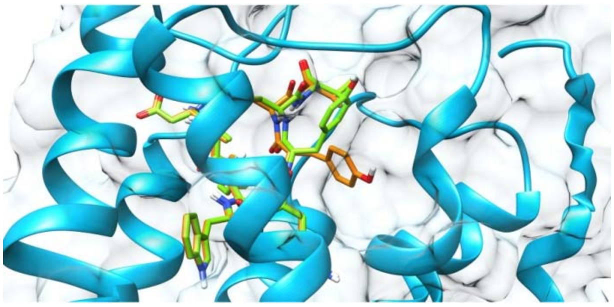
Urotensin-II and URP. What can we learn from ligand conformation?

Alfonso Carotenuto[a]

a Dipartimento di Farmacia, Università di Napoli "Federico II", Via Montesano 49, 80131, Napoli, Italy

alfonso.carotenuto@unina.it

The urotensin II receptor (UT) has long been studied mainly for its involvement in the cardiovascular homeostasis in either health or disease state [1]. The biological activities associated with UT activation are modulated by two endogenous ligands, i.e. urotensin II (UII) and urotensin II-related peptide (URP). Extensive expression of the two ligands revealed the multiple pathophysiological effects mediated by the urotensin system such as cardiovascular disorders (heart failure, cardiac remodelling, hypertension), smooth muscle cell proliferation, renal disease, diabetes, and tumour growth [1]. As recently demonstrated, UII and URP could exert different actions on transcriptional activity, cell proliferation, and myocardial contractile activities supporting the idea that UII and URP interact with UT in a distinct manner (biased agonism) [2]. We have developed a number of UII analogs, among which a superagonist named P5U and an antagonist named urantide [3]. Conformational studies, mainly by solution NMR, on novel developed UII analogs and URP reveal detailed information on the bound structure of agonists and antagonists at UT and can help to elucidate the different activation mechanisms of URP and UII.



[1] H. Vaudry, et al. *Ann. N. Y. Acad. Sci.*, 2010, **200**, 53-66.
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FAR-O17

Identification of a new benzoindol-2-one derivative as a potential modulator of p53 pathway in cancer cells

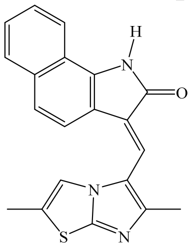
A. Graziadio[a]*, A. Locatelli*[a]*, A. Leoni*[a]*, R. Morigi*[a]*, M. Rambaldi*[a]*,*
C. Cappadone[a]*, L. Merolle*[a]*, A. Sargenti*[a]

a Dipartimento di Farmacia e Biotecnologie, FaBiT – Università di Bologna,
Via Belmeloro 6, 40126, Bologna, Italy

alessandra.graziadi3@unibo.it

“Guardian of the genome”, “Death star”, “Good cop/ bad cop”, “An acrobat in tumorigenesis” are just a few of the names that have been attributed to the p53 gene over recent years. When the first alterations of the p53 gene in human cancers were discovered, p53 started to become really popular, with the title of “molecule of the year**”** attributed by Science, in 1993.[1] This title was certainly justified, as the observation that more than one half of human cancers expressed a mutant p53. The high rate of genetic alterations in human cancers underlines the important cellular function of p53, a tumor suppressor protein that affects a signal transduction pathway leading to cell cycle arrest, apoptosis, or senescence.

In this communication we wish to describe the activity profile of compound NSC 743420 on cancer cell lines that differ in their p53 status.



NSC 743420

This derivative emerged as a new lead from a small library of Knoevenagel adducts, that were synthesized by reacting benzoindolones with imidazothiazole aldehydes properly substituted.[2] This compound showed an antiproliferative activity in the preliminary screening in the NCI 60 cell panel, with mean GI_{50} value of 0.21 µM.

In order to achieve an explanation on its activity, the compound was examined for its effect on the growth of three tumor cell lines: HT-29 colon adenocarcinoma, having a mutant p53, MCF-7 breast cancer and U2-OS osteosarcoma, having wild-type p53. The data of these biological assays suggest that the mechanism of action of the compound is not exclusive, but it involves p53-dependent and p53-independent molecular targets. The obtained results open new perspectives for the development of analogues with improved and more selective activity profiles. Also the synthesis of analogues of NSC 743420 will be discussed.

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FAR-O18

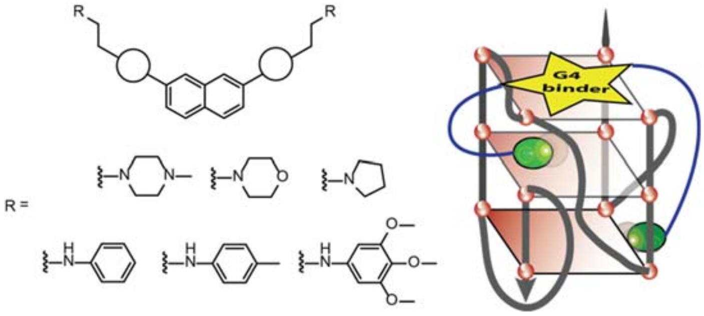
Double chained naphthalenes as G4 binders

Alessio Terenzi, Roberta Bartolotta, Carla Gentile, Annamaria Martorana,
Giampaolo Barone, Anna Maria Almerico, Antonino Lauria

Dipartimento di Scienze e Tecnologie Biologiche Chimiche e Farmaceutiche (STEBICEF),
Università di Palermo, Via Archirafi n. 32 , 90123, Palermo, Italia

alessio.terenzi@unipa.it

The interest in G-quadruplexes (G4) as key targets for novel and selective anticancer drugs is exponentially growing due to their involvement in cellular carcinogenic pathways. In particular, their presence in promoter regions of a number of oncogenes with functions in transcriptional regulation is a recent discovery with ground-breaking potential in biology and medicine [1, 2].



In this framework, our research efforts aim to design and develop binders to specific G-rich sequences in oncogenes promoters to modulate their expression. The first approached target was the human proto-oncogene c-Kit, which presents a G4 sequence (c-Kit1) with a large irregular cleft, not present in any other G4s. Computation was used to drive synthetic work, employing large databases of heterocyclic molecules and G4 isoforms as templates in the molecular modeling strategies. The designed binders herein depicted present a π-delocalized system able to stack at the top/end of the G4 and side arms able to fit specific binding pockets. These two fragments are connected by a suitable linker. The selectivity of the synthesized binders is assessed by competitive binding experiment with other G4s from telomeric and gene promoter sequences, mainly using spectroscopic techniques.

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FAR-O19

Purinergic P2X Receptors: Homology Models and Analysis of Receptor-Ligand Interaction

Diego Dal Ben

School of Pharmacy, Medicinal Chemistry Unit, University of Camerino, Via S. Agostino 1,
62032 Camerino, Italy

diego.dalben@unicam.it

The purinergic P2X receptors are ligand-gated cation channels activated by the endogenous ligand ATP and assembled as homo- or heterotrimers from seven cloned subtypes (P2X1-7). All trimer subunits share a common topology consisting in intracellular N- and C- termini, two transmembrane domains and a large extracellular domain. P2X receptors are present in virtually all mammalian tissues and regulate a large variety of responses. The development of ligands that modulate the activity of P2X receptors represents a promising strategy to obtain novel pharmacological tools for the treatment of pain, cancer, inflammation, and neurological, cardiovascular, and endocrine diseases [1]. The publication of the crystal structures of P2X4 receptor in *apo* and *ATP-bound* forms represents a key step for the analysis of the receptor structure, the interpretation of mutagenesis data, and the depiction of ligand binding and receptor activation mechanism [2,3]. In addition, the availability of ATP-competitive and selective P2X receptor ligands provides useful information for the design of new potent and selective ligands with possibly suitable pharmacokinetic profiles, with the final aim to obtain new drugs. Molecular modeling studies were performed to develop structural models of the human and rat P2X receptors in *apo* and *ATP-bound* forms. These models allowed to analyse the role of some non-conserved residues at ATP binding site and to study the receptor interaction with some non-specific or subtype selective agonists and antagonists [4].

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[2] T. Kawate, J.C. Michel, W.T. Birdsong and E. Gouaux *Nature*, 2009, **460**, 592-598.
[3] M. Hattori and E. Gouaux *Nature*, 2012, **485**, 207-212.
[4] D. Dal Ben, *submitted.*

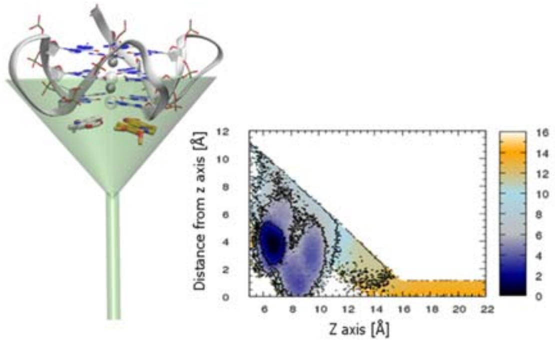
FAR-O20

DNA G-quadruplex binding of a naturally occurring antitumor agent investigated by Funnel Metadynamics

Federica Moraca[a], *Vittorio Limongelli*[b], *Stefano Alcaro*[a], *Francesco Ortuso*[a], *Anna Artese*[a] *and Michele Parrinello*[c]

a Dipartimento di Scienze della Salute, Università "Magna Græcia"di Catanzaro, Viale Europa , 88100, Catanzaro, Italia.
b Dipartimento di Farmacia, Università "Federico II" di Napoli,
via D. Montesano, 80131, Napoli, Italia.
c Dipartimento di Chimica Applicata e Bioscienze, Scienze Computazionali, ETH di Zurigo, USI Campus, via Giuseppe Buffi, 6900, Lugano, Svizzera.

fmoraca@unicz.it



An accurate estimation of the drug affinity to its target is of great help in a drug discovery strategy. Unfortunately, traditional computational methods, such as molecular dynamics (MD), are not able to investigate long time-scale events such as ligand/protein docking-undocking process, due to high energetic barriers. In this case, the use of enhanced sampling methods like Metadynamics is compulsory. In this study we present the application of the new formalism called Funnel Metadynamics [1] on a G-quadruplex/Berberine complex [2] to shed light on the binding mechanism of such ligand. Using this technique, we have been able to reconstruct the ligand binding free-energy surface (FES), identify an alternative binding mode of Berberine to G-quadruplex and also to elucidate the solvent role. Moreover the calculation of the absolute binding free energy resulted in agreement with experimental data [3].

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[3] Arora, A., Balasubramanian, C.; Kumar, N. *et al.* FEBS J., 2008, **275**, 3971-83.

FAR-O21

Combretastatine: aspetti metabolici e farmacologici

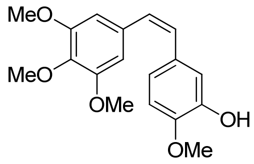
Silvio Aprile[a], *Erika del Grosso*[a], *Giorgio Grosa*[a]

a Dipartimento di Scienze del Farmaco - Università del Piemonte Orientale
"A. Avogadro"- Largo Donegani 2, 28100, Novara, Italy

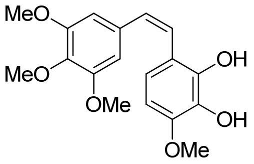
silvio.aprile@unipmn.it

Le combretastatine sono composti naturali a struttura stilbenica estratte dall'arbusto africano *Combretum caffrum* e dotate di proprietà antitumorali. Il loro meccanismo d'azione si esplica inducendo l'arresto irreversibile del proliferare della neoformata vascolarizzazione tumorale lasciando intatta la vascolarizzazione normale. Tale meccanismo prevede l'interazione delle combretastatine a livello della subunità β della tubulina con conseguente inibizione della polimerizzazione dei microtubuli. Ad oggi due combretastatine sono in fase clinica: CA-4 e CA-1 entrambe come prodrug fosfato. La CA-4 si trova in fase 3 nel trattamento del carcinoma anaplastico alla tiroide (ATC) in associazione a carboplatino e paclitaxel mentre la CA-1 è in fase1 nel trattamento della leucemia mielogena acuta refrattaria (AML) e nella sindrome mielodisplastica (MDS). La CA-1 esplica il proprio meccanismo d'azione anche attraverso la formazione di un metabolita orto-chinonico altamente reattivo il quale si è dimostrato, in fase preclinica, avere attività antitumorale.

L'attività di ricerca, si è focalizzata sullo studio *in vitro* (per mezzo di frazione epatiche subcellulari di ratto ed umane) ed *in vivo* (su ratti) del destino metabolico sia della CA-4 che della CA-1 con particolare riferimento alla caratterizzazione delle specie chinoniche generate tramite attivazione metabolica. Lo stesso approccio è stato applicato allo studio di analoghi rigidi combretastatinici sintetizzati dallo stesso gruppo di ricerca ed in collaborazione con altri gruppi. Tali derivati hanno la proprietà di non subire isomerizzazione a livello del ponte olefinico con conseguente perdita di attività. Le specie orto e para chinoniche identificate sono state valutate in funzione della loro attività antitubulinica e citotossica. E' in fase di studio l'interazione chimica tra metaboliti chinonici delle combretastatine e tubulina al fine di comprenderne a fondo il loro ruolo nel profilo farmacodinamico. Infine, si è valutata l'attività dei sistemi enzimatici riduttivi coinvolti nella riduzione delle specie chinoniche a idrochinoni.



CA-4 (Zybrestat ®)



CA-1 (OXi4503)

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[2] Theeramunkong S, Caldarelli A, Massarotti A, Aprile S, Caprioglio D, Zaninetti R, Teruggi A, Pirali T, Grosa G, Tron GC, and Genazzani AA. *J. Med. Chem.* 2011, **54**, 4977-86.

FAR-O22

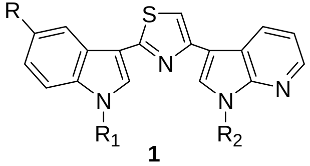
Synthesis of Nortopsentin analogues

Gloria Di Vita

Dipartimento di Scienze e Tecnologie Biologiche Chimiche e Farmaceutiche, Università degli Studi di Palermo, Via Archirafi 32, 90123 Palermo, Italy.

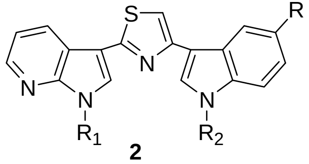
gloria.divita@unipa.it

Nortopsentins A-C, having a characteristic 2,4-bis(3'-indolyl)imidazole skeleton, showed *in vitro* cytotoxicity against P388 cells (IC_{50} values: 4.5-20.7 μM).[1] Due to the considerable biological activities shown, different analogues of nortopsentins have been reported, in which the imidazole ring of the natural compound has been replaced by other five-membered heteroclycles such as pyrazole, furan, pyrrole, thiophene, isoxazole and thiazole, and in the thiazole series also an indole ring has been substituted with an azaindole one.[2] In particular some analogues with a 7-azaindole moiety (**1**) showed antiproliferative activity against a wide spectrum of human tumor cell lines with IC_{50} at micro- to submicromolar range. They significantly reduced the growth of two experimental models of DMPM; inhibited CDK1 activity and consequently induced a marked cell cycle arrest at G_2/M compartment and showed a synergistic cytotoxic effect with paclitaxel. In our effort to search for novel antitumor compound, we synthesized 3-[4-(1*H*-indol-3-yl)-1,3-thiazol-2-yl]-1*H*-pyrrolo[*2,3-b*]pyridine (**2**), analogues in which the spacer is constituted by the thiazole ring and the indole and 7-azaindole, respectively in position 2 and 5, have been reverse (**2**). We also synthetized 7-chloro-3-[2-(1*H*-indol-3-yl)-1,3-thiazol-4-yl]-1*H*-pyrrolo[*2,3-c*]pyridine, in which one of the indole unit is replaced by a 6-azaindole moiety (**3**). All thiazole derivatives (**2**) and (**3**) will be proposed to the NCI to investigate their antitumor activity on a panel of about 60 human cancer cell lines derived from nine human cancer cell types. The biological results will be discussed.



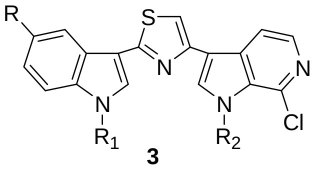
1

R= H, F, Me, OMe, F, Cl, Br
R_1= H, Me, Boc
R_2= H, Me



2

R= H, F
R_1= H, Me
R_2= H, Me, SO_2-Ph-Me



3

R= H, F, Br, OMe
R_1= H, Me, Boc
R_2= H, Me

[1] M. Alvarez, M. Salas, *Heterocycles*, 1991, **32**, 1391-1429.
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FAR-O23

Cannabinoid Receptor Ligands from Alkylresorcinols: A Structure-Affinity Relationship Study

A. Brizzi[a], F. Aiello[b], A. Ligresti[c], M. G. Cascio[d], L. Luongo[e], P. Marini[d], S. Maione[e], D. Cerretani[f], M. Elodia[g], P. P. Correale[g], R. G. Pertwee[d], F. Corelli[a], V. Di Marzo[c]

[a]Dipartimento di Biotecnologie, Chimica e Farmacia, Università degli Studi di Siena, Via A. Moro 2, 53100 Siena, Italia
[b]Dipartimento di Farmacia e Scienze della Salute e della Nutrizione, Università della Calabria, 87036, Arcavacata di Rende, Cosenza, Italia
[c]Endocannabinoid Research Group, Istituto di Chimica Biomolecolare, Consiglio Nazionale delle Ricerche, 80078, Pozzuoli, Napoli, Italia
[d]Institute of Medical Sciences, University of Aberdeen, Scotland, UK
[e]Dipartimento di Medicina Sperimentale, Sezione di Farmacologia "L. Donatelli", Seconda Università di Napoli, Via Costantinopoli 16, 80138 Napoli, Italia
[f]Dipartimento di Medicina, Chirurgia e Neuroscienze, Unità di Farmacologia, Università degli Studi di Siena, Via A. Moro 2, 53100 Siena, Italia
[g]Dipartimento di Oncologia, Unità di Radioterapia e Oncologia Medica, Università degli Studi di Siena, Via A. Moro 2, 53100 Siena, Italia

antonella.brizzi@unisi.it

Plant-derived phenolic compounds were suggested to participate in such benefits on human health and they are reported to occur not only in many higher plant families but also in some bacteria and fungi. One of these, olivetol, or 5-pentylresorcinol, is involved in the biogenesis of THC and CBD in Cannabis, two phytocannabinoids displaying several pharmacological effects, and it has been selected as the basic aromatic scaffold to design and synthesized a new class of stable and potent cannabinoid receptor ligands [1]. Moreover, the functional agonist/antagonist profile, the antinociceptive activity [2-4] and the antiproliferative effect in HT29 colon cancer cell line of the most interesting compounds have been evaluated.

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[2] A. Brizzi, M.G. Cascio, V. Brizzi et al. *Bioorg. Med. Chem.*, **2007**, 15, 5406-5416.
[3] A. Brizzi, V. Brizzi, M.G. Cascio et al. *J. Med. Chem.*, **2009**, 52, 2506-2514.
[4] A. Brizzi, M.G. Cascio, M. Frosini et al. *J. Med. Chem.*, **2011**, 54, 8278-8288.

FAR-O24

Discovery and preclinical evaluation of a pyrroloquinoxaline based broad-spectrum anticancer agent

Fedora Grande [a], *Francesca Aiello* [a], *Antonio Garofalo* [a], *Nouri Neamati* [b]

a Dipartimento di Farmacia e Scienze della Salute e della Nutrizione, Università della Calabria, Edificio Polifunzionale, 87036 - Arcavacata di Rende (Cs)
b Department of Medicinal Chemistry, College of Pharmacy, University of Michigan, North Campus Research Complex, 2800 Plymouth Road, Ann Arbor, MI 48109-2800, USA.

fedora.grande@unical.it

During the last decade, we have designed and synthesized several compounds endowed with cytotoxic properties. Among those compounds, a series of pyrroloquinoxaline derivatives, showing desirable drug-like properties and promising anticancer activity, have been identified.[3] Some of the synthesized compounds showed an interesting profile at sub-micromolar concentrations *in vitro* assays in a wide panel of tumor cell lines. In particular, one of the most active compounds (SC144) has been selected for an in depth biological investigation. An excellent *in vivo* anti-cancer efficacy was ascertained for such a derivative by studies on xenograft mice, while flow cytometry studies indicated its capability to arrest cell cycle progression at the G_0/G_1 phase. Further mechanistic investigation revealed that our compound is able to induce reactive oxygen species by inhibition of Mn-SOD. The compound showed a synergistic effect when used in combination with several conventional cytotoxic agents. SC144 was also shown able to up-regulate MDA-7/IL-24 in colon cancer cells and also to induce gp130 phosphorylation-deglycosylation in ovarian cancer. The therapeutic potential of this compound was supported by its oral bioavailability assessed in a mouse model of human ovarian cancer, in which tumor growth was suppressed without significant evidence of toxicity. SC144 has been recently marketed, for research purposes only.

[1] F. Grande, R. Yamada, X. Cao, F. Aiello, A. Garofalo, N. Neamati *Expert Opin. Inv. Drug*, 2009, **18**, 555-568.
[2] S. Xu, F. Grande, A. Garofalo, N. Neamati *Mol. Cancer Ther*. 2013, **12**, 937-949.

FAR-O25

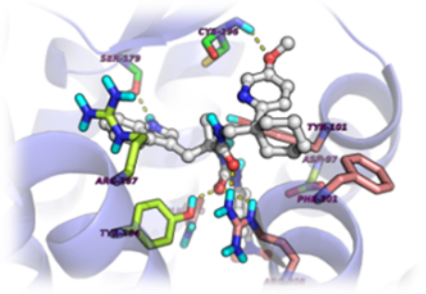
Structural determinants in the binding of BB2 receptor ligands: *in silico* and spectroscopic studies on PD176252 analogues

Antonio Carrieri[a], *Danilo Belviso*[b], *Rocco Caliandro*[b], *Enza Lacivita*[a], *Mariagrazia Perrone*[a], *Annamaria Galetta*[a], *Piero Mastrorilli*[c], *Vito Gallo*[c], *Marcello Leopoldo*[a]

[a] *Dipartimento di Farmacia-Scienze del Farmaco, Università degli Studi di Bari "Aldo Moro", Via Orabona 4, 70125, Bari, Italy*
[b] *CNR – Istituto di Cristallografia, Via Amendola 122/o, 70125, Bari, Italy*
[c] *Dipartimento di Ingegneria Civile, Ambientale, del Territorio, Edile e di Chimica, Politecnico di Bari, Via Orabona 4, 70125, Bari, Italy*

antonio.carrieri@uniba.it

The mammalian bombesin receptor family comprises three G protein-coupled receptors: the neuromedin B receptor, the gastrin-releasing peptide receptor (BB2), and the bombesin receptor subtype 3 [1]. BB2 receptor plays a role in gastrointestinal functions; however, at present the role of this subtype in normal physiology and pathological conditions is unknown due in large part to lack of specific binders for all subclasses of bombesin receptors. Here we present a study focused on the properties of the peptoid bombesin antagonist called PD176252 [2], and other structurally related analogues aiming at elucidating the causes of their different affinity towards the BB2 receptor. By means of computational techniques, based on QSAR, docking and homology building, supported by experimental data (X-Ray diffraction and NOESY-NMR) fresh insights into the binding to this class of biological target were achieved.



[1] R.T. Jensen, J.F. Battey, E.R. Spindel, R.V. Benya *Pharmacol. Rev.*, 2008, **60**, 1-42.
[2] V. Ashwood, V. Brownhill, M. Higginbottom, D.C. Horwell, J. Hughes, R.A. Lewthwaite, A.T. McKnight, R.D. Pinnock, M.C. Pritchard, N. Suman-Chauhan, C. Webb, S.C. Williams *Bioorg. Med. Chem. Lett.* 1998, **8**, 2589-259

FAR-O26

3-Aroyl-1-arylpyrroles as New Anticancer Agents

La Regina G.[a], Coluccia A.[a], Passacantilli S.[a], Famiglini V.[a], Pelliccia S.[b], Hamel E.[c], Novellino E.[b], Silvestri R.[a]

a Istituto Pasteur - Fondazione Cenci Bolognetti, Dipartimento di Chimica e Tecnologie del Farmaco, Sapienza Università di Roma, Rome, IT
b Dipartimento di Farmacia, Università di Napoli Federico II, Naples, IT
c National Cancer Institute, Frederick, USA

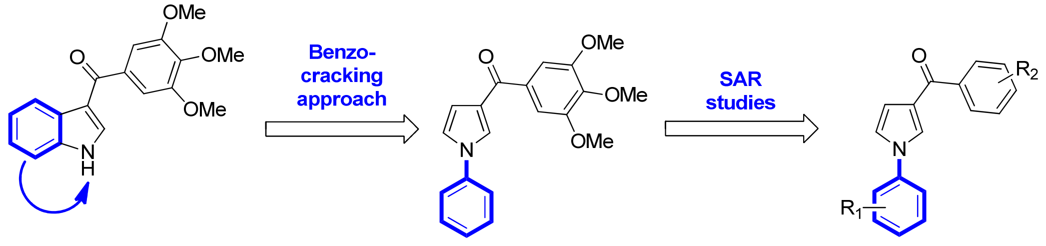
giuseppe.laregina@uniroma1.it

We developed 3-aroyl-1-arylpyrroles (ARAPs) as a new class of tubulin polymerization inhibitors. Starting from previuolsly reported arylthioindole and aroylindole antimitotic agents [1], new compounds was designed via benzocracking approach by shifting of the indole benzene ring to position 1 of the pyrrole nucleus (Chart 1).

New derivatives were prepared by microwave-assisted reaction of the appropriate pyrrole derivative with the right benzoyl chloride in the presence of $AlCl_3$ in 1,2-dichloroethane at 110 °C (150 W) for 2 min.

ARAPs exhibited a potent inhibiton of tubulin assembly and growth of a panel of cancer cells, by binding the colchicine site of tubulin. In particular, (1-(3-aminophenyl)-1*H*-pyrrol-3-yl)(3,4,5-trimethoxyphenyl)-methanone showed strong inhibition of the Pgp-overexpressing NCI-ADR-RES and Messa/Dx5 MDR cell lines and suppressed *in vitro* the Hedgehog molecular signalling pathway.

Chart 1. Design of 3-aroyl-1-arylpyrroles



R_1 = H, Me, alogen, NO_2, NH_2, NH_2 derivative, OH, O-alkyl as single or double substitutions; R_2 = H, 3,4,5-OMe_3.

[1] La Regina, G. et al.: (a) J.Med.Chem., 2004, **47**, 6120-6123. (b) J.Med.Chem., 2006, **49**, 947-954. (c) J.Med.Chem., 2007, **50**, 2865-2874. (d) J.Med.Chem., 2009, **52**, 7512-7527. (e) J.Med.Chem., 2011, **54**, 8394-8406. (f) J.Med.Chem., 2013, **56**, 123-149.

Chimica Farmaceutica

Poster

FAR-P1

An innovative formulation for topical drug delivery: preparation and characterization of gel-embedded vesicles

T. Coviello[1], A.M. Trotta[1], C. Marianecci[1], M. Carafa[1], L. Di Marzio[2], F. Rinaldi[1], C. Di Meo[1], P. Matricardi[1], F. Alhaique[1]

[1]Dipartimento di Chimica e Tecnologie del Farmaco, "Sapienza", Università di Roma,
P.le A. Moro 5, 00185, Roma, Italy
[2]Dipartimento di Farmacia, Università di Chieti "G. D'Annunzio", Via dei Vestini 31, 66100,
Chieti, Italy

franco.alhaique@uniroma1.it

The major disadvantage of transdermal and dermal drug delivery is the poor penetration of most compounds across human skin. One of the possible approaches to achieve increased skin penetration of drugs is based on the use of vesicular systems, such as liposomes and niosomes. Following previous researches (1), some innovative formulations, based on physical gels, prepared with two polysaccharides, Xanthan and Locust Bean Gum gels, loaded with non-ionic surfactant vesicles (niosomes), are described. The vesicles, composed by Tween20 and cholesterol or by Tween 85 and Span 20, were loaded with ammonium glycyrrhizate (AG), which shows anti-inflammatory activity (2). The new systems were characterized by rheological and dynamo-mechanical measurements. The addition of the the vesicles did not significantly perturb the polymeric network. The new formulations showed mechanical properties comparable with those of the commercial product indicating their suitability for topical applications. Extrusion test were also carried out. *In vitro* release experiments evidenced that the polysaccharide network protects the integrity of the vesicles and leads to their slow release. Finally, shelf live experiments for the evaluation of the gel/vesicle formulation were performed.

From the obtained results, it can be concluded that the main positive performances detected with the novel formulation can be summarized as follows:

- the niosome-embedded AG formulations modulate the diffusion of the drug;
- the injectability tests of the novel formulations showed that the extrusion forces were similar to those recorded for a commercial preparation;
- the analysed gels can be considered stable and suitable for topical applications also after a period of one year, with no need to add any kind of preservative.

(1) C. Marianecci et al., J. Pharm. Pharmaceut. Sci. **14**, 336-346 (2011)
(2) D. Paolino et al., J. Controlled Rel. **106**, 99-110 (2005).

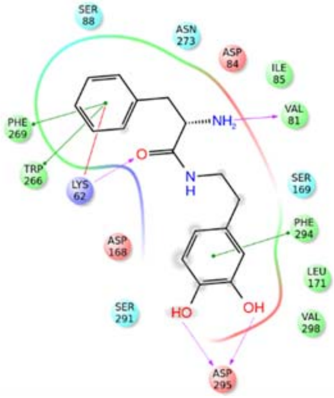
FAR-P2

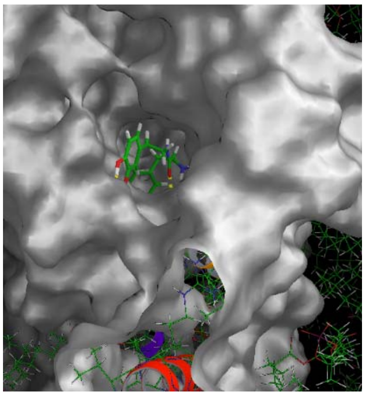
DA-Phen, a new dopamine aminoacid conjugate: *in vivo* testing and molecular modeling as dopaminergic modulator

Marco Tutone[a], *Anna Maria Almerico*[a], *Antonino Lauria*[a], *Flavia Maria Sutera*[b], *Carla Cannizzaro*[c], *Libero Italo Giannola*[a], *Viviana De Caro*[a]

[a]*Dipartimento di Scienze e Tecnologie Biologiche Chimiche e Farmaceutiche,*
Università di Palermo, Via Archirafi 32, 90123, Palermo, Italy
[b]*Dipartimento di Biomedicina Sperimentale e Neuroscienze Cliniche,*
Università di Palermo, Via del Vespro, 90127, Palermo, Italy
[c]*Dipartimento di Scienze per la Promozione della Salute e Materno Infantile*
"G.D'Alessandro", Università di Palermo, Via del Vespro 133, 90127 Palermo, Italy

annamaria.almerico@unipa.it





DA-Phen [1] was designed as potential dopaminergic active, depressive like-behavior. Spatial learning and memory assessment protocols (Forced Swim Test and Morris Water Maze) were used in order to investigate the *in vivo* potential behavioral pattern of DA-Phen on male Wistar rats. Our results strengthen the hypothesis that DA-Phen could induce adaptive responses to environmental challenges, probably due to the modulation of dopaminergic neurotransmission.

Homology modeling of GPCR D1 dopamine receptor was performed. The model, validated by means Ramachandran plot and q-mean score, was thereafter inserted in a double layer membrane. The surfaces of the binding pocket were mapped and used to perform a validated protocol of induced fit docking [2] with the aim to confirm the results obtained from the behavioral tests. DA-Phen showed docking capability higher than other known D1 agonists.

[1] Giannola L.I. *et al.*, *Pharmazie*, 2008, **63**, 704−710.
[2] Almerico A. M. *et al.*, *J. Mol. Mod*, 2012, **18**, 2885-289.

FAR-P3

Fragment deconstruction study and human thrombin-bound crystal structures of new β-D-glucose-containing anticoagulants

Cosimo D. Altomare [a], *Modesto de Candia* [a], *Giorgia Zaetta* [a], *Benny D. Belviso* [b], *Rocco Caliandro* [b]

[a] *Dipartimento di Farmacia – Scienze del Farmaco, Università degli Stdi di Bari "Aldo Moro", Via E. Orabona 4, 70125 Bari, Italy*
[b] *Istituto di Cristallografia, Consiglio Nazionale delle Ricerche, Via Amendola 122/o, 70126 Bari, Italy*

cosimodamiano.altomare@uniba.it

We recently synthesized novel glucose-conjugated dual factor Xa (fXa) and thrombin (fIIa) inhibitors, bearing 5-chlorothien-2-yl and 1-isopropylpiperidine moieties as binders of the S1 and S3/S4 enzymes' pockets, respectively, which showed potential for use in the treatment of thrombotic diseases. In particular, the β-D-glucosyl-bearing derivative proved to be a competitive inhibitor with high potency against fXa (K_i = 0.09 nM) and fIIa (K_i = 100 nM), and in vitro/ex vivo micromolar anticoagulant potency. Despite the narrower binding site groove of fIIa, the inhibitory potency of the glucosyl derivative, compared to the parent glucosyl-lacking compound, increases against fIIa (110-fold) much more than against fXa (7-fold).

Experimental deconstruction of the most potent inhibitor molecule into smaller fragments, synthesized and tested, provided us with significant insights into the enzymes' affinity contributions of the P1 and P3/P4 moieties, and a C3-alkyl-linked β-D-glucose fragment (P_G). Interestingly, our fragment deconstruction study revealed a positive cooperativity (i.e., ΔG superadditivity) of the P3/P4 and P_G fragments in both fIIa and fXa, but this effect proved to be stronger in fIIa (15.5 $kJ \cdot mol^{-1}$) than in fXa (2.8 $kJ \cdot mol^{-1}$). To understand the inhibitors' binding modes to fIIa, the crystal structures of human thrombin in complex with two glucose-based compounds were solved (pdb codes: 4NZE and 4N3L), and the crystallographic results will be presented and discussed.

[1] G. Lopopolo, M. de Candia, C. Altomare *et al. ChemMedChem* 2012, **7**, 1669-1677.

FAR-P4

Design and synthesis of CXCR4 antagonists with anti-proliferative activity

Mariateresa Badolato [a], *Francesca Aiello* [a], *Fedora Grande* [a],
Ines Barone [a], *Andrea Brancale* [b], *Stefania Catalano* [a],
Antonio Garofalo [a], *Sebastiano Andò* [a]

[a] *Dipartimento di Farmacia e Scienze della Salute e della Nutrizione, Università della Calabria, Edificio Polifunzionale, 87036 - Arcavacata di Rende (Cs), Italy*
[b] *School of Pharmacy and Pharmaceutical Sciences, Cardiff University, King Edward VII Avenue, Cardiff, CF10 3NB, UK*

mary.badolato@libero.it

CXC-chemokine receptor 4 (CXCR4) is involved in a number of physiological and pathological pathways thus representing one of the most promising target for the development of innovative therapeutic agents with a broad-spectrum of activity. In particular, a crucial role for this receptor has been hypothesized during cancer growth and progression. At data, numerous non-peptides compounds, belonging to various *N*-containing heterocyclic classes, have been shown to significantly inhibit CXCR4.[1,2] Among the chemical scaffolds identified, a very interesting class of active compounds is represented by indole derivatives, since molecular modeling experiments showed that this nucleus meets the spatial requirements for interaction with the three key residues identified in the pharmacophoric model. Herein we report the design and the synthesis of new series of indole based compounds, such as *N*-indolbenzohydrazides and 5*H*-indole[1,2-*a*][3,1]benzoxazin-5-one hydrazine derivatives, showing affinity toward the receptor. The new molecules will be subjected to various *in vitro* tests, in order to assess their capability to antagonize the effects of the CXCR4 ligand SDF-1 on anchorage-dependent breast cancer cell proliferation.

[1] F. Grande, A. Garofalo, N. Neamati *Curr Pharm Des*, 2008, **14**, 385-404.
[2] B. Debnath, S. Xu, F. Grande, A. Garofalo, N. Neamati *Theranostics*, 2013, **3**, 47-75.

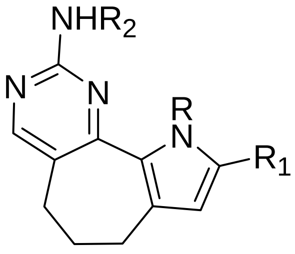
FAR-P5

Synthesis and biological evaluation of pyrrolo[3',2':6,7]cyclohepta[1,2-*d*]pyrimidin-2-amines

D. Giallombardo[a], *V. Spanò*[a], *A. Montalbano*[a], *A. Carbone*[a], *B. Parrino*[a], *P. Diana*[a], *G. Cirrincione*[a], *M. Nadai*[b], *S. N. Richter* [b], *P. Barraja*[a]

[a] *Dipartimento di Scienze e Tecnologie Biologiche Chimiche e Farmaceutiche Università degli Studi di Palermo, Via Archirafi 32, 90123 Palermo (Italy)*
[b] *Dipartimento di Medicina Molecolare, Università di Padova, Via Gabelli 63, 35121 Padova (Italy)*

paola.barraja@unipa.it



1

The photodynamic therapy (PDT) is an interesting therapeutic option for the treatment of tumors. [1] It requires systemic administration of a photosensitizing agent (PS), followed by irradiation of the tumor with light of the proper wavelength. Up to date studies are focused on the development of powerful photosensitizers that more specifically target cancer cells. [2] In consideration of the great interest in the pyrimidine nucleus, being the scaffold of many antitumor drugs, we studied in the last years pyrrolopyrimidine systems which showed promising antitumor properties either in the dark and under light irradiation. [3,4] Here we present, the synthesis of pyrrolo[3',2':6,7]cyclohepta[1,2-*d*]pyrimidin-2-amines of type **1** which were conveniently prepared by us using a versatile synthetic pathway.

The biological effect of these compounds was evaluated in tumoral cells, where the compounds displayed cytotoxicity in the micromolar range and photocytotoxicity in the nanomolar range, with an overall selectivity index for the best molecules higher than 2600. Since compounds exhibited low or no significant effect on DNA, their activity was evaluated in terms of cellular cycle perturbation and induction of apoptosis/necrosis, in order to define the mechanism of action involved in the photoinduced cell death.

[1] see for example: R. Allison et al. *Photodiagnosis and Photodynamic Therapy*, 2010, **7**, 61 – 75.
[2] see for example: D. E. Dolmans et al. *Nt. Rev. Cancer*, 2003, **3**, 380 – 387.
[3] V. Spanò et al. *Eur. J. Med. Chem.*, 2014, **74**, 340 – 357.

FAR-P6

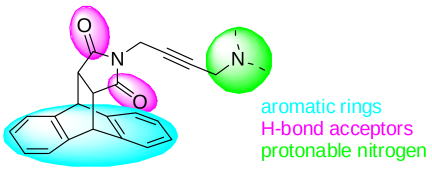
Dual inhibitors of P-glycoprotein and multidrug resistance associated protein-1 carrying a polycyclic scaffold.

A. Bisi,[a] *S. Gobbi,*[a] *L. Merolle,*[b] *G. Farruggia,*[b,c] *F. Belluti,*[a] *A. Rampa,*[a] *J. Molnar,*[d] *E. Malucelli,*[b] *C. Cappadone*[b]

Department FaBiT, University of Bologna [a]Via Belmeloro, 6, 40126 and [b]Via S. Donato, 19/2, 40127, Bologna, Italy, [c]National Institute of Biostructures and Biosystems, Via delle Medaglie D'oro, 305, 00136, Roma, Italy, [d]Institute of Medical Microbiology and Immunbiology, University of Szeged, Szeged, Hungary.

alessandra.bisi@unibo.it

Following the identification of a novel polycyclic scaffold, leading to a previously reported potent P-gp inhibitor,[1] a small series of easily affordable derivatives bearing a properly selected nitrogen-containing but-2-ynyl side chain [2] was now synthesized and tested to evaluate the MDR reverting activity on two different experimental models expressing either P-gp or MRP1. All compounds proved to be more potent P-gp inhibitors than the reference verapamil, and some of them, although not cytotoxic when tested alone, showed remarkable effects in combination with doxorubicin being able to induce apoptotic cell death, due to their reverting activity. In particular, two compounds could be regarded as non-toxic new potential chemosensitizers, being able to interfere with two different ABC proteins. Moreover, the intrinsic cytotoxicity of the lead compound could make it a good multitarget drug candidate, broadening its employment as MDR modulator. These results also seem to confirm the polycyclic core of these compounds as a potential new pharmacophoric carrier in medicinal chemistry.[1,3]



[1] A. Bisi, S. Gobbi, A. Rampa, F. Belluti, *et al. J. Med. Chem.* 2006, **49**, 3049-3051.
[2] A. Bisi, S. Gobbi, A. Rampa, *et al. Bioorg. Med. Chem.* 2008, **16**, 6474–6482.
[3] S. Bova, A. Bisi, *et al. J. Med. Chem.* 2009, **52**, 1259-1262.

FAR-P7

Study of the kinetic release of anti inflammatory drugs from electrospun nanostructured polymeric membranes

Marcello Locatelli [a,b], *Pantaleone Bruni* [a], *Vincenzo Ferrone* [a], *Stefano Narcisi* [a], *Giuseppe Carlucci* [a], *Fausto Croce* [a]

[a] *University "G. d'Annunzio" of Chieti-Pescara; Department of Pharmacy; via dei Vestini 31; 66100 Chieti (CH); Italy; m.locatelli@unich.it*

[b] *Interuniversity Consortium of Structural and Systems Biology INBB; Viale Medaglie d'oro 305; 00136 Roma; Italy.*

pantaleone.bruni@unich.it

The electrospinning process consists in extruding a polymeric solution through a fine nozzle by means of a strong applied electric field. When the electric force overcome the surface tension of the polymeric solution tiny fibers are estruded from the solution producing nonwoven membranes with individual fiber diameters ranging from 50 to 1000 nm. Electrospun fiber meshes or mats posses oustanding features such as small fiber diameters, high specific surface area and high porosity which make them suitable as promising systems for drug delivery. As the polymeric solution can be easly loaded with a wide range of biologically active compounds electrospinnig allows the realization of biodegradable, nanosized membranes with an engineered degradation rate which can optimize the drug delivery within the body. In the present study, electrospun nanostructured polymeric membranes, formed by a blend of poly (D,L-lactide) (PDLLA) and poly (ethylene oxide) (PEO, loaded with the anti inflammatory drugs ketoprofene and ibuprofene have been produced The mats have been characterized by scanning electron microscopy (SEM), and differential scanning calorimetry (DSC). Moreover, the kinetics of the release of the two compounds either when individually or togheter present in the membrane has been evaluated i*n vitro* by utilizing a validated HPLC-UV/Vis assay. The study has demonstrated that two-step kinetics dominates the release of the two compounds from the membrane and that when the compounds are present at the same time in the membrane the time scale of the release is influenced.

FAR-P8

Design, Synthesis, Crystallographic Studies, and Biological Appraisals of New Tankyrase Inhibitors

Emidio Camaioni[a], Paride Liscio[ad], Stefania Asciutti[b], Andrea Carotti[a], Antonio Macchiarulo[a], Martina Ferri[a], Tobias Karlberg[c], Herwig Schuler[c], Stuart A. Aaronson[b], Benedetto Natalini[a], Roberto Pellicciari[d]

a Dipartimento di Scienze Farmaceutiche, Università di Perugia, Via Liceo, 1, 06123, Perugia, Italia
b Department of Oncological Sciences, Mount Sinai School of Medicine, 1425 Madison Ave, New York 10029, United States
c Department of Medical Biochemistry and Biophysics, Karolinska Institutet, S-17177 Stockholm, Sweden
d TES Pharma, via P. Togliatti 22bis, 06073 Località Terrioli, Corciano, Italy

emidio.camaioni@unipg.it

The human genome encodes two tankyrases, TNKS-1 and TNKS-2 which are members of the poly(ADP-ribose) polymerases (PARPs) family. By having an active role in telomere maintenance and Wnt pathway regulation, TNKSs take part in the complex arena of processes responsible of growth and progression of tumors. Inhibition of TNKSs activity appears therefore to be a promising strategy in the treatment of cancer. As an extension of our work in the field, we have recently reported the design, synthesis and biological appraisals of novel potent and selective TNKSs inhibitors [1]. Structure based optimization of the starting hit compound N-(4-chlorophenethyl)-6-methyl-[1,2,4]triazolo[4,3-b]pyridazin-8-amine (NNL) led us to disclose 4-(2-(6-methyl-[1,2,4]triazolo[4,3-b]pyridazin-8-ylamino)ethyl)phenol, a low nanomolar selective TNKSs inhibitor working as NAD isostere as ascertained by crystallographic analysis (PDB code 4M7B). Furthermore, cellular assays pinpoint [1,2,4]triazolo[4,3-b]pyridazine class of derivatives as powerful pharmacological tools for the unravelling of TNKS implications in physio-pathological conditions which imply Wnt pathway aberration.

[1] P. Liscio P, A. Carotti, S. Asciutti, T. Karlberg, D. Bellocchi, L. Llacuna, A. Macchiarulo, S.A. Aaronson, H. Schüler, R. Pellicciari and E. Camaioni *J.Med.Chem.* 2014, **57**, 2807-2812.

FAR-P9

Synthesis of novel scandium and yttrium complexes having potential antitumor activity

Caporale A[1a], *Palma G*[2b], *Puoci F*[3c], *Arra C*[2b], *Longo P*[4d], *Sinicropi MS*[3c], *IacopettaD*[3c], *Caruso A*[3c], *Marra N*[1a], *Saturnino C*[1a]

a Department of Pharmacy, University of Salerno, Via Giovanni Paolo II 132, 84084, Fisciano (SA), Italy.
b IRCCS (National Cancer Institute, IRCCS,"G.Pascale" Foundation), Via Mariano Semmola, 52-108,
c Department of Pharmacy, Health and Nutritional Sciences, University of Calabria, Arcavacata's Campus, via Pietro Bucci, 87036 Arcavacata di Rende (CS), Italy.
d Department of Chemistry and Biology, University of Salerno, Via Giovanni Paolo II 132, 84084, Fisciano (SA), Italy

acaporale@unisa.it

The design of new metal complexes as anticancer agents has received considerable interest in recent year, to overcome the limitations of toxicity and drug resistance of cis-platinum. The attention of medicinal chemists focused on lanthanides and group III metals complex stabilized by various ligands [1], [2].Thus, group III metal complexes are the target of this project. In line with the ongoing research projects were synthesized 7 novel scandium and yttrium complexes and they were tested for their cytotoxic activity on B16F10 (Melanoma cell-line) and DU145 (Prostatic carcinome cell-line toward MTT test assay. CAM-2 and CAM-3 have demonstrated an effective reduction in the growth on both cell lines even at a 5 µm concentration. On the other hand, CAM-5, CAM-6 and CAM-7 showed a small reduction of cell growth.

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[2] C. Saturnino, M. Napoli, G. Paolucci, M. Bortoluzzi, A. Popolo, A. Pinto, P. Longo Eur.J.Med.Chem, 2010, 45, 4169-4174.

FAR-P10

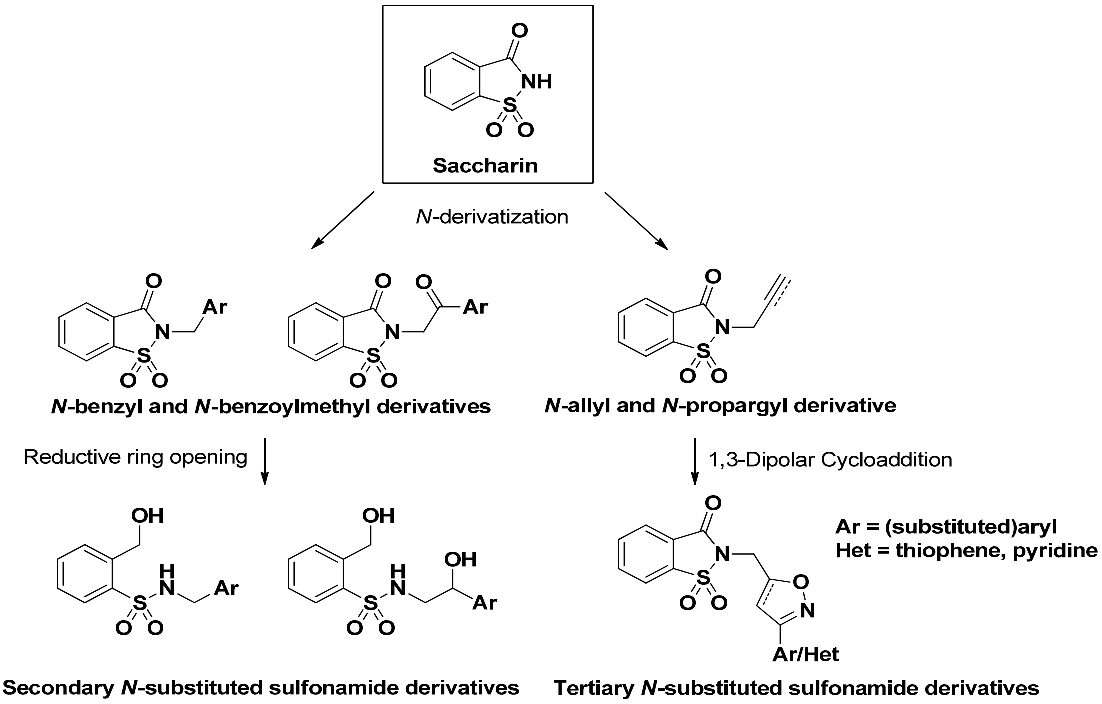
New selective saccharin-based inhibitors of the tumor-associated carbonic anhydrases IX and XII

Simone Carradori[a], *Melissa D'Ascenzio*[a], *Daniela Secci*[a], *Federica De Cosmi*[a], *Mariana Farella*[a], *Mariangela Ceruso*[b], *Daniela Vullo*[b], *Claudiu T. Supuran*[b,c]

[a]*Dipartimento di Chimica e Tecnologie del Farmaco, Sapienza Università di Roma, P.le A. Moro 5, 00185, Rome, Italy*
[b]*Laboratorio di Chimica Bioinorganica, Università degli Studi di Firenze, Via della Lastruccia 3, 50019, Sesto Fiorentino (Florence), Italy*
[c]*Section of Pharmaceutical and Nutraceutical Sciences, Università degli Studi di Firenze, Neurofarba, Via U. Schiff 6, 50019, Sesto Fiorentino (Florence), Italy*

simone.carradori@uniroma1.it

Carbonic anhydrase IX and XII were found to be over-expressed in hypoxic tumors, both in primary and in metastatic cell-lines, and represent potential targets for the development of new diagnostic and therapeutic drugs. On the basis of the atypical pharmacophoric sulfonamide moiety contained in the saccharin scaffold, we designed and evaluated novel secondary and tertiary *N*-substituted derivatives as potent and selective inhibitors of these isoenzymes.



FAR-P11

Legume proteins: ACE-inhibitory activity of enzymatic hydrolysates

Giovanna Boschin[a], *Graziana Maria Scigliuolo*[b], *Donatella Resta*[b], *Anna Arnoldi*[a,b]

[a] *Dipartimento di Scienze Farmaceutiche (DISFARM), University of Milan, Via Mangiagalli 25, 20133 Milan, Italy*
[b]*HPF-Nutraceutics s.r.l., Via Balzaretti 9, 20133 Milan, Italy*

anna.arnoldi@unimi.it

The enzymatic hydrolysis of some food proteins (in particular milk) produce peptides able to inhibit angiotensin-converting enzyme (ACE), which is involved in the renin-angiotensin system for the regulation of blood pressure [1].
In this work, the ACE-inhibitory activity of hydrolysates obtained by pepsin digestion of some legume proteins, such as chickpea, common bean, lentil, lupin, pea, and soybean were investigated, by using the tripeptide hippuryl-histidyl-leucine (HHL), as model peptide, and HPLC-DAD, as analytical method. Soybean and lupin were the most active, with IC_{50} values of 224 and 226 µg/mL, respectively [2].
Moreover three different lupin species (*Lupinus albus*, *L. angustifolius*, *L. luteus*) were studied with the final goal of selecting the best enzyme/species combination for an efficient production of ACE-inhibitory peptide mixtures. Different enzymes were tested: trypsin, chymotrypsin, corolase PP, umamizyme, and flavourzyme. Pepsin gave peptides with the best activity followed by pepsin + trypsin, chymotrypsin, trypsin, corolase PP, umamizyme, and flavourzyme [3]. This investigation confirms that lupin proteins may be a source of ACE-inhibitory peptides, and foresees the application of lupin proteins into functional foods or dietary supplements.

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FAR-P12

Metal complexes: synthesis and preliminary biological studies

Anna Rita Cappello[a], *Anna Caruso*[a,b], *Domenico Iacopetta*[a], *Dhanya Dhanyalayam*[a], *Francesco Puoci*[a], *Ortensia Ilaria Parisi*[a,b], *Pasquale Longo*[d], *Maria Stefania Sinicropi*[a], *Carmela Saturnino*[c]

a Dipartimento di Farmacia e Scienze della Salute e della Nutrizione, b DIMES
Università della Calabria, Via Pietro Bucci, 87036 - Arcavacata di Rende (Cs), Italia
c Dipartimento di Farmacia, d Dipartimento di Chimica Università di Salerno, Via G. Paolo II, 84084 – Fisciano -Salerno, Italia

anna.caruso@unical.it

Metal-based drugs chemistry represents a very attractive field of research which offers several possibilities for the design of new therapeutic agents not readily available. Properties as the wide range of coordination numbers or the intrinsic properties of the cationic metal ion and ligand itself may be exploited to obtain compounds with a wide spectrum of biological properties.

The growing interest led to the synthesis of many Au and Ti compounds with different molecular structures, which have been tested for their anticancer[1] and antibacterial activity.[3] Here we report the synthesis and the preliminary biological studies of a new class of metal complexes.

The compounds have been tested on five different cellular lines, namely breast (MCF-7 and SKBR3), cervical (HeLa), endometrial (Ishikawa), Leydig (R2C) cancer cell lines. Amongst the complexes tested, only the Ag- and Au-based compounds showed an interesting antiproliferative activity on all cell lines, even though the mechanism by which they exert their effects is still under consideration. Moreover, the same newly synthesized compounds showed antimicrobial properties against Gram +ve (*S. aureus*, *S. pneumoniae*) and Gram –ve (*K. pneumoniae*, *P. aeruginosa*, *E. coli*) organisms.

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FAR-P13

A resveratrol derivative induces authophagic cell death in human breast cancer MCF-7 cell line

Adele Chimento[a], *Carmela Campana*[a], *Maria Stefania Sinicropi*[a], *Carmela Saturnino*[c], *Anna Caruso*[a,b], *Pietro Rizza*[a], *Rosa Sirianni*[a], *Ivan Casaburi*[a], *Ortensia Ilaria Parise*[a,b], *Francesco Puoci*[a], *Marina Sala*[c], *Pietro Campiglia*[c], *Vincenzo Pezzi*[a]

a Dipartimento di Farmacia e Scienze della Salute e della Nutrizione, b DIMES,
Università della Calabria, Via Pietro Bucci, 87036 - Arcavacata di Rende (Cs), Italia
b Dipartimento di Farmacia, Università di Salerno, Via G. Paolo II, 84084 – Fisciano - Salerno, Italia

anna.caruso@unical.it

Resveratrol derivatives represents an important group of compounds which may considered as potential new anticancer drugs.[1] In this study we aimed to investigate the specific mechanism underlying inhibitory effects of a thiazolidin-4-one (MS7) resveratrol derivative on MCF7 breast cancer cell proliferation. First we confirm our previous results indicating the ability of MS7 to inhibit MCF7 cell growth examining its long-term effects on clonogenic survival. In vitro colony formation assay showed a reduced clonogenicity of MS7 treated cells in a concentration-dependent manner. In addition, performing flow cytometry analysis we found that MS7 caused cell cycle arrest at G2 phase and changes in the expression of cell cycle markers such as cyclin D1 and B1. We investigated also whether MS7 could induce apoptosis in our breast cancer cell model. WB analysis and laddering assay showed that MS7 not determine the appearance of caspase cleaved forms and DNA fragmentation. In contrast, expression of autophagic cell death markers, such as Beclin, LC3-II, Uvrag, Ambra were increased after MS7 treatment. In addition, MS7 autophagic cell death was confirmed by acridin orange assay. Based on our results we conclude that MS7 exibit promising anti-cancer activity by triggering authophagic cell death. The understanding of molecular mechanisms behind biological activity of MS7 could be useful to design future therapies employing this resveratrol derivative in breast cancer treatment.

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FAR-P14

Carbazole derivatives with potential interfering activity on Aβ aggregation

Anna Caruso[a,b], *Francesca Di Cristo*[c], *Pasquale Longo*[d], *Camillo Rosano*[e], *Domenico Iacopetta*[a], *Roberta Ricciarelli*[f], *Barbara Marengo*[f], *Maria Stefania Sinicropi*[a], *Carmela Saturnino*[c]

a Dipartimento di Farmacia e Scienze della Salute e della Nutrizione, b DIMES, Università della Calabria, Via Pietro Bucci, 87036 - Arcavacata di Rende (Cs), Italia
c Dipartimento di Farmacia, d Dipartimento di Chimica, Università di Salerno, Via G. Paolo II, 84084 – Fisciano -Salerno, Italia
e Biopolimeri e Proteomica IRCCS AOU San Martino - IST Istituto Nazionale per la Ricerca sul Cancro, Via Largo Benzi 10, 16132 - Genova, Italia
f Dipartimento di Medicina Sperimentale sezione di Patologia, Università di Genova, Via L.B. Alberti 2 16132 - Genova, Italia

anna.caruso@unical.it

The neuropathological hallmarks of Alzheimer disease include abundant deposits of amyloid β (Aβ) peptides organized in senile plaques, accumulation of hyperphosphorylated tau protein in neurofibrillary tangles, and extensive neuronal degeneration and loss.[1] Besides, cholinergic abnormalities have been observed in AD as, for instance, a reduction in acetylcholine receptor levels or dysfunctions of cholinergic signal transmission, which are of critical importance in brain areas involved in learning, memory, and emotional responses.[2] For this reason, we have synthesized a library of carbazole derivatives here investigated *in silico* and *in vitro* for their ability to prevent the aggregation of Aβ peptides. The synthesized compounds were underwent to molecular docking simulation and cell-based analyses in order to verify their potential interfering activity on Aβ aggregation. All together, the obtained results indicate that the two most promising compounds in docking simulations also exhibited the higher activity *in vitro*. Other studies are ongoing for a better understanding of the underlying mechanism by which the molecules act in our cell-based system.

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FAR-P15

Nuovi composti policiclici di interesse farmaceutico

Anna Caruso[a,b], *Carmela Saturnino*[c], *Domenico Iacopetta*[a], *Maria Stefania Sinicropi*[a]

a Dipartimento di Farmacia e Scienze della Salute e della Nutrizione, b DIMES,
Università della Calabria, Via Pietro Bucci, 87036 - Arcavacata di Rende (Cs), Italia
c Dipartimento di Farmacia, Università di Salerno, Via G. Paolo II, 84084 – Fisciano - Salerno, Italia

anna.caruso@unical.it

Tra gli eterocicli azotati, gli alcaloidi a nucleo carbazolico rappresentano una classe di derivati naturali dalle molteplici attività biologiche.[1] Essenzialmente, essi sono potenti antitumorali, ma possiedono anche attività antimicrobica, anti-Alzheimer, antinfiammatoria ed antistaminica.[2] La funzionalizzazione del nucleo carbazolico, mediante la messa a punto di semplici vie sintetiche, ha consentito di ottenere le nuove serie: 6-aril, 3-acil (e aroil) e 9-alchil-1,4-dimetil-9*H*-carbazoli,[1] *N*-(1,4-dimetil-9*H*-carbazol-3-il) guanidine[3] e *N*-(1,4-dimetil-9*H*-carbazol-3-il)-3,4,5-trimetossibenzamidi (e uree).[4] Inoltre, pirimido[5,4-b]carbazoli,[5] benzofuro (e benzotieno) chinazolinoni ed indoli 3,5-sostituiti[6] sono stati studiati, quali nuovi analoghi strutturalmente correlati. Il profilo citotossico dei composti preparati è stato valutato utilizzando saggi *in vitro* (ad esempio MTT, formazione di colonie, citofluorimentria, ecc.). Alcune delle molecole sintetizzate hanno mostrato profili farmacologici interessanti a concentrazioni sub-micromolari.

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FAR-P16

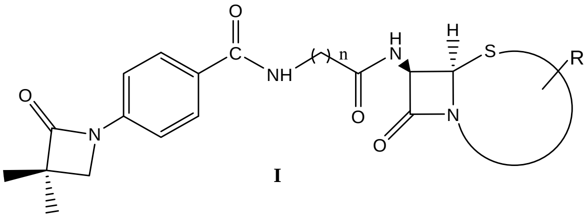
Sintesi e attività antimicrobica di nuovi derivati β-lattamici

Marco Fiorillo[a], Anna Caruso[a,b], Margherita De Rosa[c], Annunziata Soriente[c], Angelamaria Caporale[d], Anna Rita Cappello[a], Vincenza Dolce[a], Domenico Iacopetta[a], Francesco Puoci[a], Ortensia Ilaria Parisi[a,b], Carmela Saturnino[d], Maria Stefania Sinicropi[a]

a Dipartimento di Farmacia e Scienze della Salute e della Nutrizione, b DIMES,
Università della Calabria, Via Pietro Bucci, 87036 - Arcavacata di Rende (Cs), Italia
c Dipartimento di Chimica, d Dipartimento di Farmacia, Università di Salerno, Via G. Paolo II, 84084 – Fisciano -Salerno, Italia

anna.caruso@unical.it

Gli antibiotici sono una delle classi di farmaci più importanti e ampiamente utilizzati. Tuttavia, l'antibiotico-resistenza è diventata una minaccia per la salute pubblica globale.[1] A questo proposito, vi è un crescente interesse scientifico verso lo studio di molecole di origine naturale e di nuova sintesi in grado, non solo di esprimere la loro azione antibatterica mediante meccanismi specifici, ma anche dotate di caratteristiche farmacocinetiche favorevoli e di una bassa tossicità. Oggetto della presente ricerca è stato la preparazione e lo studio delle proprietà antimicrobiche di nuove molecole (**I**), quali potenziali strumenti terapeutici utili nel trattamento di malattie causate da patogeni resistenti.



I

Il derivato denominato **A93b** ha mostrato eccellente attività nei confronti dei batteri Gram+, i valori di MIC riscontrati contro *Staphylococcus aureus* sono stati gli stessi di quelli riportati in letteratura per la Ceftazidima. I ceppi batterici Gram-, invece, sono risultati resistenti ad **A93b**.

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FAR-P17

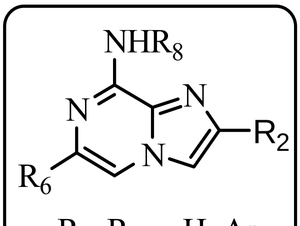
Imidazo[1,2-a]pyrazine core for the design of new adenosine receptor antagonists: optimization of A_3 affinity and structural exploration to target the A_{2A} subtype

Daniela Catarzi[a], Vittoria Colotta[a], Flavia Varano[a], Lucia Squarcialupi[a], Katia Varani[a]

a Dipartimento di Neuroscienze, Psicologia, Area del Farmaco e Salute del Bambino, Sezione di Farmaceutica e Nutraceutica, Universita' di Firenze, Via U. Schiff 6, 50019 Sesto Fiorentino (FI), Italy
b Dipartimento di Scienze Mediche, Università di Ferrara, C.so Giovecca, 203, 44100 Ferrara, Italy

daniela.catarzi@unifi.it

Adenosine is an endogenous nucleoside that modulates many physiological processes by interacting with four adenosine receptors (ARs), namely A_1, A_{2A}, A_{2B} and A_3, that are members of the G-protein coupled receptor superfamily. There is concrete evidence that both A_3 and A_{2A} AR could be promising therapeutic targets in many neurodegenerative diseases [1]. In fact, A_3 and A_{2A} antagonists are reported to have neuroprotective activity in stroke and in Parkinson's disease, respectively [1,2]. Thus, our research group focused on the identification of bicyclic scaffolds that suitably decorated could lead to the development of new AR antagonists [3-5]. In the present study, selected substitution on the imidazo[1,2-a]pyrazine core skeleton produced potent and selective human A_3 AR antagonists. Preliminary results also encouraged the structural exploration of this versatile scaffold to target the A_{2A} subtype.



R_2, R_6 = H, Ar
R_8 = H, COAr

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FAR-P18

Physicochemical characterization of non ionic surfactant vesicles forming innovative supramolecular nanocarriers

Martina Di Francesco[a,*], *Rosita Primavera*[b], *Matteo Ciancaioni*[b], *Donato Cosco*[a], *Luisa Di Marzio*[b], *Christian Celia*[b,c], *Donatella Paolino*[a], *Massimo Fresta*[a,*]

[a]*Department of Health Sciences, University of Catanzaro "Magna Graecia", Via S. Venuta, 88100 Catanzaro, Italy*
[b]*Department of Pharmacy, University of Chieti - Pescara "G. d'Annunzio", Via dei Vestini 31, 66013 Chieti, Italy*
[c]*Department of Nanomedicine, The Methodist Hospital Research Institute, 6670 Bertner Ave., Houston, TX 77030, USA*

martina.difrancesco89@gmail.com; *fresta@unicz.it*

The use of nanotechnology, such as the development of nanocarriers for drug delivery, has received great attention owing to the potential that nanocarriers can theoretically act as "magic bullets" and selectively target affected organs and cells while sparing normal tissues. During the last decades surfactants brought an increasing interest among the scientists working in the area of drug delivery systems. Niosomes forming by hydrophilic surfactants gained particular interesting as nanocarriers to deliver hydrophilic and/or hydrophobic compounds. In fact, Niosomes show similar physicochemical features compared to liposomes, but they require less production costs and are stable over a longer period of time in different conditions. Basically, Niosomes are synthetized using combinations of hydrophobic surfactans and cholesterol and few contributions are actually available about the use of hydrophilic surfactants forming Niosomes. The aim of this work was to synthetize and physicochemical characterize Niosomes forming by self-assembling hydrophilic surfactants and cholesterol. Size, shape, narrow size distribtuion and zeta potential of innovative supramolecualr nanocarriers were carried out. Moreover, hydrophobic probe was used as molecular model to evaluate the entrapment efficiency of these nanocarriers. Results demonstrated that hydrophilic surfactants can form innovative Niosomes, which could be used as suitable drug delivery systems for potential therapeutic treatments.

FAR-P19

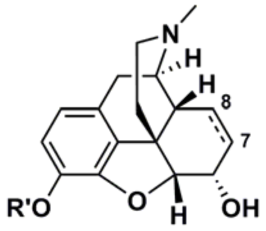
(Trans)dermal delivery of opioids: a structure-permeability relationship

Umberto Musazzi [a], *Carlo Matera* [a], *Francesco Cilurzo* [a], *Clelia Dallanoce* [a],
Giulio Vistoli [a], *Federica Vacondio* [b]; *Paola Minghetti* [a], *Marco De Amici* [a]

[a] *Dipartimento di Scienze Farmaceutiche, Università degli Studi di Milano, Via G. Colombo 71, 20131, Milano, Italia*
[b] *Dipartimento di Farmacia, Università degli Studi di Parma, Parco Area delle Scienze 27/A, 43100, PARMA, , Italia*

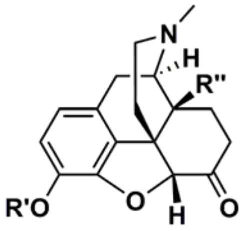
francesco.cilurzo@unimi.it

Recent studies showed that morphine is locally effective in the local treatment of post herpetic neuralgia. However, no information has been available in literature on the ability of human skin to retain morphine derivatives. The present study investigated the effect of four different substituents (i.e., 3-methoxyl, 6-carbonyl, 14-hydroxyl groups and 7,8-didehydro), on in vitro penetration through human skin. The effect of the selected substituents and their synergistic effects, statistically evaluated, were elucidated in relation to physico-chemical parameters and molecular dynamic simulations.



R' = H, (7,8-didehydro) **(1)** Morphine
R' = H **(2)** Dihydromorphine

R' = CH_3, (7,8-didehydro) **(5)** Codeine
R' = CH_3 **(6)** Dihydrocodeine



R' = H, R'' = OH **(3)** Oxymorphone
R' = H, R'' = H **(4)** Hydromorphone

R' = CH_3, R'' = OH **(7)** Oxycodone
R' = CH_3, R'' = H **(8)** Hydrocodone

The 3-methoxyl group, determining a significant increase of flux and at the same time a reduction of skin retention, plays a key role in governing the penetration of morphine derivatives. Moreover, the docking analyses suggested that a ceramide-based computational model might be suitable for describing the affinity of opioid to be retained into the human epidermis.
The overall results suggested that hydromorphone could be a good alternative to morphine since it has a greater affinity for human epidermis as well as a relatively higher potency.

FAR-P20

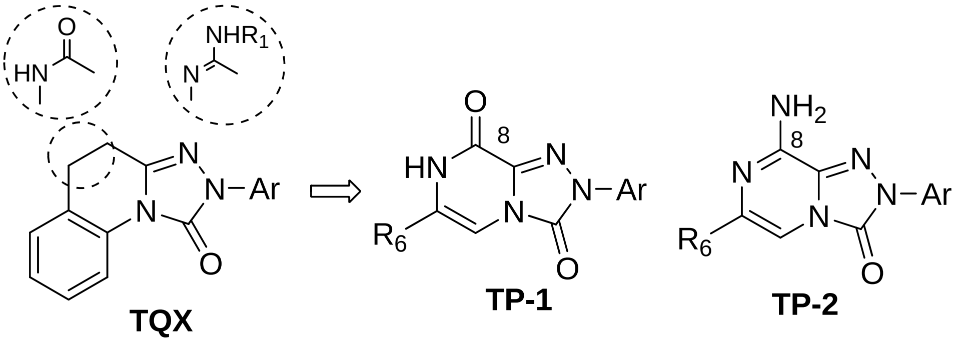
1,2,4-Triazolo[4,3-*a*]pyrazin-3-one as a new scaffold to develop potent adenosine receptor antagonists

Vittoria Colotta[a], *Lucia Squarcialupi*[a], *Daniela Catarzi*[a], *Flavia Varano*[a], *Rosaria Volpini*[b], *Michela Buccioni*[b], *Diego Dal Ben*[b]

a Dipartimento di Neuroscienze, Psicologia, Area del Farmaco e Salute del Bambino, Sez. di Farmaceutica e Nutraceutica, Università di Firenze, Via Ugo Schiff 6, 50019 Sesto Fiorentino (FI), Italia
b Scuola di Scienze del Farmaco e dei Prodotti della Salute, Università di Camerino, Via S. Agostino, 62032 Camerino, Italia

vittoria.colotta@unifi.it

The neuromodulator adenosine exerts its physiological functions by activation of four G-protein-coupled receptors, known as A_1, A_{2A}, A_{2B} and A_3. Adenosine receptor (ARs) antagonists emerged as useful therapeutic agents in a wide range of pathologies [1]. In particular, A_{2A} and dual A_1/A_{2A} AR antagonists proved to be effective in the treatment of Parkinson's disease (PD), while A_3 AR antagonists demonstrated anti-inflammatory and anti-asthmatic activity [1]. To continue our research on AR ligands, we designed the 1,2,4-triazolo[4,3-*a*]pyrazin-3-ones **TP-1** and **TP-2**, as simplified analogues of our previously reported 1,2,4-triazolo[4,3-*a*]quinoxalin-1-one derivatives **TQX** [2,3]. Some potent AR antagonists, with different degrees of selectivity, were identified in both the 8-oxo- **(TP-1)** and 8-amino **(TP-2)** sets. Docking studies at human ARs are in progress to rationalize the obtained affinities and to guide the design of new **TP** derivatives.



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FAR-P21

New modulator of the tumoural immuno escape via Indoleamin 2,3-dioxygenase (IDO) inhibition.

Antonio Coluccia[a], *Giuseppe La Regina*[a], *Alato Okuno*[b] *Osamu Takikawa*[b]
Romano Silvestri[a]

a Dipartimento di Chimica e Tecnologia del Farmaco, Sapienza Università di Roma, Piazzale Aldo Moro, 5 Cap 00182, Roma, Italy
b National Institute for Longevity Sciences, National Center for Geriatrics and Gerontology 35 Gengo, Morioka, Obu, Aichi 474-8511, Japan.

antonio.coluccia@uniroma1.it

Indoleamine 2,3-dioxygenase (IDO) is a heme-containing enzyme implicated in the regulation of immunological responses and tolerances contributing to tumor immune surveillance escape making IDO inhibition an attractive area of anti cancer research. Herein, we report a virtual screening campaign that led to the identification of a new IDO inhibitor (**8** IC_{50} = 17,5 μM). With the aim to access the pharmacophore structural requirements of our hit compound and to optimize the IDO inhibition potency a structure activity relationship studies was carried out. The IDO inhibition potency was optimized to 7 μM for derivative **15,** which is to our knowledge, more active than compounds already in clinical trials.

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FAR-P22

Molecular Modeling Studies on A_{2B} Adenosine Receptor and its Ligands

Diego Dal Ben, Michela Buccioni, Catia Lambertucci, Gabriella Marucci, Claudia Santinelli, Andrea Spinaci, Ajiroghene Thomas, Rosaria Volpini

School of Pharmacy, Medicinal Chemistry Unit, University of Camerino, Via S. Agostino 1, 62032 Camerino, Italy

diego.dalben@unicam.it

A_{2B} Adenosine Receptor (A_{2B}AR) agonists are studied as possible therapeutic tools for a variety of pathological conditions. To date, medicinal chemistry efforts have led to the development of two structural families of ligands based on nucleoside or non-nucleoside (pyridine) scaffolds [1-3]. Among them, only a limited number of compounds are potent agonists of this receptor, in most cases with a low or no selectivity versus the other adenosine receptor subtypes.

To simulate the binding mode of these molecules at the human A_{2B}AR, 3D models of this receptor were developed by using two recently published crystal structures of the closely related human A_{2A}AR in complex with two different agonists as templates. The developed models were employed as targets for molecular docking studies of the two structural families of agonists. Results suggest a set of common interaction points between the nucleoside and non-nucleoside agonists and the receptor binding site. This conserved pattern of interaction between the A_{2B}AR and its agonists could provide useful data for the design and the development of A_{2B}AR agonists belonging to nucleoside or non-nucleoside structural families [4].

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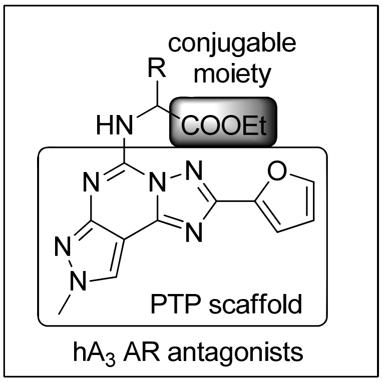
FAR-P23

Conjugable A_3 adenosine receptor antagonists: probing the 5 position of the pyrazolo[4,3-*e*][1,2,4]triazolo[1,5-*c*]pyrimidine scaffold

Stephanie Federico[a], *Sara Redenti*[a], *Karl-Norbert Klotz*[b],*Stefano Moro*[c],*Giampiero Spalluto*[a]

a Dipartimento di Scienze Chimiche e Farmaceutiche, Università degli Studi di Trieste, Via Licio Giorgeri 1, 34127, Trieste, Italia
b Institut für Pharmakologie, Universität of Würzburg, Versbacher Strasse 9, 97078, Würzburg, Germany
c Molecular Modeling Section, Dipartimento di Scienze Farmaceutiche, Università degli Studi di Padova, via Marzolo 5, 35131 Padova, Italy.

sfederico@units.it



A_3 adenosine receptors (ARs) belong to the superfamily A of G-protein coupled receptors. When activated, A_3 AR could inactivate adenylyl cyclase or stimulate phospholipase C or D.[1] Antagonists for the A_3 AR are promising agents for the treatment of asthma, inflammation and glaucoma.[1] In addition detectable hA_3 AR antagonists are useful in ligand discovery and receptor localization imaging. A simple strategy in order to obtain such antagonists is to link fluorophore, or other detectable groups, to a conjugable hA_3 AR antagonist.[2] Herein, we report the exploration of new possible aminoacid spacers at the 5 position of the well-known pyrazolo[4,3-*e*][1,2,4]triazolo[1,5-*c*]pyrimidine (PTP) scaffold as site of linkage for functionalizing moieties, that can be useful in the study of the physio-pathological role of A_3 AR.

[1] S.L. Cheong, S. Federico, G. Venkatesan, A.L. Mandel, Y.M. Shao, S. Moro, G. Spalluto and G. Pastorin *Med. Res. Rev.*, 2013, **33**, 235-335.
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FAR-P24

Design, Virtual Screening and Synthesis of Potential Microsomal Prostaglandin E_2 Synthase-1 (mPGES-1) Inhibitors

Antonio Foglia, Simone Di Micco, Stefania Terracciano, Carmela Saturnino, Raffaele Riccio, Ines Bruno, Giuseppe Bifulco

Department of Pharmacy, University of Salerno, via Giovanni Paolo II, 132, 84084 Fisciano, Italy

afoglia@unisa.it

Microsomal prostaglandin E_2 synthase 1 (mPGES-1), a member of the MAPEG (membrane-associated proteins involved in eicosanoid and glutathione metabolism) superfamily, is an inducible enzyme that couples with cyclooxygenase-2 for the biosynthesis of the bioactive lipid metabolite prostaglandin E_2 (PGE_2). Taken into account the involvement of mPGES-1 in the development of various human cancer, including colon, lung, stomach, pancreas, prostate and brain tumors, and in inflammatory disorders. It is considered as an attractive target for anti-cancer and inflammatory therapy[1]. With the aim of identifing new mPGES-1 inhibitors, we performed an in silico screening by molecular docking using LigBuilder v2.0 software and the X-ray crystal structure of mPGES-1 [2]. Following computational docking suggestions, we are currently involved in the synthesis of a small collection of new 3,5-disubstituted isoxazoles through 1,3-dipolar cycloaddition. In particulary, the synthesis of the selected compounds will be accomplished through a one-pot three-step process, utilizing a regioselective copper(I)-catalyzed cycloaddition reaction between in situ generated nitrile oxides and terminal alkynes.

[1] M.Nakanishi, V. Gokhale, E.J. Meuillet, D.W.Rosenberg. Biochimie, 2010, **92**, 660-664.
[2] T. Sjögren, J. Nord, M. Ek, P. Johansson, G. Liu, S. Geschwindner Proc. Natl. Acad. Sci. U.S.A., 2013, **110**, 3806-3811.

FAR-P25

Lubeluzole: from anti-ischemic to chemosensitizing agent

C. Franchini[a], M. M. Cavalluzzi[a], R. Gualdani[b], M. A. De Salvia[c], M. Piarulli[a], C. Bruno[a], A. Lovece[a], A. Carrieri[a], A. Rosato[a], M. Viale[d], M. R. Moncelli[b], G. Lentini[a].

a Dipartimento di Farmacia – Scienze del Farmaco, Università degli Studi di Bari 'Aldo Moro', Via E. Orabona 4, 70125, Bari, Italia

b Dipartimento di Chimica 'U. Shiff', Università di Firenze, Via della Lastruccia 3, 50019, Firenze, Italia

c Dipartimento di Scienze Biomediche e Oncologia Umana, Università degli Studi di Bari 'Aldo Moro', Piazza Giulio Cesare 11, 70124, Bari, Italia

d IRCCS Azienda Ospedaliera Universitaria San Martino, IST Istituto Nazionale per la Ricerca sul Cancro (IRCCS SMIST), L.go R. Benzi 10, 16132, Genova, Italia

carlo.franchini@uniba.it

Lubeluzole, a neuroprotective anti-ischemic drug, and its enantiomer were recently reported as chemosensitizing agents in combination with either doxorubicin or paclitaxel.[1] The synergistic effects of lubeluzole for both drugs were observed over a wide concentration window (0.005–5 μM), the lowest limit being at least 40 times lower than human plasma concentrations related to heart-conduction disorders. In this work, data on lubeluzole synergistic antimicrobial activity against some microorganisms affecting the gastro-intestinal tract will be reported. The results obtained studying the activity of lubeluzole on colonic contractile responses will be shown. New analogues designed in order to potentiate the chemosensitizing effects and reduce the unwanted side interaction with hERG channels will be presented.

[1] M. M. Cavalluzzi, M. Viale, C. Bruno, A. Carocci, A. Catalano, A. Carrieri, C. Franchini, G. Lentini *Bioorg.Med.Chem.Lett.* 2013 **23**, 4820–4823.

FAR-P26

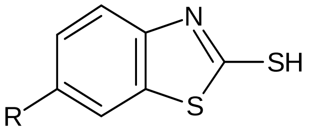
1,3-Benzothiazoles as Antimicrobial Agents

C. Franchini, A. Carocci, A. Catalano, I. Defrenza, A. Carrieri, F. Corbo

Dipartimento di Farmacia-Scienze del Farmaco, Università degli Studi di Bari "Aldo Moro", Via Orabona n. 4, 70125, Bari, Italy

carlo.franchini@uniba.it

One of the major problems we are facing today in the context of infectious diseases is the relentless increase and spread of antimicrobial resistance. Thus, studies for the identification of novel targets and drugs for the treatment of infectious diseases are at the forefront. We focused our attention on antimicrobials bearing a benzothiazole nucleus. In the past, our research group was interested in the study of a series of 2-mercapto-1,3-benzothiazoles (**1**) and the corresponding isosters, 2-amino-1,3-benzothiazoles (**2**). All the compounds were tested for their *in vitro* antimicrobial activity against bacteria strains and *Candida* species. Interestingly, the two series showed antibacterial activity against Gram positive and negative and/or antifungal activity, depending on the characteristics of the substituent at the 6-position of the aryl moiety.[1, 2,3] In general, we observed that the isosteric substitution of SH with NH_2 brought to the loss of activity against both Gram positive and negative bacteria, while, quite surprisingly, the compounds often exerted interesting antifungal activity. Basing on these positive results, we decided to study a new series of 1,3-benzothiazoles obtained by introducing a hydrazine moiety at position 2 of the aryl moiety (**3**). In order to improve structure-activity relationship studies on 2-amino-1,3-benzothiazoles new compounds belonging to this class were synthesized and tested as antimicrobials.



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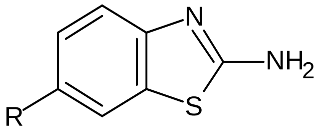

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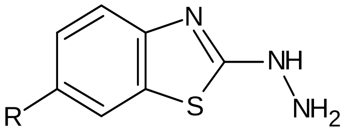

series **3**

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FAR-P27

Chromones as CYP11B inhibitors for the treatment of hormone-related diseases

Gobbi S.,[1] Hu Q.,[2] Rampa A.,[1] Belluti F.,[1] Hartmann R. W.,[2] Bisi A.[1]

[1]Department of Pharmacy and Biotechnologies, University of Bologna, Via Belmeloro, 6, I-40126 Bologna, Italy [2]Pharmaceutical and Medicinal Chemistry, Saarland University, P.O. Box 151150, & HIPS, D-66041 Saarbrücken, Germany

silvia.gobbi@unibo.it

Steroid hormones are known to play an essential role in the regulation of crucial physiological processes, but their abnormally increased levels have proved to be involved in the development of several hormone-related diseases. Thus, the search for inhibitors of cytochrome P450 (CYP) enzymes catalyzing the closely related biosyntheses of the different steroid hormones has gained researchers' attention during the past decades. Recently we focused on 11β-hydroxylase (CYP11B1) and aldosterone synthase (CYP11B2) as attractive therapeutic targets [1]. These enzyme isoforms, sharing a high degree of sequence homology, respectively catalyze key steps in the biosyntheses of cortisol, whose overproduction can cause diseases such as hypercortisolism and Cushing's syndrome[2] and aldosterone, involved in hypertension and cardiac diseases such as congestive heart failure or myocardial fibrosis [3].

In the search for potential ligands for these enzymes, and further exploiting the idea of flavonoid-like scaffolds as privileged structures, a small library of chromone derivatives carrying a pyridyl- or imidazolylmethyl substituent in positions 2 or 3 and small substituents in position 7 was designed. Some potent inhibitors were obtained, active in the nanomolar range in particular on CYP11B1, endowed with reasonable selectivity towards the related CYP11B2.

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[3] Brilla, C. G. *Cardiovasc. Res.* 2000**, 47** (1), 1-3.

FAR-P28

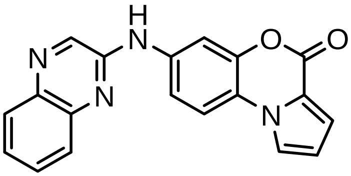
Identification of two novel benzo[*b*]pyrrolo[1,2-*d*][1,4]oxazin-4-one derivatives acting as GPER antagonists

Fedora Grande [a], *Silvia Avino* [a], *Maria Francesca Santolla* [a], *Francesca Aiello* [a], *Maria Grazia Perri* [a], *Camillo Rosano* [b], *Mariateresa Badolato* [a], *Filomena Vigliatore* [a], *Antonio Garofalo* [a], *Marcello Maggiolini* [a]

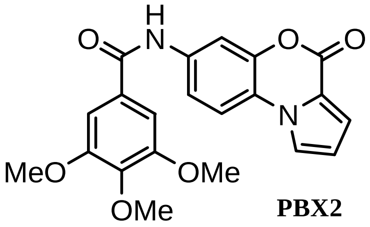
a Department of Pharmacy, Health and Nutritional Sciences,
University of Calabria, Rende (Cs), Italy
b U.O.S. Biopolymers and Proteomics - Irccs AOU San Martino,
IST-National Institute for Cancer Research, Genova, Italy

fedora.grande@unical.it

The G-protein estrogen receptor (GPR30/GPER) is implicated in a number of key cellular processes in both normal and malignant cells. In particular, the function of GPER has been associated with aggressive features of breast cancer. Currently, only a few compounds have been shown to act as GPER agonists or antagonists. On the basis of data obtained by docking simulations carried over the active site of the receptor with known ligands, we have designed a new class of potential antagonists with an aminopyrrolobenzoxazine moiety linked to a variable bulky aromatic nucleus. These compounds were prepared by reaction of newly synthesized 7-amino-4*H*-benzo[*b*]pyrrolo[1,2-*d*][1,4]oxazin-4-one with suitable chloro-derivatives. In particular, the quinoxaline and the trimethoxybenzoyl analogs, named **PBX1** and **PBX2** respectively, showed promising properties in preliminary tests on receptor and thus will be in-depth investigated by various *in vitro* assays.[1]



PBX1



PBX2

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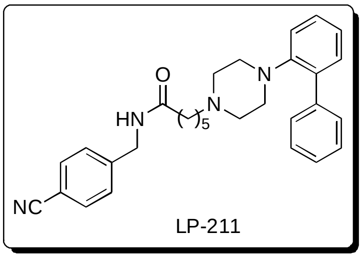
FAR-P29

Towards metabolically stable serotonin 5-HT$_7$ receptor ligands: structural modification of LP-211 and *in silico* prediction model

Enza Lacivita[a], *Mauro Niso*[a], *Sabina Smusz*[b], *Grzegorz Satala*[b], *Roberto Perrone*[a], *Andrzej J. Bojarski*[b], *Marcello Leopoldo*[a]

a Dipartimento di Farmacia-Scienze del Farmaco, Università degli Studi di Bari, Via Orabona, 4, 70125, Bari, Italy
b Department of Medicinal Chemistry, Institute of Pharmacology Polish Academy of Sciences, Smetna 12, 31-343, Kraków, Poland

enza.lacivita@uniba.it; *marcello.leopoldo@uniba.it*



LP-211

Serotonin 5-HT$_7$ receptors (5-HT$_7$Rs) are expressed in functionally relevant regions of the brain suggesting a role in many pathophysiological processes, such as depression, mood disorders, modulation of learning and memory [1]. During last years, our research group has been involved in the development of selective 5-HT$_7$ receptor ligands and the most relevant outcome is represented by LP-211, a brain penetrant selective 5-HT$_7$R agonist. However, LP-211 is transformed *in vivo* into the main metabolite 1-(2-biphenyl)piperazine that retains affinity for the 5-HT$_7$R [2]. Since the pharmacology of this metabolite has been poorly explored, it is unknown if its presence can revert or attenuate the action of the LP-211 *in vivo*. On such basis, the availability of novel 5-HT7R agonists with improved pharmacokinetic properties is desirable. Following this aim, we manipulated the chemical structure of LP-211 to improve overall pharmakocinetic properties, leaving unchanged the structural features that are responsible for affinity, selectivity and agonistic properties towards the 5-HT$_7$R. In parallel, machine learning methods have been applied to build an *in silico* model for the prediction of metabolic stability of the newly designed compounds.

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[2] Hedlund et al Neurosci. Lett. 2010, 481, 12-16.

FAR-P30

P1 Receptor Ligands: Design, Synthesis, and Biological Activity of New Adenosine Analogues

Catia Lambertucci, Michela Buccioni, Diego Dal Ben, Gabriella Marucci, Claudia Santinelli, Andrea Spinaci, Ajiroghene Thomas, Rosaria Volpini.

School of Pharmacy, Medicinal Chemistry Unit, University of Camerino, via S. Agostino 1, 62032 Camerino (MC) Italia

catia.lambertucci@unicam.it

The A_{2A} adenosine receptor ($A_{2A}R$) crystal structures allowed to know the specific interactions of the receptor with the co-crystallized ligands [1]. In particular, polar interactions are formed by the ligand with Asn253 and Glu169 residues, while the aromatic scaffold of the bound molecule forms π-stacking bonding with Phe168. Furthermore, water molecules are distributed in a network of reciprocal interaction and they play a role as a "bridge" in the ligand-receptor contact [2]. Comparative sequence analysis between the A_{2A} and A_3 subtypes shows that, among the residues mentioned above, only Phe168 and Asn253 are conserved in these receptors. In contrast, the Glu169 of $A_{2A}R$ is replaced by Val169 in the A_3R [3].

Based on these observations, an amino and alkylamino groups have been introduced at N^6-position of known A_{2A} ligands. New compounds were tested at human A_1, A_{2A}, A_{2B}, and A_3 receptors transfected in CHO cells. Preliminary results show that new derivatives present pronounced affinity and potency at the A_3R subtype and reduced interaction with the $A_{2A}R$, contrary to what had been expected. Surprisingly, these compounds behave as $A_{2A}R$ agonists but show an antagonist profile at the A_3R.

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[2] G. Lebon, T. Warne, P. C. Edwards, K. Bennett, C. J. Langmead, A. G. W. Leslie, C. G. Tate *Nature*, 2011, **474**, 521-525.
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FAR-P31

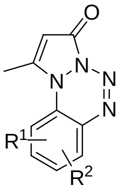
Pyrazolo[1,2-*a*]benzo[1,2,4]triazepin-3,6(7*H*)dione, a new ring system with antiproliferative activity

Francesco Mingoia [a], *Riccardo Delisi* [b], *Alessio Terenzi* [b],
Annamaria Martorana [b], *Anna Maria Almerico* [b], *Antonino Lauria* [b]

a Istituto per lo Studio dei Materiali Nanostrutturati (ISMN- CNR), Via U. La Malfa 153, 90146 Palermo, Italy.
b Dipartimento di Scienze e Tecnologie Biologiche Chimiche e Farmaceutiche (STEBICEF), Università di Palermo, Via Archirafi 32, 90123 Palermo, Italy.

antonino.lauria@unipa.it

Recently a new series of pyrazolo[1,2-*a*]benzo[1,2,3,4]tetrazin-3-one derivatives **1** have been synthesized and evaluated for their anticancer potential. Several of the new synthesized derivatives screened against more than 50 types of human tumor cell lines (NCI), showed promising antiproliferative activity reaching in some cases sub-micromolar values [1].



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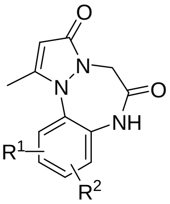

2

Furthermore, by optimization studies, new designed derivatives, effective on apoptosis induction, cell cycle arrest and antiproliferative activity, were proposed as new promising anticancer candidates [2]. Here, following our research interest on tuning the biological profile of pyrazolo fused tricycles, we planned to carry out a series of structural modification switching to the new ring system Pyrazolo[1,2-*a*]benzo[1,2,4]triazepin-3,6(7*H*)dione **2** in order to verify the electronic effect resulting from ring expansion. Therefore, in the present study, we designed and synthesized a set of eight new derivatives of type **2** containing selected functional groups. The preliminary NCI one dose screening (10 μM) evidenced moderate antiproliferative activity [GI%: 23 against SNB75 (CNS cancer); 18 against CCRF-CEM (leukemia); 15 against NCI-H322M (NSCLC)]. Further *in silico* optimization studies are in progress.

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[2] F. Mingoia et al, Eur. J. Med. Chem., 2013, 64, 345-356.

FAR-P32

Analytical tools for the identification of new synthetic drugs of abuse in seized material

Laura Mercolini [a], *Michele Protti* [a], *Marco Polito* [b], *Salvatore Sgrò* [b],
Lucia Maini [c], *Xavier Arnes Novau* [d], *Maria Augusta Raggi* [a]

[a] *Laboratory of Pharmaco-Toxicological Analysis,*
Department of Pharmacy and Biotechnology (FaBiT),
Alma Mater Studiorum - University of Bologna, Bologna (Italy)
[b] *Agenzia delle Dogane e dei Monopoli - DID Emilia Romagna-Marche -*
Laboratori e Servizi Chimici, Bologna (Italy)
[c] *Department of Chemistry "G. Ciamician",*
Alma Mater Studiorum - University of Bologna, Bologna (Italy)
[c] *Agencia Tributaria, Laboratorio de Aduanas, Barcelona (Spain)*

laura.mercolini@unibo.it

Drug addiction is one of the most alarming problems all over the world that, despite years of intense antidrug policies, does not seem to fade away. On the contrary, new emerging dangerous drugs of abuse are continually designed and synthesised to elude controls. The Laboratory of Pharmaco-Toxicological Analysis of the University of Bologna, in collaboration with "Agenzia delle Dogane e dei Monopoli" of Bologna, "Agencia Tributaria" of Barcelona and the Department of Chemistry of the University of Bologna, developed an effective analytical strategy to process an unknown white powder sample, seized by "Guardia di Finanza" of Bologna. Both qualitative and quantitative tests have been carried out by means of several combined analytical methodologies, based on LC-MS/MS, GC-MS, FT-IR, Single Crystal X-ray diffraction and X-ray powder diffraction. The active ingredient was found to be 4-Methylethcathinone (4-MEC), a very powerful stimulant and entactogen drug, belonging to the class of phenethylamines, quantified in approximately 70% by weight. The remaining 30% was found to be starch, used as cutting agent.

Analytical assays are now in progress on other suspicious specimens, like for example a new illicit product, marketed as "bath salts", recently seized at the Bologna "G. Marconi" airport. From some preliminary results, the crystals contain pentedrone, a stimulant synthetic molecule related to the class of cathinones. Further analyses are underway in order to assign the exact chemical structure and confirm the compound identity.

FAR-P33

Developing novel polyamine conjugates for selective anticancer therapy

Anna Minarini

Dipartimento di Farmacia e Biotecnologie, Alma Mater Studiorum-Università di Bologna,
Via Belmeloro 6, 40126, Bologna, Italy

anna.minarini@unibo.it

The holy grail of anticancer therapy is to deliver the cytotoxic agent to the cancer cell selectively and minimise the exposure to normal cells. Today there are several methods of targeting drugs to the appropriate site but many, such as monoclonal antibodies, are expensive and time consuming to develop.

In recent years, extensive research has been devoted to the design of anticancer-polyamine conjugates since it was shown that rapidly proliferating and cancer cells display elevated intracellular polyamine content linked to increased activity of a specific polyamine transport system (PTS).[1] Although, there is limited molecular knowledge regarding the identity and protein components of the PTS found in animal cells, it is known that the PTS is able to transport large substituent groups attached to a polyamine backbone. A successful example of the application of this strategy is the design of F14512, an etoposide-spermine conjugate, currently undergoing phase I clinical trials.[2] The spermine moiety of F14512 functions both as a target vector for etoposide and as a subsidiary DNA anchor, leading to a reinforced inhibition of topoisomerase II.

Our concept was therefore to use endogenous transport pathways that are up-regulated naturally in cancer cells to deliver novel cytotoxic intercalating agents[3] more effectively to these cells and to assess the efficacy of these agents in terms of cytotoxicity and epigenetic changes. Different polyamine chains have been used to make hybrid drug molecules or conjugates in order to improve both the cellular import and the affinity for DNA. This study should help to better characterise the PTS and identify the optimal structural requirements for polyamine binding to the transporter.

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FAR-P34

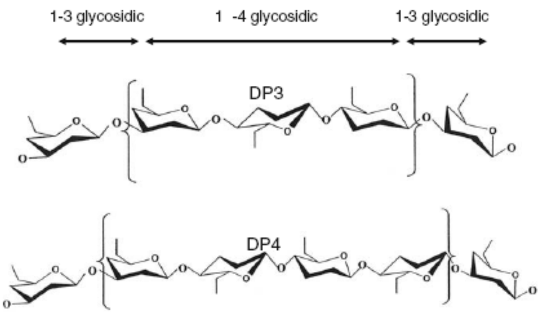
In vitro digestion of beta glucan enriched pasta and antioxidant potential of digesta

Alessandra Montalbano, *Patrizia Diana, Paola Barraja, Anna Carbone, Virginia Spanò, Barbara Parrino, Luisa Tesoriere, Alessandro Attanzio, Girolamo Cirrincione*

Dipartimento di Scienze e Tecnologie Biologiche e Farmaceutiche (STEBICEF), Università degli Sudi di Palermo,Via Archirafi 32 , 90123, Palermo, Italy

alessandra.montalbano@unipa.it

(1→3-1→4) Beta glucan is a linear polysaccharide endowed with a wide range of health benefits including lowering serum cholesterol, regulating blood glucose levels and conferring anti-cancer activities.[1] For this reason there has been a growing interest in beta glucan enriched food. A simulated oral, gastric and small intestinal digestion [2] of pasta enriched with 5% beta glucan was performed in order to assess the influence of pH and matrix enzyme degradation on stability and bioaccessibility of the polysaccharide. Beta glucans were assayed in post oral, post gastric and post intestinal (PI) digesta. Water soluble fraction (bioaccesible) derived from PI ultracentrifugation was isolated and its antioxidant capacity was studied through ABTS cation radical decoloration and Folin assays. With respect to not enriched pasta, the bioaccesible fraction of the beta glucan enriched one showed an antioxidant capacity 20% higher. Further details and results will be discussed.



[1] B. S. Ghotra, T. Vasanthan and F. Temelli *Food Research International*, 2008, **41**, 957-963.

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FAR-P35

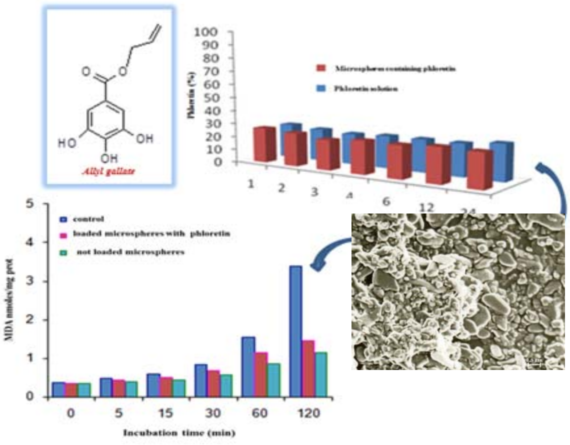
Preparation and biological activities of gallic acid-based microspheres for phloretin transdermal delivery

Roberta Cassano, Francesco Puoci, Nevio Picci, Sonia Trombino

Department of Pharmacy, Health and Nutritional Sciences, University of Calabria, Via Pietro Bucci , 87036, Rende, Italy

sonia.trombino@unical.it

Polymeric microspheres based on gallic acid, a molecule with antioxidant properties were prepared. The compound has a chemical structure with two different functional groups, carboxylic and oxydrilic, both susceptible of derivatization and so able to provide polymerizable derivatives. On the basis of these characteristics, microspheres potentially useful for the administration of phloretin, were obtained. Phloretin is a dihydrochalcone flavonoid found in green apples with many biological and pharmacological properties, such as potent antioxidant activity in scavenging radicals, inhibition of lipid peroxidation and antiproliferative effects. The new biopolymer was characterized by Fourier transform infrared spectroscopy. The content of phenolic groups were determined. Its ability in inhibiting lipid peroxidation in rat liver microsomal membranes, induced in vitro by a source of free radicals, that is tert-butyl hydroperoxide, was studied. The microspheres were also characterized for swelling the behaviour, phloretin loading efficiency and transdermal release.



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FAR-P36

Antihypertensive activity of *Polyphenolic* Compounds from Olive *Mill Wastewater*

Ortensia Ilaria Parisi[a,b], *Donatella Restuccia*[a], *Ivan Casaburi*[a], *Sonia Trombino*[a], *Roberta Cassano*[a], *Paola Avena*[a], *Nevio Picci*[a], *Vincenzo Pezzi*[a] *and Francesco Puoci*[a]

[a] *Dipartimento di Farmacia e SSN, Università della Calabria Edificio Polifunzionale , 87036 , Rende, Italia*

[b] *Dipartimento di Ingegneria Informatica, Modellistica, Elettronica e Sistemistica - DIMES, Università della Calabria, 87036 , Rende, Italia*

ortensiailaria.parisi@unical.it

As with other aspects of cardiovascular diseases, there is a reduced incidence of hypertension in populations that consume the Mediterranean diet, and adherence to the Mediterranean diet is inversely related to systolic and diastolic blood pressure[1]. Several studies have demonstrated the antihypertensive properties of olive oil. It was found, indeed, that intravenous administration of olive oil extract reduced systolic, diastolic, and mean arterial blood pressures in normotensive rats[2]. Epidemiological data from studies in three Mediterranean countries – Italy, Greece, and Spain – as well as non-Mediterranean countries, suggest a protective effect for monounsaturated fatty acids or olive oil, while non-Mediterranean countries show little or no positive effects[3].

Anyway, during olive oil production, large volumes of water are generated and subsequently discarded. Olives contain a variety of bioactive components, and some of them, according to their partition coefficients, end up in the water phase.

The current investigation aimed at evaluating the *in vitro* antihypertensive activity and other biological properties.

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FAR-P37

Enzyme immobilization on smart polymers: *catalysis on demand*

Giuseppe Cirillo[a], Fiore Pasquale Nicoletta[b], Manuela Curcio[a], Umile Gianfranco Spizzirri[a,], Nevio Picci[a], Francesca Iemma[a]*

a Department of Pharmacy, Health and Nutritional Sciences, University of Calabria, I-87036 Rende (CS), Italy
b Department of Chemistry and Chemical Technologies, University of Calabria, I-87036 Rende (CS), Italy

g.spizzirri@unical.it

A new approach for the synthesis of hydrogel films with thermo-sensitive enzymatic activity is reported. Pepsin (PEP) was covalently immobilized on thermo-responsive hydrogels by radical polymerization in the presence of N-isopropylacrylamide and poly-(ethylene glycol) dimethacrylate 750, acting as functional monomer and crosslinking agent, respectively [1]. Hydrogels showing lower critical solution temperatures between 32.9 and 36.1°C were synthesized by UV-irradiation of reaction batches differing in the PEP/monomers ratio. The derivatization degree was expressed as mg of PEP per gram of matrix and found to be in the range of 6 to 11% as assessed by Lowry method [2]. Using bovine serum albumin as a substrate, kinetics parameters were determined by Lineweaver–Burk plots and the catalyst efficiency evaluated [3]. Hydrogels with the highest water affinity at 25°C were found to be the most effective catalysts, with an efficiency reduction of only 27% with respect to the free PEP. Thermal stability experiments highlight he ability of the hydrogels to preserve the catalytic sites at temperatures above the LCST. The activity was recovered at room temperature and maintain for ten consecutive cycles. Thus, on-off devices could be manufactured and successfully employed in complex reaction batches requiring high temperatures without affecting the catalytic activity of enzymes.

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FAR-P38

Towards Tuberculosis Treatment with Next Generation BM635 Analogs

Giovanna Poce[a], Salvatore Alfonso[a], Martina Cocozza[a], Raquel Fernandez-Menendez[b], Lluis Ballel [b], Robert H. Bates[b], Scott G. Franzblau[c], Eric J. Rubin[d], Mariangela Biava[a]

a Dipartimento di Chimica e Tecnologie del Farmaco, Sapienza Università di Roma, piazzale Aldo Moro 5, 00185, Rome, Italy
bDiseases of the Developing World (DDW) Tres Cantos Medicines Develpment Campus (TCMDC) GlaxoSmithKline, Severo Ochoa 2, 28760, Tres Cantos Madrid, Spain
cDepartment of Medicinal Chemistry and Pharmacognosy, University of Illinois at Chicago, 833 S. Wood Street, IL 60612-7231, Chicago, US
dDepartment of Immunology and Infectious Diseases, Harvard School of Public Health, HIM 10484 Blackfan Cir, MA 02115, Boston, US

giovanna.poce@uniroma1.it

Despite enormous efforts have been made in the hunt for new drugs, tuberculosis still remains the first bacterial cause of mortality worldwide, therefore, new shorter and simpler drug regimens with bactericidal mechanism that differ from those of current drugs are needed. We have identified a class of 1,5-diphenyl pyrroles endowed with high antitubercular activity, whose hit compound was **BM212**. A hit expansion campaign, initiated for improving likeness to a drug, led to the optimized **BM635** that proved to be a highly potent anti-mycobacterial compound with MIC of 0.12 μM against virulent *M. tuberculosis* H37Rv, 15 times more potent than isoniazid (MIC, 1.8 μM). **BM635** was progressed to *in vivo* studies in an acute murine tuberculosis infection model. The resulting ED_{99} of 49 mg/kg, found for **BM635**, is within the range of commonly employed tuberculosis drugs, demonstrating the potential of this chemical series.[1] Here we describe the hit-to-lead chemistry process for identifying new analogs with improved potency, reduced off-target activities, and physiochemical/metabolic properties suggestive of reasonable *in vivo* pharmacokinetics. Moreover we describe the target identification and validation process applied for defining the molecular target for **BM212**.

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FAR-P39

New strategies for the analysis of synthetic cannabinoids in seized and biological samples

Laura Mercolini [a]*, Michele Protti* [a]*, Marco Zanella* [b]*,*
Marcello D'Elia [b]*, Maria Augusta Raggi* [a]

[a] *Laboratory of Pharmaco-Toxicological Analysis, Department of Pharmacy and Biotechnology (FaBiT), Alma Mater Studiorum - University of Bologna,*
Via Belmeloro 6 Bologna, Italy
[a] *Gabinetto Regionale di Polizia Scientifica dell'Emilia Romagna, Polizia di Stato,*
Via Volto Santo 3, Bologna, Italy,

mariaaugusta.raggi@unibo.it

In recent years law enforcement agencies and public opinion have witnessed a new phenomenon that is revolutionising the trends in drug abuse: a large number of new synthetic psychoactive substances are being added at an astonishing rate to traditional ones. Their regulation is problematic, as the efforts to control one chemical often lead to the diffusion of several other structural analogues.

A large part of these compounds, known as "designer drugs", is represented by synthetic cannabinoids, and in particular by JWH series, whose most popular compounds on the illegal market are JWH-018, JWH-073, JWH-081, JWH-200 and JWH-250.

In order to prevent and fight the diffusion and consumption of these new illicit drugs, it is useful to have at disposal reliable analytical methods able to carry out their identification and quantitation in unknown seized materials and in different biological samples (blood, urine, saliva and hair).

The aim of this study is the development of an analytical strategy for the fast identification of new synthetic cannabinoids by means of high resolution mass spectrometry, also coupled to liquid chromatography (LC-MS/MS) for quantitative purposes. This strategy involve an accurate study of characteristic fragmentation patterns, since the accurate selection of mass spectrometric parameters for the identification of specific fragments will lead to the discernment between structural analogues.

Moreover, the optimization of the chromatographic setup and the compilation of an in-house MS and MS/MS spectra database will be carried out in order to perform sound screenings of unknown compounds in seized materials and biological matrices.

FAR-P40

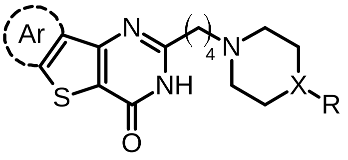
Thieno[3,2-*d*]pyrimidine as a scaffold for 5-HT$_7$ receptor ligands

Giuseppe Romeo[a], *Maria N. Modica*[a], *Loredana Salerno*[a], *Valeria Pittalà*[a], *Sebastiano Intagliata*[a], *Alfredo Cagnotto*[b], *Mario Salmona*[b], *Maria A. Siracusa*[a]

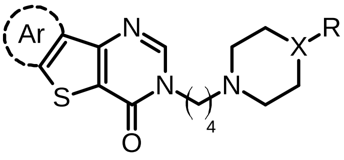
[a]*Dipartimento di Scienze del Farmaco, Università di Catania., Viale A. Doria 6, 95125, Catania, Italia*
[b]*IRCCS – Istituto di Ricerche Farmacologiche "M. Negri", Via La Masa 19, 20156, Milano, Italia*

gromeo@unict.it

The 5-HT$_7$ receptor (5-HT$_7$R) is the last member of the serotonin (5-HT) receptors family. It is widely diffused in the human body and it is particularly expressed in CNS. The 5-HT$_7$R plays a role in a number of physiologic functions and it seems to be involved in some CNS disorders, such as anxiety, depression, Fragile X syndrome [1]. Recently, evidences for its role in depression have been found: antidepressant action of the drug Amisulpride has been clearly linked to its potent antagonism at 5-HT$_7$R. In recent years, our research group has been involved in the development of new ligands for the serotonin 5-HT$_{1A}$ and 5-HT$_7$ receptors. In particular, compounds of the **A** type, based on the (benzo)thieno[3,2-*d*]pyrimidine scaffold and with an arylpiperazine moiety as terminal fragment on the side chain in the 2-position, behaved as good 5-HT$_7$R ligands [2]. Here we present the synthesis and the binding properties of a new series (**B**) of (benzo)thieno[3,2-*d*]pyrimidine compounds in which the side chain has been shifted to the 3-position. Some of novel compounds displayed improved affinity and selectivity for the 5-HT$_7$R over the 5-HT$_{1A}$R.



A



B

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FAR-P41

Monitoring of synthetic opioids in classical and alternative biological matrices for abuse evaluation

Maria Addolorata Saracino, Laura Mercolini, Michele Protti,
Agnese Samorì, Elena Capelli, Maria Augusta Raggi

Laboratory of Pharmaco-Toxicological Analysis, Department of Pharmacy and
Biotechnology (FaBiT), Alma Mater Studiorum - University of Bologna,
Via Belmeloro 6 Bologna, Italy

maria.saracino5@unibo.it

Synthetic opioids are widely used in the clinical practice to treat acute pain, to alleviate the severe disabling pain of terminal conditions (such as cancer) and to control the chronic pain of degenerative conditions (such as rheumatoid arthritis). Some drugs belonging to the class of synthetic opioids are also used in the treatment of heroin dependence. Fentanyl is a potent, synthetic analgesic opioid with a rapid onset and short duration of action, mainly used to induce anesthesia. Methadone is used as an analgesic drug and a maintenance anti-addictive and reductive preparation in opioid dependency treatments.

Some of these opioid drugs are also commercialized on the illegal market as drugs of abuse, generating a severe problem that adds to the already complicated reality of heroin addiction.

In order to contain and control this alarming phenomenon, it is evident the need for reliable, rapid and feasible analytical methods for the detection and quantitation of synthetic opioids in biological fluids from suspected abusers.

The matrices of choice for this purpose are whole blood and plasma, but the obvious limitations due to their invasive sampling and their complicated transportation and storage, have led to the development of alternative procedures, based on the use of innovative biological samples, such as Dried Blood Spots (DBS).

The aim of the present study is the development, validation and application of original analytical methods based on liquid chromatography coupled to spectrophotometric (HPLC-UV), spectrofluorimetric (HPLC-F) and electrochemical (HPLC-ED) detection, for the determination of fentanyl and methadone in classical and alternative biological matrices, thus monitoring those cases of illicit consumption.

FAR-P42

In silico investigation of a novel cyclic NDI derivative against duplex and G-quadruplex DNA

Carmine Talarico, Anna Artese, Giosuè Costa, Federica Moraca, Lucia Parrotta, Francesco Ortuso and Stefano Alcaro

[a] *Dipartimento di Scienze della Salute, Università "Magna Græcia" di Catanzaro, Campus "S. Venuta", Viale Europa, 88100 Catanzaro, Italia.*

carmine.talaricox@gmail.com

Over the last decades, a large number of telomeric G-quadruplex ligands have been extensively studied as promising anticancer drugs.[1] Recently, biological studies have revealed naphthalene diimides (NDI) derivatives as compounds provided with antiproliferative activity.[2] Moreover, linear molecules characterized by the NDI scaffold have been shown to intercalate into DNA. Subsequently, further structural modifications were applied in order to increase the specificity for G-quadruplex over duplex DNA. In this work, we present a molecular recognition study of a novel designed cyclic NDI derivative (Fig.1) against duplex and G-quadruplex DNA in order to evaluate its selectivity.[3] This protocol helped us to get further insight into the binding interactions of such molecule and to evaluate its thermodynamic profile.

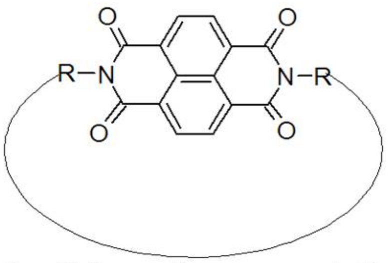
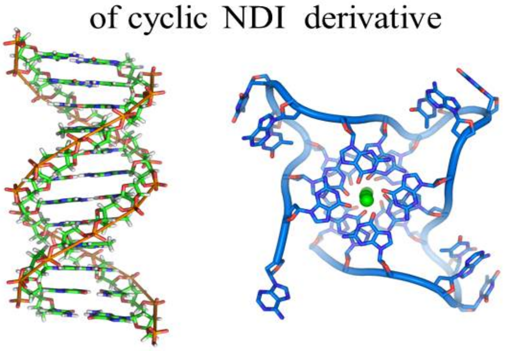


Fig. 1 – Schematic representation of cyclic NDI derivative



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FAR-P43

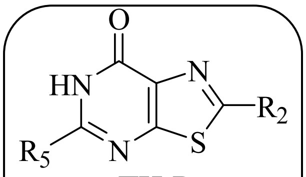
Exploring the 7-oxo-thiazolo[5,4-d]pyrimidine scaffold for the design of new adenosine A_3 receptor antagonists.

Flavia Varano[a], *Daniela Catarzi*[a], *Vittoria Colotta*[a], *Lucia Squarcialupi*[a], *Katia Varani*[b], *Diego Dal Ben*[c]

[a] *Dipartimento di Neuroscienze, Psicologia, Area del Farmaco e Salute del Bambino, sez. di Farmaceutica e Nutraceutica, Università di Firenze, Via Ugo Schiff 6, 50019, Sesto Fiorentino (FI), Italia*
[b]*Dipartimento di Scienze Mediche Istituto di Farmacologia, Università di Ferrara, via Fossato di Mortara 17-19, 44121 Ferrara, Italia*
[c]*Scuola di Scienza del Farmaco e dei Prodotti della Salute, Università di Camerino, Via S. Agostino 1, 62032 Camerino (MC), Italia*

flavia.varano@unifi.it

Adenosine is an endogenous nucleoside that mediates a wide range of physiological responses by interaction with specific adenosine receptors (ARs), namely A_1, A_{2A}, A_{2B} and A_3. ARs blockade results beneficial in several human pathologies. In particular, selective A_3AR antagonists could be useful in the treatment of ischemic and inflammatory diseases [1]. In our laboratory, much effort has been directed toward the development of new A_3AR antagonists belonging to correlated classes of heterocyclic compounds [2,3], such as the herein reported 7-oxo-thiazolo[5,4-d]pyrimidines **TH-P**. Preliminary binding results show that some of the newly synthesized **TH-P** derivatives possess A_3AR nanomolar affinities and a complete selectivity vs the other ARs. Molecular modeling analysis is in progress to interpret the obtained biological results.



TH-P

R_2 = arile, eteroarile
R_5 = CH_3, C_6H_5

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FAR-P44

New ligands for the dual receptor GPR17

*Rosaria Volpini, Michela Buccioni, Diego Dal Ben, Catia Lambertucci,
Gabriella Marucci, Claudia Santinelli, Andrea Spinaci, Ajiroghene Thomas*

*School of Pharmacy, Medicinal Chemistry Unit, , University of Camerino, Via S. Agostino 1,
62032 Camerino, Italy*

rosaria.volpini@unicam.it

The recently de-orphanized GPR17 is a peculiar G protein-coupled receptor showing a dual pharmacology. In fact, it is specifically activated by two unrelated families of inflammatory mediators: extracellular nucleotides and cysteinyl-leukotrienes, which are massively released upon different types of injury [1]. It has been recently reported that it is pathologically activated during acute CNS injury, thus contributing to early necrotic death inside the lesion, but in the days and weeks after injury, it may initiate cell repair mechanisms [1]. Hence, GPR17 may represent a novel target for human neurodegenerative diseases like stroke, trauma, and multiple sclerosis. Recently, it has been reported that 2-phenylethynylATP behaves as strong agonist ($EC_{50} = 0.036$ nM) of GPR17 while N^6-methylATP possesses antagonist behaviour [2]. Starting from these observations, new ATP analogues, including acyclic nucleotides, have been designed and synthesized. The new compounds were tested on GPR17 transfected cells by using an innovative and non-radioactive functional cAMP assay [3], where they proved to be potent ligands for the receptor. Hence, they could be efficacious tools for the further characterization of GPR17 and for studying its role in neurodegeneration processes.

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FAR-P45

Lupin peptides induce the LDL receptor / SREBP2 pathway at HEPG2 cell line

Carmen Lammi[a], *Chiara Zanoni*[a], *Graziana M. Scigliuolo*[2], *Alfonsina D'Amato*[3], *Anna Arnoldi*[a]

[a]*Department of Pharmaceutical Sciences, University of Milan, Via Mangiagalli 25, 20133 Milan, Italy;*
[b]*HPF-Nutraceutics SRL, Via Balzaretti 9, 20133 Milan, Italy,*
[c]*Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Polytechnic of Milan, Milan, Italy*

carmen.lammi@unimi.it

Lupin is a protein-rich grain legume, which provide some health benefits, particularly in the area of dislipidemia prevention. Previous experiments in suitable animal models and in mild hypercholesterolemic individuals have shown that the consumption of lupin proteins may be useful for controlling total and low-density-lipoprotein (LDL) cholesterol levels [1-2]. With the objective of providing evidences that peptides generated by the digestion of lupin proteins may be responsible of the observed activities and for investigating the mechanism of action, HepG2 cells were treated with lupin peptides obtained either by pepsin (P) or trypsin (T) hydrolysis and molecular and functional investigations were performed on the LDL receptor / SREBP2 pathway. For the first time, this report provides the experimental evidence that peptides obtained from the hydrolysis of lupin proteins are able to interfere with the HMGCoAR activity, up-regulating the LDL receptor and SREBP2 proteins via the activation of PI3K/Akt/GSK3β pathways and increasing the LDL-uptake at HepG2 cell line.

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FAR-P46

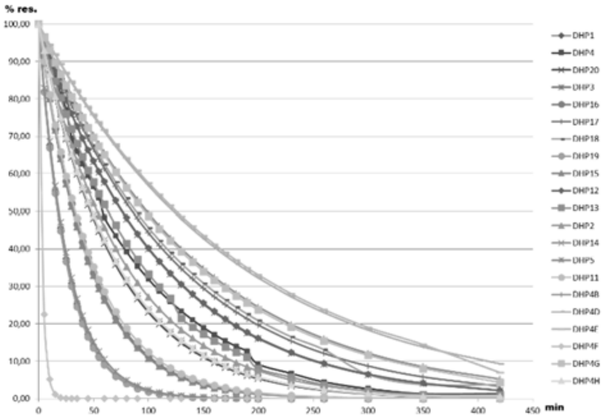
QSPR studies applied in the prediction of photosensitivity of 1,4-dihydropyridine drugs newly synthesized

Giuseppina Ioele, Michele De Luca, Roberta Rizzuti, Gaetano Ragno

Department of Pharmacy, Health and Nutritional Sciences,University of Calabria, 87036 - Arcavacata di Rende (Cs).

giuseppina.ioele@unical.it

A Quantitative Structure Property Relationships (QSPR) model is proposed to establish a mathematical correlation between the molecular structure and the light stability of 21 new 1,4-dihydropyridine compounds. These molecules are characterized by a high tendency to degradation when exposed under the light, furnishing in the most of cases a related oxidation product from aromatization of the pyridinic ring[1]. In the present work, photodegradation was forced in accordance with the ICH international rules[2], and degradation kinetics was monitored by spectrophotometric and MCR techniques. The photodegradation rate combined with a series of descriptors related to the chemical structures were computed by multivariate modeling analysis. The defined model could be used in the design of new and more photostable drugs as well as in the development of new photoprotective systems.



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FAR-P47

Conversion of simvastatin to their active metabolite for pharmaceutical and biochemical investigations

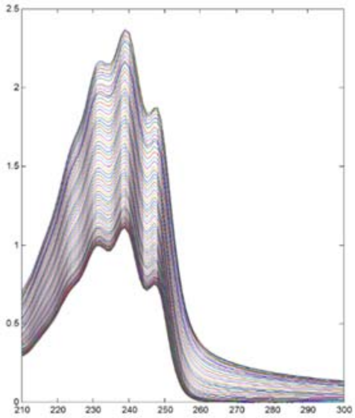
Michele De Luca, Emanuela Martello, Luigina Muto, Giuseppina Ioele, Anna Rita Cappello, Vincenza Dolce, Gaetano Ragno

Department of Pharmacy, Health and Nutritional Sciences, University of Calabria, Rende (CS), Italy.

michele.deluca@unical.it

Simvastatin is one of the best-known inhibitors of 3-hydroxy-3-methylglutaryl (HMG-CoA coenzyme A reductase) in the process of cholesterol hepatic biosynthesis, resulting in increased levels of the LDL receptor in hepatocytes and improved elimination of cholesterol from the receptors LDL. The drug is an inactive lactone (prodrug) that after oral administration is rapidly hydrolyzed in vivo to the corresponding hydroxyl acid derivative. The rate of hydrolysis of the lactone ring is pH-dependent and the conversion would be strengthened in alkaline solutions.

This paper studies the behavior of simvastatin hydrolysis at different pH levels to develop a method for the quantitative and kinetic determination of simvastatin and its metabolites in eukaryotic models, for pharmaceutical and biochemical investigations. The main target is an *in vitro* easy-to-use system for screening of others congener molecules. The study for individuate novel drugs are usually long and expensive to make necessary the use of laboratory animals, so an rapid and inexpensive method to screen new molecules could be of huge support for the clinical research. The proposed kinetic study could be used, in quick and effective way, to test many new natural or synthetic statin-like inhibitors.



FAR-P48

Synthesis and antiproliferative Activity of isoxazolo[3,4-*d*]pyridazin-7(6*H*)-one derivatives

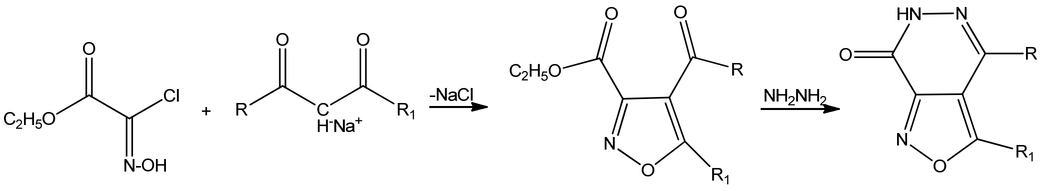
B. Maggio[a]*, G. Cancemi*[a] *, D. Raffa*[a]*, M. V. Raimondi*[a]*, F. Plescia*[a]*,*
S. Cascioferro[a]*, M. G. Cusimano*[a]*, M. Lauricella*[b]*, D. Carlisi*[b]*, G. Daidone*[a]

a Dip. STEBICEF, Università di Palermo, Via Archirafi 32, 90123, Palermo, Italy
c Dip. Di Biomedicina Sperimentale e Neuroscienze, Università di Palermo, Via del Vespro 129 , 90127, Palermo, Italy

giuseppe.daidone@unipa.it

A screening conducted by NCI (USA) on compounds available in our laboratory allowed to discovery 3,4-diphenylisoxazolo[3,4-*d*]pyridazin-7(6*H*)-one **1a** [1] as an hit compound with a good antiproliferative activity, with IC_{50} values often of sub-micromolar order.

We synthesized some analogs of this hit and also performed some molecular transformations with the aim to identify more potent agents and to understand which structural elements are important for the antitumor activity.



2 **3 a-g** **4 a-g** **1 a-g**

a: R= C_6H_5 R_1= C_6H_5; **b**: R= CH_3 R_1= CH_3; **c**: R= C_6H_5 R_1= CH_3; **d**: R= C_6H_4-CH_3 R_1= C_6H_4-CH_3;
e: R= C_6H_4-CH_3 R_1= C_6H_5; **f**: R= C_4H_3O R_1=C_6H_5 ; **g**: R= C_4H_3O R_1= C_6H_4-CH_3;

We identified another good antiproliferative compound, the 3,4-di(*p*-tolyl)isoxazolo[3,4-*d*]pyridazin-7(6*H*)-one **1d**, and ascertained the importance of the presence of aril, and not alkyl, groups on the isoxazolo-pyridazionone moiety for the antitumor activity. Studies on the cell cycle alteration and on some cellular target (ATM, procaspase-2 proteins and H2AX histone) demonstrated that **1d** is able to produce an increase of the cell population in S fase and to induce cellular death by apoptosis, probably damaging the DNA with double strand breaks. UV-vis titration, viscosity and circular dichroism measurements showed that the compound is able to give an interaction with the DNA double strand.

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FAR-P49

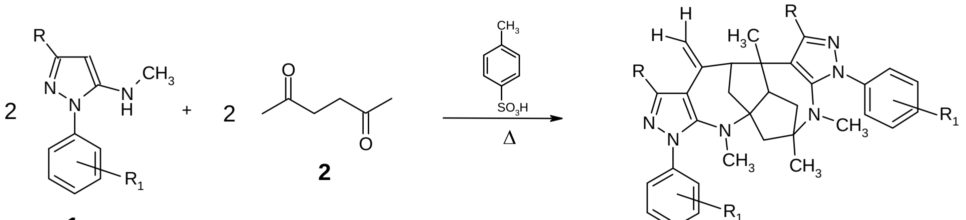
Synthesis and antiproliferative Activity of a natural like glucosyl polycyclic compound

B. Maggio[a]*, M.V. Raimondi*[a]*, S. Cascioferro*[a]*, M.C. Scherrmann*[b]*, N. Prosa*[b]*, M. Lauricella*[c]*, D. Carlisi*[c]*, and G. Daidone*[a]

a Dip. STEBICEF, Università di Palermo, Via Archirafi 32, 90123, Palermo, Italy
b Université Paris-Sud, ICMMO Bât 420, 91405 Orsay Cedex, France
c Dip. Di Biomedicina Sperimentale e Neuroscienze, Università di Palermo, Via del Vespro 129 , 90127, Palermo, Italy

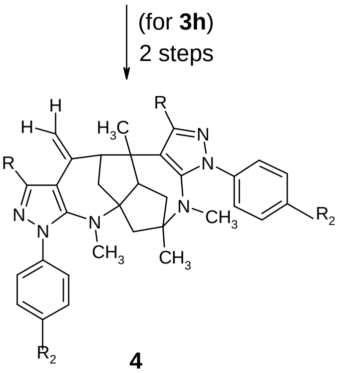
giuseppe.daidone@unipa.it

Previously we reported the synthesis of new polycyclic compounds **3a,g** [1]. Some of them resulted to be endowed with antiproliferative activity when tested against the NCI panel of human tumoral cell lines. In continuing the above research we prepared by Sonogashira reaction, starting from **3h,** the glucosyl derivative **4.** Compound **4** showed antiproliferative activity in the range 0.47-5.43 μM against all the tumoral cell lines of the NCI panel. Cytofluorimetric analyses performed on MDA-MB231 cells showed that **4** is able to induce cell cycle arrest at G2/M phase. Moreover, the compound induced morphological signs of differentiation, decreased the level of cyclin B1, a cyclin involved in G2/M transition, while increased the level of cyclin-dependent kinase (CDK) inhibitor p21WAF1.



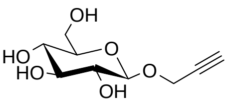
1a-g **2** **3a-h**

1,3	a	b	c	d	e	f	g	h
R	H	CH_3	Ph	CH_3	CH_3	CH_3	CH_3	CH_3
R_1	H	H	H	3-Cl	4-OCH_3	4-CH_3	4-Cl	4-I



4

4: R = CH_3, R_2 =



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FAR-P50

Contributo Ritirato

FAR-P51

Metallic core nano-devices as drug delivery systems

Licciardi M.[a], Palumbo F.S.[a], Mauro N.[a], Scialabba C.[a], Cavallaro G.[a], Giammona G.[a]

[a]*Dipartimento di Scienze e Tecnologie Biologiche Chimiche e Farmaceutiche*

mariano.licciardi@unipa.it

Metallic core nanoparticles (MCNPs) are core-shell systems of nanometric size containing both a therapeutic and/or a diagnostic agent physically loaded in a polymer coating. Among the potential applications, MCNPs are widely used for cancer diagnosis, for example MRI, and cancer therapy, being they are able to load high amount of drug avoiding toxicity and other painstaking side effects arising owing to high drug concentration in other body districts.[2] Among MCNPs gold NPs and magnetite (Fe_2O_3) have been successfully used for the above mentioned purposes. Magnetite is a very promising candidate as core material, being biocompatible and biodegradable.[3] In the nanometric size it exhibits superparamagnetic behavior, namely it is strongly magnetized when an external magnetic field is applied but no residual magnetization exists upon removal of the magnetic fieled.[2] Differently, gold nanoparticles have been proposed in cancer therapy for the photothermal therapy for the destruction of cancer cells or tumor tissue and tumor imaging.[3] Recently, superparamagnetic iron oxide and gold nanoparticles coated with biocompatible and functional copolymers have been prepared and characterized, and proposed as anticancer drug delivery systems.

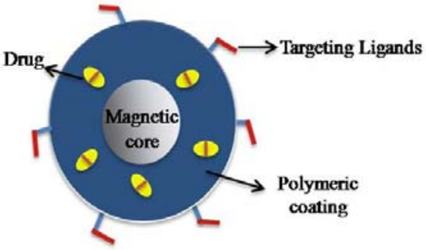

Figure 1. Schematic representation of a model MCNPs

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FAR-P52

Hyaluronic acid functionalized derivatives for the production of versatile biomaterials for regenerative medicine applications

F.S. Palumbo , M. Licciardi, C. Fiorica, F. Calascibetta, G. Pitarresi, G. Giammona

Dip. di Scienze Biologiche Chimiche e Farmaceutiche Università di Palermo

fabiosalvatore.palumbo@unipa.it

A series of functionalized hyaluronic acid (HA) derivatives have been designed for processing into biomaterials for regenerative medicine applications[1,2]. A patented chemical procedure[3] has been exploited to link as pendant chains to the HA backbone a) other extracellular matrix (ECM) polymers or short sequences simulating ECM cues, such as heparin, elastin or RGD peptides, b) hydrophobic chains. The functionalization with proteins (elastin, RGD peptides) improve HA cells adhesivity and mechanical properties. Moreover, the crosslinking process of the obtained derivatives with heparin produce hydrogels able to incorporate and control the release of heparin binding growth factors. The hydrophobic functionalization gives to the polymer self assembling properties exploited to obtain physically crosslinked biomaterials. Hydrophobic coils make such materials sensible to the ionic strength and to the presence of cyclodextrins and represent useful cargoes to entrap hydrophobic drugs. All these functionalized HA derivatives shows a greater versatility for processing strategies and are suitable for the production of scaffolds having ideal characteristics for cartilage regeneration and for stem cell culturing purposes.

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FAR-P53

Target-fishing applied to a new class of antifungal compounds

Giorgio Maccari[a], *Davide Deodato*[a], *Alexandru Casian*[a] *and Maurizio Botta*[a].

a Dipartimento di Biotecnologie, Chimica e Farmacia, Università di Siena, Via Aldo Moro 2, Cap 53100, Siena, Italia

giorgio.maccari@gmail.com

The epidemiology of fungal infections is an evolving issue since the late 1960s when, as a consequence of the development of antibiotic therapies, a drastic rise of mycoses was observed. Today, fungal infections represent a major global health threat and the increasing incidence of invasive and opportunistic mycoses is often associated with excessive morbidity and mortality. Fungal infections have increased in incidence during last decades often as a result of advanced medical treatments and of the increasing number of immunocompromised patients.

During studies on antifungal compounds we found that some macrocyclic amidinoureas derivatives were endowed with a good activity against wild-type and resistant *Candida* species.[1,2]

By using computational chemistry and biological assays we have identified chitinase as the biological target of our compounds. Chitin is the main component of the fungal cell wall, it is a polymer of N-acetylglucosamine (GlcNAc) with a β-1,4 linkage between monomers. Family 18 chitinases are the enzymes responsible for chitin degradation; they have been validated as a potential target for the design of new therapeutic agents active against fungal infections.

On the basis of these results we have prepared a new series of compounds with improved biological activity against clinical isolates of candida.

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FAR-P54

Synthesis of novel linear guanilated polyamines and macrocyclic aminidoureas

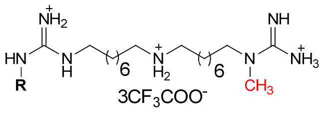
Alexandru Casian[a], *Giorgio Maccari*[a], *Maurizio Botta*[a,b]

a Dipartimento Biotecnologie,Chimica e Farmacia, Università degli Studi di Siena Via A. Moro 2, 53100, Siena, Italy

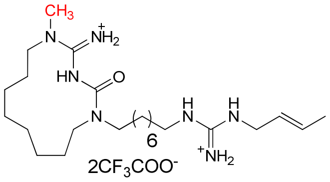
b Sbarro Institute for Cancer Research and Molecular Medicine, Center for Biotechnology, College of Science and Technology, Temple University, BioLife Science Bldg, Suite 333, 1900 N 12th Street, Philadelphia, PA 19122, USA

alexandru.casian@unisi.it

Guazatine (a mixture of guanidines and polyamines used in agriculture as fungicide) has demonstrated a very interesting behavior acting as a fungicide towards *albicans* and *non-albicans* Candida strains [1]. On the basis of such results, two natural components of guazatine, showing good antifungal activity toward Candida strains, were chosen as models for the synthesis of new linear and macrocyclic derivatives[2,3]. A very valuable information has been collected until now regarding the SAR studies performed on the linear polyamines and macrocycle amindinoureas compounds. The aim of the reported work was to obtain new derivatives by introducing a methyl group on one amino moiety that is part of guanidine function.



R= benzyl, propargyl, but-2-enyl, methyl cyclopropyl



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FAR-P55

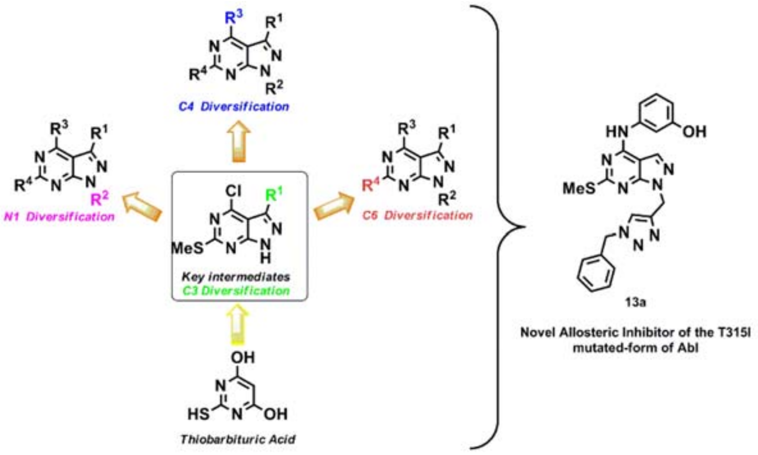
Exploring the chemical space around pyrazolo[3,4-*d*]pyrimidine scaffold: towards novel allosteric inhibitors of T315I-mutated Abl

Giulia Vignaroli [a], *Martina Mencarelli* [a], *Maurizio Botta*[a]

a Dipartimento di Biotecnologie, Chimica e Farmacia, Università degli Studi di Siena, Via Aldo Moro 2, 53100 Siena, Italy

giuliavignaroli@yahoo.it

A library of pyrazolo[3,4- *d*]pyrimidines, endowed with a high level of molecular diversity, has been developed applying a synthetic sequence that allowed C3, N1, C4, C6 substitution. The enzymatic screening of this 'privileged scaffold'- based compound collection, validated the use of a diversity-oriented approach in a field characteristically explored by target-oriented synthesis. In fact, several compounds showed high activity against the selected kinases (i.e. Src, Abl *wt* and T315I mutated-form), furthermore and interestingly a new compound has emerged as an allosteric inhibitor of the T315I mutated-form of Abl, opening up new opportunities for the development of a novel class of non-competitive inhibitors of Abl (T315I).



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Chimica Fisica

Keynote

CHF-K1

From hydrocarbons to solar energy: unfolding trends for chemistry

Nicola Armaroli[a]

Istituto per la Sintesi Organica e la Fotoreattività, Consiglio Nazionale delle Ricerche Via Gobetti 101, 40129, Bologna, Italy

nicola.armaroli@isof.cnr.it

The unprecedented improvement of the quality of life occurred in some regions of the world during the last century has been predominantly powered by fossil fuels, which still provide over 80% of our primary energy supply. This share has to be drastically reduced to curb the effects of a catastrophic climate change. The chief candidate to phase out the oil-gas-coal age is solar energy, which is available in several direct and indirect forms and is by far the most abundant, sustainable, and safe energy source we can rely on [1,2]. The transition to a solar-powered civilization will be a long and difficult process in which some key trends can be already envisaged: (1) growing share of electricity in energy end use [3]; (2) increase of efficiency in energy production [1,2]; (3) establishment of technologies for the manufacturing of solar fuels [4]; (4) recycling the equipment used for converting renewable energy flows that is often made of materials available in limited supply [5]. Solutions to the tremendous challenge of energy transition require the mobilization of huge human and economic resources in several scientific and technological fields, with chemistry playing a prominent role. In this broader context, some research results from our laboratories in the fields of materials for solar energy conversion and efficient lighting technologies will be illustrated [6,7].

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CHF-K2

Spectroscopic characterization of photosynthetic reaction centers embedded in ABA tri-block polymersomes

R. R. Tangorra,[a] *A. Operamolla,*[a] *F. Milano,*[b] *O. Hassan Omar,*[c] *J. Henrard,*[d] *R. Comparelli,*[b] *F. Italiano,*[b] *A. Agostiano,*[a,b] *G. M. Farinola,*[a,c] *and M. Trotta*[b]

[a] *Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro", Via Orabona 4 , 70125, Bari, Italia* [b] *Istituto per i processi Chimico-Fisici, Via Orabona 4, 70125, Bari, Italia;* [c]*, Istituto di Chimica dei Composti Organometallici, Via Orabona 4, 70125, Bari, Italia;* [d] *. Department of Chemistry and Namur Research College (NARC), University of Namur (UNamur), Rue de Bruxelles 61, Namur, Belgium*

r.tangorra@ba.ipcf.cnr.it

The highly efficient photoconversion ability of the photosynthetic molecular machinery is continuously spurring the assembly of artificial devices, using the photoconverting proteins for technological applications[1]. It is hence of paramount importance to have a robust, durable and versatile scaffold to be loaded with the integer and fully active photoconverter. In this communication, the photosynthetic reaction center (RC) from the bacterium *R. sphaeroides* R26 is reconstituted in synthetic block co-polymer vesicles where it retains its full functional activity. In particular, amphiphilic symmetric block co-polymer, based on poly(2-methyloxazoline)-poly(dimethylsiloxane)-poly(2-methyloxazoline) (ABA) self-assemble in water, forming the polymerosomes[2]. The protein loading of polymerosomes was obtained, for the first time, by using the so-called micelle-to-vesicle transition (MVT) method[3], a mild and highly biocompatible technique employed for membrane protein insertion in liposomes. Interestingly, spectroscopic and enzymatic data, directly obtained from the embedded protein, indicate that the RC tends to accomodate in the external portion of the ABA, *i.e.* the PMOXA facing the bulk solution rather than the expected random orientation in the central PDMS core. These organic vesicles show a photoactivity twice as large to the analogue phospholipid vesicles.

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CHF-K3

From Nano- to Mesostructures: Governing the hierarchical self-assembly of supramolecular architectures

Mariano Venanzi

Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Via della Ricerca Scientfica 1, 00133, Roma, Italia

venanzi@uniroma2.it

The building-up of supramolecular structures is determined by a complex interplay of dynamical and structural factors, including the interactions between the molecular building blocks, the differential solvation of monomeric and aggregated species, the presence of chemical groups giving rise to specific site-to-site interactions (aromatics, charged groups, hydrogen bonding donor-acceptor atoms). All these factors govern the formation of aggregates of different size and morphology (nanospheres, fibrils, nanotubes).

In this contribution we report on the aggregation properties of two classes of bio-inspired compounds that gather the two principal features that make Nanotechnology the privileged field of action of modern system chemistry: The well-established synthetic procedures that enable to endow molecular scaffolds with entirely new properties (the whole is smarter than the single components) and the knowledge of the structural and dynamical features that rule the aggregation of the components in the final supramolecular architecture.

In the first example we show that is possible to modulate the aggregation propensity of peptide foldamers, i.e. peptide assuming few specific constrained conformations, by varying length and composition of the peptide chain. We will also show that a single residue substitution dramatically changes the conformational landscape of the peptide building block and this effect propagates to nano- and mesoscopic dimension.[1]

In the second example, we describe how the suitable substitution of a porphryin scaffold can drive the mechanistic course of the self-assembly process, leading to amplification of physical properties, i.e. chirality, but also electric conductivity, to a mesoscopic scale.[2]

This bottom-up strategy is what enables the chemists to mark the route that leads from the very single molecule to millimetric fibers.

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CHF-K4

Cells meet organic devices: Something to learn from simulations

Marco Dallavalle, Francesca Lugli, Stefania Rapino, Francesco Zerbetto

a Dipartimento di Chimica "G. Ciamician", Universita' di Bologna, V. F. Selmi 2, 40126, Bologna, Italia

francesco.zerbetto@unibo.it

Neuro-electronics is a rapidly developing field that interfaces the living with electronic devices. In its simplest form it couples cells, actually neurons, to the working of devices such as transistors with the intent of modifying the response of the organisms themselves or of detecting some of their activities by the variation of the device response. Further complexity is added by the medium of operation necessary to keep the cells viable. The combination of these systems generates something that, by any standard, is exceedingly complicated to apprise quantitatively. And yet, in order to understand the overall behavior, simulations appear to be desirable. The issue is whether they are at all possible and if they are what can be done in terms of computer chemistry.

In this communication, I review the effort that is being carried out in my group aimed at understanding various features of the interaction of cells with organic surfaces and devices. Simulations are carried out at different levels of computational theory that include mesoscopic modelling and finite differences approaches. The collaboration with experimental groups is also described.

CHF-K5

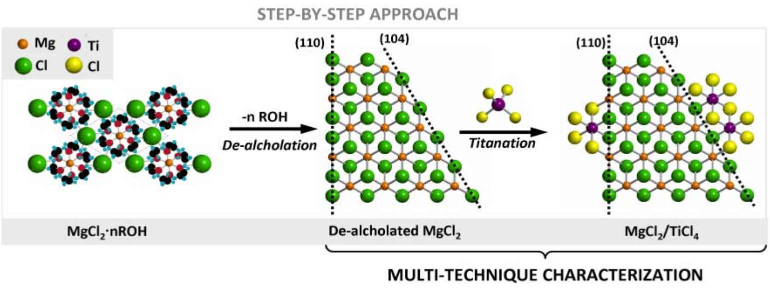
A new life for an evergreen: new experimental approaches for Ziegler-Natta catalysts

Elena Groppo[a], *Thushara K.S.*[a], *Alessandro Piovano*[a], *Kalaivani Seenivasan*[a], *Erik Gallo*[a], *Carlo Lamberti*[a], *Silvia Bordiga*[a]

a Dipartimento di Chimica, Università di Torino, Via Quarello 15, 10125 Torino, Italia

elena.groppo@unito.it

Covering still increasing volumes of the polyolefin production sector (that is approaching 150 MTons/year), heterogeneous Ziegler-Natta (ZN) catalysts are among the most productive and versatile catalytic systems in use in chemical industry. Their versatility can be traced back to the complexity of their chemical composition,[1,2] which consists of: i) the active phase, usually a transition metal halide of the 4th periodic table group; ii) a $MgCl_2$-based phase that increases the dispersion of the active phase; iii) electron donor molecules, which influence the selectivity in the α-olefins polymerization, and iv) the co-catalyst, usually an aluminum alkyl (such as AlR_3, R = alkyl chain). With nearly 80 years of history, this process is often considered as mature. Nonetheless, the structure of the active sites at a molecular level is far from being understood, and this hampers a rational design of new and more efficient catalysts. In this contribution it is shown that, although certainly well-established, there is still much room for new developments in the field of ZN catalysis. New experimental approaches are proposed, based on the synergic application of several characterization techniques (mainly spectroscopic), which have the potential to correlate the structure of the active sites at a molecular-level with the catalytic activity in olefin polymerization.[3] A step-by-step approach is followed. At first, the structural and surface properties of $MgCl_2$ supports obtained from de-alcholation of different $MgCl_2$-ROH adducts (R = MeOH, EtOH) are explored. In a second step, the interaction and reactivity of $TiCl_4$ with said $MgCl_2$ is investigated. Then, formation of active Ti sites through interaction with aluminum alkyls is examined and finally ethylene polymerization is followed in situ.



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Chimica Fisica

Oral

CHF-O1

Photocatalytic Hydrogen Production

Gian Luca Chiarello, Elena Selli

Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milano, Italy

gianluca.chiarello@unimi.it

Hydrogen can be photocatalytically produced mainly by two processes, *i.e.* either by the direct splitting of water into H_2 and O_2 [1], or by the photoreforming of organic compounds into H_2 and CO_2 [2]. Here, both routes will be presented.

Very active, high surface TiO_2 nanoparticles, also modified with noble metals and doped with fluorine, have been synthesized in continuous and single step by flame spray pyrolysis (FP) [3]. Their photoactivity was tested in an expressly set up, closed recirculation apparatus where the illuminated photocatalyst bed was continuously fed with methanol/water vapors. The FP-made materials showed an activity superior to that of commercial benchmark TiO_2. The rate of H_2 evolution increased upon noble metal addition on TiO_2, Pt being the most effective co-catalyst followed by Au and Ag, in line with their work function values. Indeed, noble metal nanoparticles are able to capture photopromoted electrons, thus increasing the efficiency of the electron-hole pairs separation. H_2 production rate was further improved by fluorine doping able to favor the indirect methanol photo-oxidation mechanism by increasing surface hydroxyl radical formation.

Moreover, separate production of H_2 and O_2 was obtained in a recently set up two compartment Plexiglas cell [1], which allows the simultaneous measurement of photocurrent. O_2 evolves from an illuminated thin TiO_2 layer, either deposited by radio frequency magnetron sputtering (RF-MS) or grown by anodization of a titanium foil, in contact with a NaOH solution, while H_2 evolves at the Pt counter electrode in contact with a H_2SO_4 solution. The rutile phase, predominant when TiO_2 was deposited at 600°C by RF-MS, appears in this case to be more active than the anatase phase, present in higher amount when deposited at 450°C, due to the better capability of the rutile phase to absorb light at longer wavelength.

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CHF-O2

Colloidal nanocrystals for energy conversion applications

R. Comparelli[a], *F. Petronella*[a], *A. Truppi*[a,b], *E. Binetti*[a,c], *A. Panniello*[a],
M.Striccoli[a], *A. Agostiano*[a,b], *M. Lucia Curri*[a] …

[a] *CNR-IPCF, U.O.S. Bari, c/o Dip. Chimica Via Orabona 4 70126 Bari*
[b] *Università degli Studi di Bari "A.Moro" Dip. Chimica Via Orabona 4 70126 Bari*
[c] *CNR-ICBM, Via Sommarive, 14, 38123 Trento,*

r.comparelli@ba.ipcf.cnr.it

Nanostructured wide band gap semiconductors (TiO_2, ZnO), are potential candidates for heterogeneous photocatalysis and energy conversion applications owing to their designable and tunable properties. Nonetheless, wide band gap semiconductors can be activated only by UV light, thus limiting the fraction of useful solar spectrum to ~4%. In addition, the efficiency of e^-/h^+ generation is affected by the competition between their undesired recombination and interfacial charge transfer. Current efforts in the field of designing and synthesis of photoactive materials aims at improving charge separation, inhibiting charge carrier recombination and enhancing the photoactivity in the visible region. Such goals can be achieved by suitably modifying the properties of the particles by surface treatments including surface modification of semiconductor particles with narrow band gap semiconductors, noble metals or doping with metal or non-metal ions.[1] We have investigated synthesis and characterization of nanostructured and shape controlled TiO_2-based photoactive materials and their application in photocatalysis and energy conversion. In particular, bifunctional catalysts have been prepared, namely TiO_2/CNTs, TiO_2/Ag, TiO_2/Fe_2O_3/Ag,. The obtained results point out the high photoactivity of nanosized catalysts and the possibility to shift their photoactivity in the visible range.[2-5]

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CHF-O3

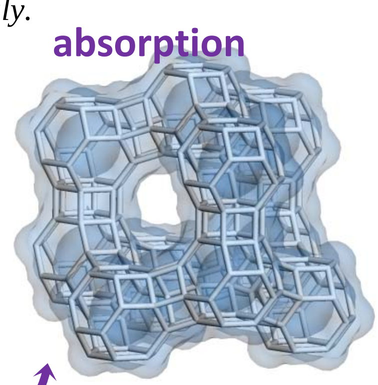
Carbon dioxide capture and recycling in microporous materials

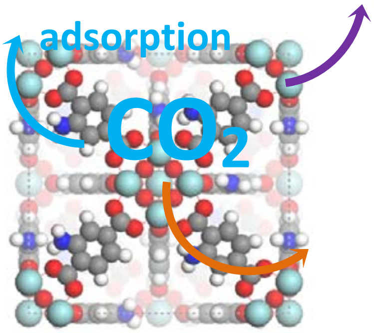
Jenny G. Vitillo[a,b], *Jayashree Ethiraj*[a], *Filippo Giordanino*[a], *Valentina Crocellà*[a], *Gabriele Ricchiardi*[a], *Elena Groppo*[a], *Marcello Baricco*[a], *Francesca Bonino*[a], *Sachin Chavan*,[c] *Silvia Bordiga*[a]

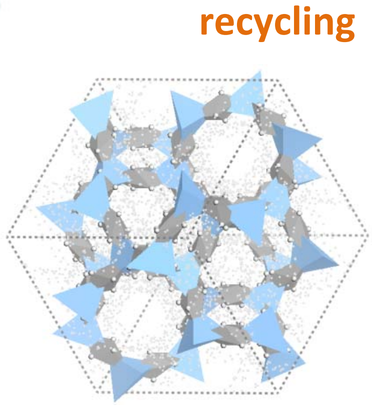
[a]*Dipartimento di Chimica, Università di Torino and NIS Centre, Via Giuria 7, I-10125 Torino, Italy.* [b]*Dipartimento di Scienza e Alta Tecnologia, Università degli Studi dell'Insubria, Via Lucini 3, 22100 Como, Italy.*
[c] *Department of Chemistry, University of Oslo, P.O. Box 1033, N-0315 Oslo, Norway*

jenny.vitillo@uninsubria.it

Carbon dioxide is generally recognized as the most important greenhouse gas. Its monotonic increasing trend is at the basis of the increasing research interest in materials that capture CO_2, either by physical ad-sorption or by dissociative chemi-sorption. Nevertheless, being the annual amount of CO_2 released of the order of gigatons [1], to find an effective way to reuse it as valuable chemical reagent is a key point in the global warming research. However, the low oxidation state of carbon strongly hinders CO_2 reactivity. In the present work, different original strategies aimed to increase the performances of materials used in all the steps of carbon dioxide recycling life are presented. In particular, the possibility to increase affinity of microporous materials for storage and separation toward CO_2 was explored by introduction of chemical functionally as amines and by metal oxide coating. In the end, the CO_2 reduction on a microporous phase of γ-$Mg(BH_4)_2$ is reported, showing high yield and unprecedented fast kinetics.







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CHF-O4

Porous and Layered Solids for the development of Innovative Quasi-Solid Electrolytes for DSSC Applications

Daniele Costenaro[a], Chiara Bisio[a], Giorgio Gatti[a], Toby B. Meyer[b], Michael Graetzel[c], Leonardo Marchese[a]

a Dipartimento Scienze e Tecnologie Avanzate, Università del Piemonte Orientale "A. Avogadro", Viale Michel 11, 15121 Alessandria, Italy
b SOLARONIX SA, Rue de l'Ouriette 129, Aubonne, 1170, Switzerland
c Laboratoire de Photonique et Interfaces, Ecole Polytechnique Fédérale de Lausanne, Station 6, CH-1015 Lausanne, Switzerland

chiara.bisio@unipmn.it

Dye-sensitized solar cells (DSSC) have attracted the interest of the scientific community for their potential high solar conversion efficiency and for the possibility to prepare devices with low cost materials and processes[1]. Recent studies have shown that the use of a gel- or quasi-solid electrolyte leads to a significant increase in energy-conversion efficiency and long term stability of DSSC type devices[2]. In our approach, solids with controlled properties and chemical composition were selected to understand the role of particles in final DSSC performances. Interesting results were obtained by using porous and layered materials as additives for DSSC electrolytes. Synthetic saponite-clay materials were prepared by hydrothermal treatment of a gel with various dilution conditions in order to obtain particle with size from *ca.* 200 nm to 50 nm and solids with different textural and surface properties. The addition of saponite in DSSC devices led to an increase of solar cell efficiencies up to 8% with respect to the reference cell[3]. Besides layered solids, silica-based materials with different structural properties (amorphous silica, monodispersed silica particles and ordered mesostructured silicas) are synthetized and modified with basic groups in order to decrease the recombination processes at the interfaces[4]. Interesting results were obtained by using functionalized materials as additives for DSSC electrolytes.

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CHF-O5

Chalcogenide thin film solar cells on flexible substrates

S. Binetti[a], *A. Le Donne*[a], *P. Garattini*[a], *S. Tombolato*[a], *R. Mereu*[a], *M. Meschia*[b], *M. Acciarri*[a]

a Milano-Bicocca Solar Energy Research Center (MIB-SOLAR), Dept. of Materials Science,
University of Milano-Bicocca, via Cozzi 55, Milano (Italy)
b Voltasolar s.r.l, Via dell'Artigianato 8, 22078 Turate, Como (Italy)

simona.binetti@unimib.it

In the frame of chalcogenide thin films for PV, Cu(In,Ga)Se_2 (CIGS) is the most promising in terms of record efficiency (i.e. 20.4 %, which is very near to that of Si solar cells) and stability. However, CIGS cost is still higher than that of Si since it relies on rare elements (i.e. In and Ga). Cu_2ZnSnS_4 (CZTS), in which In and Ga are replaced by low cost elements (i.e. Zn and Sn), is very promising in terms of reduced cost and sustainability. However, an intense research activity to optimize the growth process and the material quality is still necessary before transferring the device on the market.

The research activity at MIB-SOLAR is aimed at solving cost and sustainability problems of chalcogenide thin films. As far as the reduction of Watt peak cost of CIGS is concerned, a new low cost method for its deposition on flexible substrates has recently been developed, in collaboration with a small enterprise. This method relies on a hybrid sputtering-evaporation approach which provides a scalable process combining the advantages of both techniques. The cylindrical geometry of the deposition chamber can be exploited for a roll to roll process on flexible organic substrates. Both the absorber layers grown at 450°C on polyimide substrates and the solar cells based on them were systematically investigated by several techniques. The results revealed efficiency up to 12%, high deposition rates and good control of Ga grading and Na content, for further optimization. This method can be applied also to deposit CZTS films, however, the real low-cost potential of CZTS could be more efficiently exploited if combined with a scalable, non-vacuum deposition method. This work reports also on CZTS grown by dip coating of a solution of metals and thiourea followed by sulphurization treatment at temperature suitable for polyimide substrates.

CHF-O6

A complete study on synthetic analogues of anthocyanins as bio-inspired sensitizers for dye-sensitized solar cells

Giuseppe Calogero[a], Ilaria Citro[a], Antonio Bartolotta[a],Gaetano Di Marco[a], A. Sinopoli[b], Stefano Caramori[c], Carlo Alberto Bignozzi[c], Vesselin Petrov[d], Ana M. Diniz[d] A. Jorge Parola[d], Fernando Pina[d],

a CNR-IPCF, viale F. Stagno D'Alcontres 37, 98158, MESSINA, IT
b Dipartimento di Chimica, Università di Ferrara, Via L. Borsari 46, 44100 Ferrara, IT
c Department of Chemical and Biological Science, University of Huddersfield, Huddersfield, HD1 3DH., UK
d REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

calogero@me.cnr.it

Here we present a computational and spectroscopic study on a family of cheap, non-toxic, environmentally friendly flavylium sensitizers. We followed a bio-inspired strategy and with the adequate structural modifications of the 2-phenyl-1-benzopyrylium core (flavylium) prepared quasi-natural biomimetic dyes. With this strategy we prepared a series of new anthocyanin analogues. Among these, in the 7-(N,N-diethylamino)-3’,4’-dihydroxyflavylium (AD65),which is our best sensitizer, the diethylamine acts as an electron donor (D), the catechol moiety complexing with Ti(IV) in ring B behaves as an acceptor (A) and the benzopyran systems (rings A and C) constitute a π bridge defining a D–π–A structure similar to a “push and pull” sensitizer. More recently, with AD65 we obtained a solar conversion efficiency of 3.6% with an open circuit voltage of 0.4 V and a short-circuit current density of 16 mA/cm^2. In order to improve the DSSC performances, part of our strategy involves extending the absorption range to the near-IR regime in order to attain good overlap with the solar emission spectrum and to produce large photocurrent responses. So, with this aim, we introduced modifications in the flavylium backbone such as the so-called styrylflavylium and/or naphtoflavylium able to reduce the HOMO–LUMO energy gap of the sensitizer. We prepared and assembled all the DSSC’s components and fully characterized their photovoltaic performances.

CHF-O7

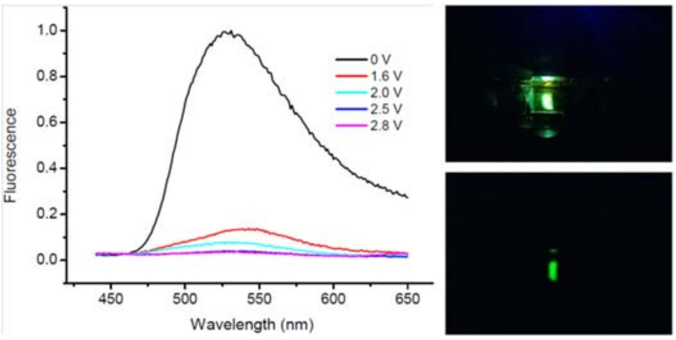
Gel polimerici elettrofluorocromici

<u>Sante Cospito</u>, Amerigo Beneduci, Massimo La Deda, Giuseppe Chidichimo

*Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabira, Via P. Bucci ,
87036, Arcavacata di Rende (CS), Italia*

sante.cospito@unical.it

L'elettrofluorocromismo (EFC) è un cambiamento ottico della fluorescenza causato dall'applicazione di campi elettrici.[1] Materiali, la cui fotoluminescenza può perciò essere modulata reversibilmente per via elettrochimica, sono potenzialmente impiegabili in display, sensori e memorie ottiche.[2] Tradizionalmente i dispositivi elettrofluorocromici (EFCD) si basano su architetture multistrato a base di polimeri semiconduttori e gel polimerici elettrolitici.[2-4] Qui presentiamo il primo esempio di EFCD a singolo strato basato su un gel polimerico contenente un tienoviologeno, il cui EFC è già stato investigato in fase liquido-cristallina.[5] L'applicazione di voltaggi sempre più riduttivi "spegne" l'emissione del materiale fino alla quasi totale scomparsa (vedi figura). Tale fenomeno è totalmente reversibile per migliaia di cicli di vita (fino a 5000). Il contrast ratio ($I_f/I_0 = 35$) tra i più elevati riportati in letteratura, i rapidi tempi di risposta ed un'eccellente efficienza di colorazione (CE = 560 cm^2 C^{-1}), uniti alla semplicità di processo e costruzione della cella, rendono questo materiale tra i più attraenti finora presentati.



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CHF-O8

pH-related features and photostability of 4-thiothymidine in aqueous solution: an investigation by UV-Visible, NMR, FT-IR-ATR and ESI-MS analysis

V. Rizzi[a], *I. Losito*[a,c], *A. Ventrella*[a], *P. Fini*[,b], *P. Semeraro*[a], *A. Agostiano*[a,b], *F. Longobardi*[a], *P. Cosma*[a,b]

a Università degli Studi "Aldo Moro" di Bari, Dip. Chimica, Via Orabona, 4- 70126 Bari, Italy
b Consiglio Nazionale delle Ricerche CNR-IPCF, UOS Bari, Via Orabona, 4- 70126 Bari, Italy
c Centro Interdipartimentale SMART, Via Orabona, 4- 70126 Bari, Italy

vito.rizzi@uniba.it

Sulphur modified nucleic acid bases or the corresponding nucleotides have been often employed to study protein–nucleic acid interactions, with the aim of determining the substrate specificity of various enzymes involved in nucleic acid metabolism [1]. Additionally, photo-crosslinking with modified oligonucleotides has been successfully applied in the mapping of ribosomes, ribozymes, and proteins [2]. Among other important applications of sulfur-containing nucleobases, the use of thiopurine prodrugs, such as azathioprine (Aza), 6-mercaptopurine (6-MP) and 6-thioguanine (6-TG), in the treatment of cancer, inflammatory conditions, viral diseases and in the therapy of organ transplant patients has been reported for almost five decades. In particular, more recently, *in vitro* and *in vivo* studies have indicated 4-thiothymidine as a promising photochemotherapeutic drug [3]. In spite of such amount of research involving 4-thiothymidine, only limited information is available on its behavior in an aqueous environment (representing a model system for more complex biological environments). A comprehensive investigation on this aspect has been thus carried out in our laboratories using several complementary techniques, namely UV-VIS, FTIR and 1H-NMR spectroscopies and ElectroSpray Ionization Mass Spectrometry (ESI-MS). The main results of this study will be the object of the present communication.

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CHF-O9

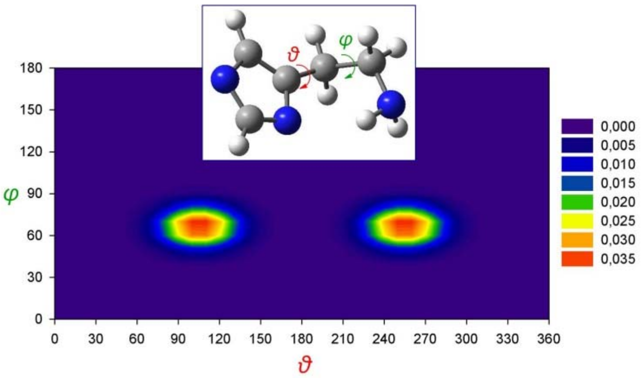
Probing the experimental conformational equilibrium of neurotransmitters by NMR in weakly ordering phases

Maria Enrica Di Pietro[a], *Giuseppina De Luca*[a], *Giorgio Celebre*[a]

a) Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Via P. Bucci, 87036, Rende (CS), Italy

mariaenrica.dipietro@unical.it

Neurotransmitters are key biological molecules ensuring a correct communication throughout our brain and body and changes in their levels are involved in multiple diseases. To rationalize their biological activity and design suitable analogues, a thorough understanding of the molecular spatial arrangement in solution is crucial. [1] To this end, NMR spectroscopy combined to the use of weakly ordering media can represent a valuable strategy, since the anisotropic dipolar interactions that influence the experimental spectra give access, *via* a proper theoretical treatment, to unique structural and conformational details. [2] This contribution report preliminary results found for a small biogenic amine neurotransmitter, ***histamine***, by combining the NMR analysis in the nematic PBLG/$CDCl_3$ phase [3] with the AP-DPD theoretical approach [4].



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CHF-O10

Laser ablation of fullerite in liquid by femtosecond laser source

Angela De Bonis[a], *Mariangela Curcio*[a], *Agostino Galasso*[a], *Jiulietta Rau*[b],
Antonio Santagata[c], *Roberto Teghil*[a]

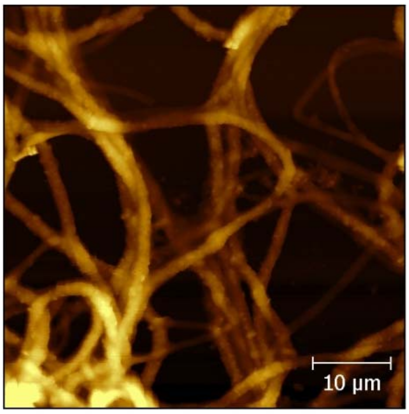
a Dipartimento di Scienze, Università della Basilicata, Viale dell'Ateneo Lucano, 10 85100,Potenza, Italy
b CNR - ISM, Via del Fosso del Cavaliere, 100 – 00133 Roma, Italy
c CNR-ISM, UOS Tito Scalo, C.da Santa Loja, Tito(Pz), Italy

angela.debonis@unibas.it

The laser ablation in liquid is a technique attracting a growing interest in the scientific and technological communities due to the possibility of obtaining stable nanoparticles in liquid media [1]. The ablation of carbon based targets is of particular importance due to the possibility to obtain different carbon allotropes by varying the experimental parameters [2].

We have investigated the ablation of a fullerite target in water and H_2O_2 by a femtosecond laser sources (Nd:glass 527nm, 250fs and 10 Hz), studying the ablation dynamic by shadowgraphic technique and the obtained products by transmission electron and scanning electron microscopies, by X-ray photoelectron and micro-Raman spectroscopies.

In particular, we report that during the femtosecond laser ablation the collapse of the fullerene cages can occur with the consequent formation of graphene oxide (GO) or reduced graphene oxide (r-GO) in H_2O_2 and water, respectively. Moreover, the self assembling of r-GO in solution and the formation of microtubes have been observed.



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CHF-O11

The effect of dopant lanthanide ions on the luminescent performances of lanthanum and gadolinium oxycarbonates

V. Caratto[1,2] *L. Panzeri*[3,4,] *M. Fasoli*[3], *M. Martini*[3,4], *I. Miletto*[5], *E. Bottinelli*[5], *E. Gianotti*[6], *F.Locardi*[1], *E. Sanguineti*[1], *M. Pani*[1] , *C. Artini*[1], *R. Masini*[7], *E. Franceschi*[1], *G. A. Costa*[1]

1 DCCI, University of Genova, Genoa. 2 DISTAV, University of Genova, Genoa 3Department of Material Science, University of Milano-Bicocca, Milan. 4INFN section of Milano-Bicocca, Milan. 5Department of Chemistry, University of Torino, Turin. 6Department of Science and Technological Innovation, University of Piemonte Orientale, Alessandria. 7CNR-IMEN, Genoa, Italy

caratto@chimica.unige.it

Compounds containing lanthanide ions are very attractive for application in the field of luminescence. A very interesting phenomenon, which can occur, is the persistent luminescence, in which the long-lasting emission of material persists for a long time after the removal of the excitation source. Promising compounds are the mixed rare earths oxycarbonates ($RE_2O_2CO_3$, RE=rare earth) and oxides (RE_2O_3, RE=rare earth) doped with one or more optically active lanthanide ions [1]. To date we successfully synthesized $Gd_2O_2CO_3$ and $La_2O_2CO_3$ in hexagonal form, doped with Eu^{3+},Sm^{3+}, Dy^{3+},Yb^{3+}, or Ho^{3+} which present interesting optical characteristics. All the samples were characterized by X-ray powder diffraction to confirm the obtainment of the hexagonal form for each composition. The aim was the study of how i) size, ii) crystalline phase, iii) nature of the host material, iv) nature and concentration of the dopant ion, influenced the UV-Vis-NIR absorption and luminescent properties of the materials. Gadolinium oxycarbonate doped with Yb^{3+} showed the phenomenon of persistent luminescence measurable up to 140 hours; moreover, the decay was independent of temperature [2]. Gadolinium oxycarbonate doped with Yb^{3+} was tested in vitro with biological molecules. This work is funded by Prin 2012.

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CHF-O12

Spectroscopic investigation of the pH controlled inclusion of Doxycycline and Oxytetracycline antibiotics in cationic micelles and their Mg^{2+} driven release

Cesaretti Alessio[a], *Catia Clementi*[a], *Benedetta Carlotti*[a], *Pier Luigi Gentili*[a], *Raimondo Germani*[a], *Fausto Elisei*[a]

Dipartimento di Chimica Biologia e Biotecnologie, Università di Perugia, Via Elce di Sotto 8, 06123, Perugia, Italia

catia.clementi@unipg.it

This work presents a steady-state and time-resolved UV-visible spectroscopic investigation of two antibiotics belonging to the family of tetracyclines (Doxycycline and Oxytetracycline) in the micellar medium provided by p-dodecyloxybenzyltrimethylammonium bromide (pDoTABr). The spectroscopic analysis have been performed in absorption and emission with femtosecond time resolution, and at pH 5.0 and 8.7 where Doxycycline and Oxytetracycline are present in their neutral-zwitterionic and monoanionic forms, respectively. The results unambiguously indicate that when Doxycycline and Oxytetracycline are in their zwitterionic form, they are entrapped within the micelle, while when they are in their monoanionic form, they preferentially show a strong one-to-one interaction with the positively charged surfactant heads. Thus, the pH of the solution controls the inclusion of the investigated drugs into the micelle by inducing an appreciable modification of their spectroscopic and dynamical properties after photo-excitation. Interestingly, the entrapped drugs are still able to strongly bind Mg^{2+} cations, crucial in determining the biological functioning of tetracyclines. The femtosecond resolved measurements reveal that the drugs are efficiently pulled out of the micelles by Mg^{2+}. In fact, magnesium-tetracyclines complexes are detected in the aqueous phase. The present study suggests the potential promising use of ammonium surfactants micelles embedding Doxycycline and Oxytetracycline as “smart” drug delivery systems allowing their pH controlled inclusion and Mg^{2+} induced release.

CHF-O13

Contributo Ritirato

CHF-O14

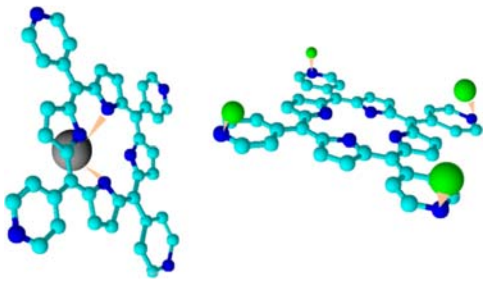
A Spectroscopic Investigation about the Selective Interaction of Mercuric and Cupric Ions with a Porphyrin Active Layer

S. Bettini,[a] *R. Pagano,*[b] *L. Valli,*[a] *and G. Giancane*[c]

a Department of Biological and Environmental Sciences and Technologies, DISTEBA, University of Salento, Via per Arnesano, I-73100 Lecce, Italy.
b Department of Engineering of Innovation, University of Salento, Via Monteroni, I-73100 Lecce, Italy.
c Department of Cultural Heritage, University of Salento, Via Birago 64, I-73100 Lecce, Italy.

gabriele.giancane@unisalento.it

The interaction mechanisms between a tetra-pyridyl substituted porphyrin and Hg(II) and Cu(II) ions have been investigated by means of different spectroscopic techniques. Investigations by means of reflection spectroscopy carried out on the porphyrin Langmuir floating film and by polarization modulation infrared reflection adsorption spectroscopy at the air-water interface evidenced the active role played by the pyridyl substituents of the porphyrin in the interaction with the analyte. Such a behavior seems to be very selective towards Cu^{2+} and Hg^{2+} ions, as demonstrated by the infrared measurements in difference mode. UV-Vis and IR characterizations suggest a deeply different interaction between the active molecules and the two analytes: in fact the interaction of Hg^{2+} ions with the tetrapyrrolic derivative molecules involves both the pyridyl substituents and the central bite of the ring [1]; on the contrary in the case of Cu^{2+} ions, spectroscopic evidences suggest that the cupric ions just interact with the porphyrin peripheral substituents. A relevant fluorescence quenching of LS film is observed when even a 0.5 nM $HgCl_2$ or a 0.5 nM of $CuCl_2$ aqueous solution is fluxed on the LS film.



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CHF-O15

Interaction between cyclodextrins (CDs) and textile dyes

Paola Semeraro[a], Paola Fini[b], Vito Rizzi[a], Angela Agostiano[a,b], Pinalysa Cosma[a,b], E. Franco[c], R. García[c], M. Ferrándiz[c], E. Núñez[d], J. Antonio Gabaldón[d], I. Fortea[d], E. Pérez[e], M. Ferrándiz[e]

[a] *Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro", Via Orabona 4,70126, Bari, Italia*

[b] *Dipartimento di Chimica, Consiglio Nazionale delle Ricerche CNR-IPCF, UOS Bari, Via Orabona 4, 70126 Bari, Italia*

[c]*Biotechnology Department. Textile Industry Research Association (AITEX), Plaza Emilio Sala, 1- 03801 Alcoy, Spain*

[d]*Departamento Ciencia y Tecnología de Alimentos, UniversidadCatólica San Antonio de Murcia, Avenida de los Jerónimos s/n, 30107 Guadalupe, Murcia, Spain*

[e]*Colorprint Fashion, SL, Avda. Fco. Vitoria Laporta, s/nApdo. Correos 104, 03830 Muro de Alcoy (Alicante), Spain*

pinalysa.cosma@uniba.it

Textile industry is one of the most pollutant ones employing high quantities of water containing a variety of chemical pollutants, among which the most important are textile dyes. Azo ones are known to be very toxic and mutagenic for living organisms, thus treatment of wastewater containing dyes is one of the most important ecological problems. In this view cyclodextrins (CDs) appear useful having an high capacity to include guest molecules, herein dyes, in their cavities [1]. Consequently the goal (objectives of an European project of the LIFE+ Program named DYES4EVER (Demonstration of cyclodextrin techniques in treatment of waste water in textile industry to recover and reuse textile dyes) of this work is a comprehensive investigation of host-guest interaction types by means of spectroscopy techniques, by Differential Scanning Calorimetry and Cyclic Voltammetry.

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CHF-O16

Structural modification of proteins adsorbed on silica nanoparticles: effect of the surface functionalization

G. Alberto, *F. Catalano, G. Martra*

Department of Chemistry and NIS Interdepartmental Centre, via P. Giuria 7, 10125 Torino (Italy)

gabriele.alberto@unito.it

The biological response elicited in cells by a material is strongly affected by the conformation, density and orientation of plasma proteins that adsorb on its surface, actually constituting new "bioactive sites" available for the interaction with cellular receptors [1]. Type and extent of possible conformational changes in adsorbed proteins depend, in turn, on the peculiar physical-chemical surface properties of the materials. In these respect the events occurring after the interaction of Bovine Serum Albumin (BSA), which represent the major constituent (60%) of the serum proteins, with omogeneous spherical pure (hydroxyl-rich) silica and ammine-functionalized silica nanoparticles were investigated by two main complementary approaches: the measurement of the adsorbed amounts and the investigation of the structure of adsorbed proteins.

In order to quantitatively asses the degree of surface covering, the surface area actually available for protein adsorption for both materials was determined by studying the agglomeration state of NPs when suspended in protein solutions (Dyamic Light Scattering and ζ potential measurements). As for the structural investigation of the interface layer, complementary spectroscopic techniques sensitive to different levels of the protein structure were used: modifications of secondary structures were investigated by CD-UV, whereas features of aromatic aminoacids residues were investigated by photoluminescence spectroscopy.

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CHF-O17

Hydrogel composite membranes for protein crystallization

S. Majidi Salehi[a,b]*, E. Fontananova*[a]*, E. Curcio*[b]*, E. Drioli*[b]*, R. Caliandro*[c]*, B. D. Belviso*[c]*, G. Di Profio*[a]

(a) Institute on Membrane Technology, National Research Council of Italy, Via P. Bucci c/o, Cubo 17/C, 87036 Rende (CS), Italy.
(b) Department of Environmental and Chemical Engineering, University of Calabria, Via P. Bucci Cubo 45/A, 87036 Rende (CS), Italy.
(c) Institute of Crystallography, National Research Council of Italy, Via G. Amendola 122/o, 70126 Bari, Italy.

g.diprofio@itm.cnr.it

Combination of polymeric hydrogel materials and porous membranes, which leads to composites with stimuli responsive properties, has been increasingly prevalent in the field of membrane separations [1]. In protein crystallization, hydrogel composite membranes are used as heterogeneous growing media to provide the suitable environment for the formation of crystals with greater size, fewer effects and enhanced diffraction properties [2]. Among different preparation methods, photo-initiated grafting of hydrogel onto a porous support has a much interest due to low cost, mild reaction conditions, selectivity to absorb UV light without affecting the bulk polymer [3]. In this work, preparation of hydrogel composites based on polypropylene and polyethersulfone membranes, via photo-initiated graft polymerization, has been investigated. Acrylic acid and 2-Hydroxyethyl methacrylate as functional monomers and Ethylene glycol dimethacrylate as a crosslinker have been used. The effect of monomer concentration, monomer mixture composition and UV irradiation time on composites preparation has been studied. Furthermore, the performance of prepared hydrogel membranes in membrane protein crystallization was evaluated.

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CHF-O18

Formation and self-assembly of long polypeptides on oxides: from prebiotic to fine chemistry

G. Martra, C. Deiana, Y. Sakhno, P. Ivanchenko, M. Fabbiani

Department of Chemistry and Interdepartmental Centre ''Nanostructured Interfaces and Surfaces-NIS'', University of Torino, via P. Giuria 7, 10125 Torino, Italy

gianmario.martra@unito.it

The polymerization of amino acids under abiotic conditions is among the topics addressed when investigating the origin of life. Since the seminal Bernal's hypothesis, the possibility of mineral surfaces acting as adsorbents for amino acids and as catalysts for their condensation to form peptides has been considered [1]. However, the following issues remain unresolved: i) the limited extent of the catalytic oligomerization (up to 6 monomers) when unactivated amino acids are considered and ii) the mobility of the oligomers on the catalytic surface to form organized structures. Here, we report on the first observation of the sequential occurrence of catalytic formation of polypeptides (poly-Gly) up to 16 or 11 units long on TiO_2 or SiO_2 surfaces, respectively, via successive monomer feedings from a vapor phase, and self-assembling of the formed polypeptides into closely packed aggregates containing both helical and β-sheet-like patches by subsequent hydration [2]. Such effective catalytic action of the oxides considered stimulated the interest towards the investigation of the surface reaction mechanism. The activation of carboxylic groups towards amidation by interaction with the surface of ionic-covalent oxides was then disclosed [3], as well as the possibility to exploit this catalytic effect in an innovative, sustainable synthesis of molecules of pharmaceutical interest (ca. 65% of drugs contains at least one amide bond) [4].

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CHF-O19

Shear-induced Multilamellar Vesicles

Luigi Gentile[a,b]*, Giuseppe A. Ranieri*[a]*, Norman J. Wagner*[c]*, Ulf Olsson*[b]

a Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Pietro Bucci 12C, 87036, Arcavacata di Rende (CS), Italia

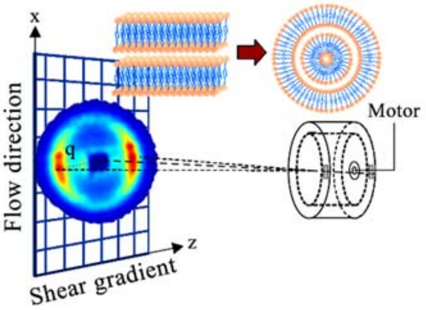
b Department of Chemistry, Division of Physical Chemistry, Lund University, Getingevägen 60, 87036, SE-221 00 Lund, Sweden

c Department of Chemical and Biomolecular Engineering, University of Delaware, Academy Street 150, 19716, SE-221 00 Newark, Delaware, USA

luigi.gentile@unical.it

In the lamellar phase (Lα), surfactants are organized in essentially flat and infinite bilayers, which are stacked with one-dimensional order with a thickness of the water-layer in the order of nanometers. In many systems, these layered structures are found to be unstable under shear flow and the structure transforms to multi-lamellar vesicles (MLVs), also called "onions" [1].

By means of rheology, rheo-Nuclear Magnetic Resonance, rheo-Small Angle Light and Neutron Scattering we are able to describe in details the formation mechanism of the MLV in model systems based on nonionic polyoxyethylene alkyl ether surfactants (C_nE_m). The mechanism details are coming mainly from a novel small angle neutron scattering sample environment that enables tracking the lamellae alignment in the velocity-velocity gradient (1-2) [2] plane during MLV formation, which was tracked independently using flow small angle light scattering commensurate with rheology. During the lamellar-to-multilamellar vesicle transition the primary Bragg peak from the lamellar ordering was observed to tilt and this gradually increased with time leading to an anisotropic pattern with a primary axis oriented at ~25° relative to the flow direction [3].



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CHF-O20

Membranes for Human Bioengineered Skin Substitutes

S. Salerno[a], A. Messina[a], A. Bader[b], E. Drioli[a] and L. De Bartolo[a]

[a]*Institute on Membrane Technology, National Research Council of Italy, ITM-CNR, c/o University of Calabria, Via P. Bucci, cubo 17/C, I-87030 Rende (CS), Italy*
[b]*Biomedical-Biotechnological Center, BBZ, University of Leipzig, Germany*

l.debartolo@itm.cnr.it

The realization of bioengineered skin substitutes is a major issue to restore functional and esthetical integrity from diseases and to develop *in vitro* skin models for toxicological tests. Polymeric semipermeable membranes are able to support cell adhesion and growth, providing a selective transport of nutrients and metabolites. In this study we investigated biodegradable membranes of chitosan (CHT), polycaprolactone (PCL) and a synthetic blend of CHT-PCL prepared by phase inversion process for the regeneration of human bioartificial skin equivalents. Membranes were characterized in order to evaluate the biodegradability, morphological and physico-chemical properties, which are important in the cell interactions. Human epidermal, dermal, and dermal/epidermal substitutes were realized on all the developed membranes by culturing human keratinocytes and human dermal substitutes in homotypic and organotypic systems. Membranes display different surface properties that affected cell adhesion and proliferation. In particular, the different functional groups and surface wettability influenced the skin regeneration by modulating the cell proliferation and influencing the differentiation towards a specific skin layers (fig.1). These bioengineered constructs provide an interesting approach for manipulating in vitro skin tissue reconstruction providing a valid tool for therapeutic and drug-screening applications.

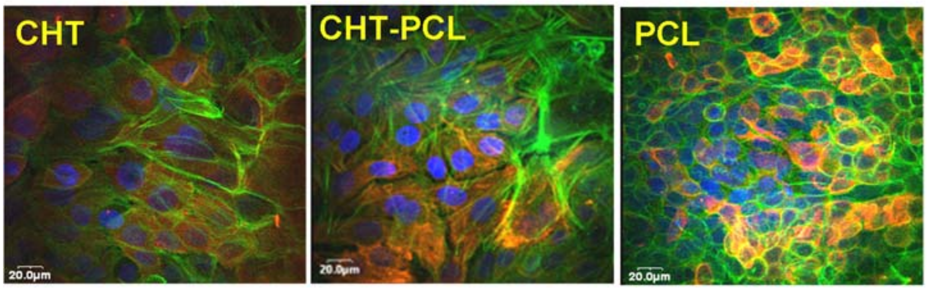

Fig. 1 Differentiation of specific epidermal layers on different membranes: outermost layers on CHT and CHT-PCL and complete proliferative layers on PCL.

CHF-O21

Computational methods to determine peptide orientation in membranes

A. Farrotti[a], *G. Bocchinfuso*[a], *A. Palleschi*[a], *N. Rosato*[b], *B. Bechinger*[c], *L. Stella*[a]
a Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Via della ricerca scientifica Snc, 00133, Roma, Italia
bDipartimento di Medicina Sperimentale e Chirurgia, Università di Roma Tor Vergata, Via Montpellier 1, 00133, Roma, Italia
cIstituto di Chimica, Università di Strasburgo,F-67000, Strasburgo, Francia

stella@stc.uniroma2.it

Molecular dynamics simulations represent a powerful tool to characterize the interactions between membrane-active peptides and lipid bilayers, but suffer from sampling problems due to their relatively short time-lengths. In order to overcome time-scale limitations, we carried out simulations with different methods: the "minimum-bias" approach [1,2], performed both with an all-atoms (AA) and a coarse-grained (CG) force-field, and potential of mean force (PMF) calculations. We used these methods to determine the position of the artificial antimicrobial peptide LAH4 in a POPC membrane. As demonstrated by solid-state NMR experiments, the presence of four His residues in its sequence allows LAH4 to change its orientation in the bilayer from in-plane to transmembrane, by increasing the pH from acidic to basic values [3]. In both AA and CG "minimum-bias" simulations, the peptide inserted in the membrane when its His residues were neutral, while charged His side-chains interacted with phospholipid headgroups. Similarly, free-energy profiles for the insertion of LAH4 into the bilayer, obtained with PMF calculations, revealed a deep free-energy minimum in correspondence of the bilayer center for LAH4 with neutral His. On the contrary, the free energy profile of charged His LAH4 exhibited a maximum in the same position. In conclusion, we determined the expected membrane-inserted orientation for neutral His LAH4. By contrast, while some inserted structures were observed also for LAH4 with charged His, this peptide showed a greater propensity to interact with the bilayer surface.

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CHF-O22

Sorption of organic pollutants onto natural zeolites: isosteric and standard enthalpy

V. Leone, P. Iovino, S. Salvestrini, S. Capasso

Department of Environmental, Biological and Pharmaceutical Sciences and Technologies,
Second University of Naples, Via Vivaldi 43, 81100 Caserta, Italy

stefano.salvestrini@unina2.it

Thermodynamic parameters of sorption processes give fundamental information on the mechanisms involved and are essential data for the design and management of sorption/desorption plants. Here, we report a study of equilibrium sorption of some non-ionic organic pollutants (benzyl alcohol, toluene, phenol, cyclohexanol and cyclohexane) onto a zeolitic tuff rich in phyllipsite and chabazite minerals (PCT). Details of PCT chemical and mineralogical composition are in Capasso et al. [1]. Sorption experiments were carried out in batch at four different temperatures.
The sorption isotherms for toluene (Fig. 1a) and cyclohexane show that PCT is an effective sorbent for these hydrocarbon compounds; on the contrary, the PCT sorption capacity for hydroxyl compounds (phenol, cyclohexanol and benzyl alcohol) was of the same order of magnitude as the experimental errors.

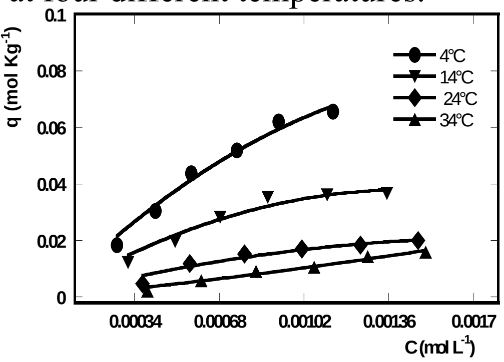

Figure 1: (a) Sorption isotherms for toluene onto the zeolitic tuff at the temperatures indicated.

Plots of the logarithm of the equilibrium concentrations in solution against 1/T at constant amount sorbed allowed to calculate the isosteric enthalpies of sorption [2]. Extrapolation at zero amount sorbed gave the standard enthalpy of sorption.
The results indicate that sorption on PCT is exothermic and the interaction energy between non-hydroxyl compounds and tuff decreases with the amount sorbed.

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CHF-O23

Nb(V)-containing saponite clay: a catalyst for the oxidative abatement of chemical warfare agents simulants

Chiara Bisio,[a,b] Fabio Carniato,[a] Rinaldo Psaro,[b] Leonardo Marchese,[a] Matteo Guidotti[b]

[a]Dipartimento di Scienze e Innovazione Tecnologica, Università del Piemonte Orientale "Amedeo Avogadro", Viale T. Michel 11 – 15121, Alessandria, Italia. [b]CNR-Istituto di Scienze e Tecnologie Molecolari, Via C. Golgi 19, 20133 Milano, Italia

fabio.carniato@mfn.unipmn.it

The oxidative abatement of pollutants and toxic chemical warfare agents (CWA) is conventionally achieved via stoichiometric reactions based on the use of strong oxidants with high environmental impact or via thermal degradation. In this work, a class of heterogeneous catalysts able to promote selective oxidation of toxic organosulfur chemical agents into non-noxious products with reduced environmental impact is proposed. A novel Nb(V)-containing saponite clay (Nb-SAP) was identified as potential catalyst for the CWA oxidative abatement. The synthesis method was modified to allow the insertion of Nb(V) ions within the inorganic framework, thus obtaining a bifunctional catalyst with strong oxidizing properties[1] and acid character.[2] This solid was compared to a Na-exchanged Nb-SAP that does not contain acid sites (Na/Nb-SAP). X-ray analysis showed that the introduction of Nb ions did not alter the trioctahedral structure of the saponite. Spectroscopic analyses provided information about the chemical nature and the delocalization of Nb(V) sites. The catalytic properties of Nb-SAP sample were evaluated at room temperature in the oxidative degradation, with H_2O_2, of (2-chloroethyl)ethyl sulfide (CEES), a simulant of sulfur mustard. The performances of Nb-SAP are compared with those of parents samples (Na-SAP, acid saponite and Na/Nb-SAP). The co-presence of Nb(V) centers and acid sites in the saponite clay was essential to have an effective and very fast decomposition of the sulfide substrate. CEES was selectively oxidized to (2-chloroethyl)ethylsulfoxide rather than to thesulfone. Nb-SAP sample resulted very promising, being able to degrade 80% of CEES in less than 8 h.

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CHF-O24

Halogen bond features revealed in the gas phase by rotational spectroscopy

Lorenzo Spada[a], Qian Gou[a], Montserrat Vallejo-Lopez[b], Andrea Staffolani[a], Alberto Lesarri[b], Emilio Josè Cocinero[c], Walther Caminati[a]

a Dipartimento di Chimica "G. Ciamician" dell'Università di Bologna, Via Selmi 2, I-40126, Bologna, Italy.
b Departamento de Química Física y Química Inorgánica, Universidad de Valladolid E-47011 Valladolid, Spain.
c Departamento de Química Física, Facultad de Ciencia y Tecnología Universidad del País Vasco, (UPV-EHU), Apartado 644, E-48940 Bilbao, Spain.

lorenzo.spada5@unibo.it

A typical halogen bond is denoted by the three dots in R–X···Y. R–X is the halogen bond donor where X is any halogen atom with an electron-poor region, R is a group covalently bound to X and Y is halogen bond acceptor with, at least, one electron-rich region [1].
In this context the high resolution microwave spectroscopy in supersonic expansion is a really suitable technique to reveal the features of the halogen bond in molecular systems free from solvent effects.
We have recently characterized with this technique the O···Cl, N···Cl and F···Cl halogen bonds through the studies of the molecular adducts of CF_3Cl with water [2], ammonia [3] and CH_3F [4].
We present here the results of microwave spectroscopy studies of additional molecular complexes, such as Pyridine ···$ClCF_3$.

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CHF-O25

Structural and electronic properties of p-doped $SrTiO_3$: a first-principles study

Leonardo Triggiani,[a,b] *Ana B. Muñoz-García,*[c] *Angela Agostiano,*[a,b] *Michele Pavone* [c]

a Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro", Via Orabona 4, 70125, Bari, Italia
b CNR-IPCF, Divisione di Bari, c/o Dip. di Chimica, Via Orabona 4, 70125, Bari
c Dipartimento di Scienze Chimiche, Università degli Studi di Napoli "Federico II", Via Cintia, 80126, Napoli, Italia

leonardo.triggiani@uniba.it

Perovskite-type mixed oxides of general formula ABO_3 are ceramic materials widely employed in heterogeneous catalysis and in solid oxide fuel cells.[1] Their ability to accommodate different dopants at A and/or B sites enables a tailored tuning of their properties and performances. For example, doped strontium titanate (STO) has been recently proposed as alternative to Ni-based cermets for solid-oxide fuel cell anodes.[2] While the available literature on STO mostly reports works on B-site doping,[3] here we focus on A-site p-doping of STO. In particular, we address the effects of Sr^{2+} substitution with aliovalent K^+ ions on STO electronic structure, oxygen vacancy formation and oxide diffusion. Hence, oxides with formulae $Sr_{1-x}K_xTiO_{3-\delta}$ have been investigated with state-of-the-art DFT-based approaches. Our results show that p-doping eases oxygen vacancy formation in STO. Detailed analyses of electronic features allow us to dissect the subtle structure-property relationships underpinning this behavior. Our insights can lay the foundations for the development of a new active STO-based material for energy conversion technologies.

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CHF-O26

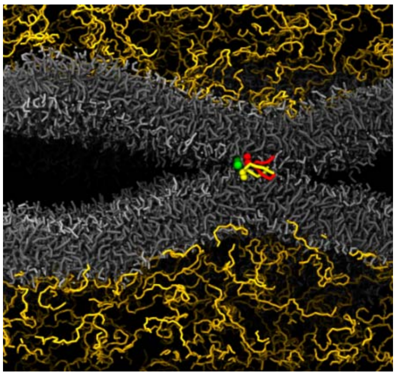
A Phenomenological Picture of the PEG and Calcium-Mediated Membrane Fusion: Theory and Simulations

M. Pannuzzo[a], *M. Karttunen*[b], *D. De Jong*[c], *S-J. Marrink*[c], *A. Raudino*[d]

a Department of Computational Biology, Universität Erlangen-Nürnberg, Staudtstr.5-91058, Erlangen, Germany
b Department of Chemistry, University of Waterloo, 200 University Avenue West, Waterloo, Ontario N2L 3G1, Canada
c Groningen Biomolecular Sciences and Biotechnology Institute & Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 7, 9747 AG Groningen, The Netherlands
d Dipartimento di Scienze Chimiche, Università di Catania, Viale A. Doria 6-95125, Catania, Italy

martina.pannuzzo@gmail.com

The mechanism of membrane fusion mediated by a non-charged water-soluble polymer (PEG) and Ca^{2+} has been investigated by means of a coarse-grained molecular dynamics simulation approach and supported by analytical predictions. A detailed view on the effects of cations and polymer on the interaction between neutral or negatively charged apposed membranes is provided, revealing a synergistic effect of Ca^{2+} and PEG on membrane fusion.



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CHF-O27

Electronic and structural features of dye-electrode interface in p-type DSSC: new insights from first-principles modeling

Ana B. Muñoz-García[a], *Michele Pavone*[a]

a Dipartimento di Scienze Chimiche, Università di Napoli Federico II, Comp. Univ. M. Sant'Angelo Via Cintia 21, 80126, Napoli, Italia

anabelen.munozgarcia@unina.it

For the last two decades dye-sensitized solar cells (DSSCs) have been challenging expensive solid-state solar panels in the quest for a cost-effective and efficient photovoltaic technology [1]. Original DSSC-based photoanodes (n-DSSCs), as pioneered by Grätzel [2], have reached efficiencies near ~13% [3]. Further developments could be achieved by combining n-DSSC with a photo-active electrode (a photocathode, i.e. a p-DSSC) in a so-called tandem cell [1]. However, the research on p- DSSCs is still in its infancy and the poor efficiencies achieved so far have hindered the foreseen development of n-DSSC/p-DSSC tandem cells [4]. In this context, a comprehensive analysis of the structure-property-function relationships in p-DSSC model systems is key to enable further progress of this technology. To this aim, computational modeling techniques can help understanding the atomic bases of p-DSSC properties and performances. Here, we report a first-principles study of a prototypical p-DSSC model made of nickel oxide and coumarin-based molecular dyes [5]. We discuss the structures and binding energies of different anchoring groups (-COOH, -CN, -NO_2, PO_3H_2) on the NiO surface. Then, we analyze the electronic features at the interface: the dye and electrode mutual interactions are tuned by the chemical nature of the anchoring group and by its anchoring mode. Our findings provide new insights on the dye-electrode interface and can benefit the design of new and better performing p-DSSCs.

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CHF-O28

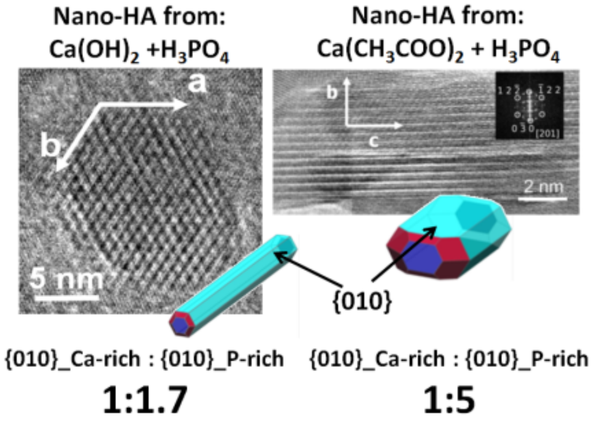
Engineering of the surface structure of nanohydroxyapatite

Y. Sakhno[a], *M. Iafisco*[b], *F. Chiatti*[a], *M. Corno*[a], *P.Ugliengo*[a], *G. Martra*[a]

a Department of Chemistry and Interdepartmental Centre "Nanostructured Interfaces and Surfaces-NIS" University of Torino, via P. Giuria 7, 10125 Torino, Italy
b Institute of Science and Technology for Ceramics (ISTEC), Faenza, Italy

yury.sakhno@unito.it

Nanohydroxyapatites are mainly limited by (010) surfaces, which actually can expose different terminations depending on the interruption of the -A-B-A-A-B-A-A-B-A- layers, where the A and B layers have the $Ca_3(PO_4)_2$ and $Ca_4(PO_4)_2(OH)_2$ chemical compositions, respectively. Hence, for a well-defined (010) slab, the most exposed layers result as ...-A-B-A, ...-A-A-B, or ...-B-A-A giving rise to the stoichiometric HA(010) and the non-stoichiometric HA(010)_Ca-rich and HA(010)_P-rich surfaces, respectively. Recently, we established a method for the recognition of such surfaces by combining B3LYP modeling and IR spectroscopy of adsorbed CO [1]. Here, we used this method for the elucidation of the structure of (010) terminations of nanohydroxyapatites prepared in the presence and in the absence of acetate ions. The combination of HR-TEM and IR spectroscopy revealed that CH_3COO^- are effective in limiting the growth of the nanoparticles along the C-axis but, importantly, affect in a large extend the relative amount of exposed HA(010)_Ca-rich and HA(010)_P-rich surfaces, which pass from 1:5 to 1:1.7 (in the presence and absence of acetates during the synthesis, respectively). This result appears relevant because these two kinds of surface terminations behave in a different way towards the adsorption of proteins [2].



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CHF-O29

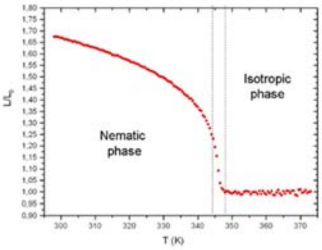
Nuovi materiali per la conversione energetica a base di elastomeri liquido cristallini

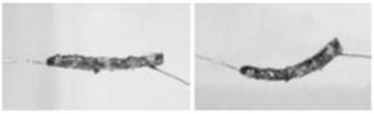
Valentina Domenici[a], Jerneja Milavec[b], Blaz Zupancic[b], Andraz Resetic[b] e Bostjan Zalar[b]

[a] Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, 56126, Pisa, Italia
[b] Department of Condensed Matter Physics, Jozef Stefan Institute, 39 Jamova Cesta, SI-1000, Ljubljana, Slovenia

valentina.domenici@unipi.it

Gli elastomeri liquido cristallini (ELC) rappresentano un eccellente esempio di materiali polimerici a memoria di forma. Le proprietà termoelastiche e termomeccaniche alla base delle loro applicazioni come attuatori, sono strettamente legate alle proprietà molecolari e di self-assembling, come chiaramente dimostrato da studi di Risonanza Magnetica Nucleare.[1] Recentemente, utilizzando film a base di ELC sono stati preparati vari materiali compositi [2,3] in grado di convertire in modo controllato energia elettrica, energia termica ed energia meccanica, aprendo la strada a nuovi dispositivi per applicazioni nel campo della micro-biorobotica e degli elettrodi flessibili. Inoltre, introducendo nella struttura degli ELC monomeri photosensibili [4] è stato possibile indurre variazioni meccaniche controllate e reversibili con stimoli luminosi.





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CHF-O30

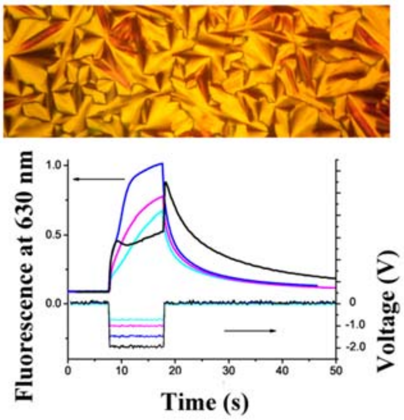
Multifunctional properties of liquid crystal thienoviologens

Amerigo Beneduci,[a] *Sante Cospito*,[a] *Bruna C. De Simone*,[a] *Daniela Imbardelli*,[a] *Massimo La Deda*,[a] *Roberto Termine*,[b] *Attilio Golemme*[a] *and Giuseppe Chidichimo*[a]

a Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Via P. Bucci, 87036 Arcavacata di Rende (CS), Italia
b CNR- IPCF UOS CS lab LiCryL Università della Calabria, Via P. Bucci, 87036, Arcavacata di Rende (CS), Italy

amerigo.beneduci@unical.it

The research in the field of electronic and photonic devices based on ordered organic semiconducting materials has been boosted by the development of new multifunctional materials.[1-3] The order characterizing liquid crystals has been exploited for improving charge mobility performances.[2] However, while in the last decade much effort has been addressed to the synthesis of hole-conducting materials (p-type), less attention has been paid on the development of electron-conducting ones (n-type). Here we show the bulk multifunctional properties of π-conjugated thienoviologen ionic liquid crystals[4] which have strong electron acceptor character and exhibit high fluorescence in the bulk state (ϕ up to 68%). Notably, the combination of their optical properties with high ionic conductivities and fast intermolecular electron transport, leads to their unique electrochromic and electrofluorochromic functions.[5] In addition to the above properties, these materials show photoconduction in glassy LC state at room temperature. The photoconductivity can be related to the reduction of the ionic liquid crystals, opening the way to the use in wider range of advanced optolectronic devices.



Electrochrofluorescence switching in Col$_r$ phase

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CHF-O31

The MgH_2 conversion reaction in a lithium cell

D. Meggiolaro[a], G. Gigli[a], A. Paolone[b], P. Reale[c], S. Brutti[b,d]

a Dip.Chimica, Sapienza Università di Roma, P.le Aldo Moro 5, 00185 Roma
b Istituto dei Sistemi Complessi (ISC-CNR), Via dei Taurini, 00185, Roma
c ENEA Centro Ricerche Casaccia, S. M. di Galeria, 00123, Cesano
d Dip.Scienze, Università della Basilicata, P.le Alteneo Lucano 10, 85100, Potenza

sergio.brutti@unibas.it

MgH_2 electrochemical conversion reaction is a valuable alternative to Li intercalation into graphite for next generation Li-ion cells [1]. MgH_2 has a theoretical capacity of 2048 $mAhg^{-1}$, 5 times larger than of graphite. The incorporation of lithium occurs by the reduction of magnesium hydride to magnesium metal nanoparticles surrounded by an amorphous matrix of lithium hydride [1,2] (hydride conversion reaction, HCR). "Going-nano" plays a key role in the promotion of the MgH2 HCR. This last effect can be thermodynamic and/or kinetic as it may involve variation of the chemical potentials of nanophases as well as drastic improvements in the ion diffusivity.

In this communication we discuss our recent results [2-3] about the MgH_2 HCR in a lithium cell. Our study combines firsts principles calculations and experiments. Advanced electrochemical tests in lithium cells (i.e. galvanostatic cycling, galvanostatic intermittent titrations, impedance spectroscopy upon cycling) as well as transmission electron microscopy and X-ray diffraction experiments have been coupled with density function theory calculations on bulk, surface and nanoclusters of MgH_2, LiH and Mg, in order to outline the main features of the HCR and the role played by surfaces.

This work is carried out in the framework of the Italian project (FIRB-Futuro in ricerca 2010) "Hydrides as high capacity anodes for lithium ion batteries".

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CHF-O32

Doped nano-titania: theoretical insight into structure-property relationships

Michele Ceotto [a], *Leonardo Lo Presti* [a,b,c], *Laura Loconte*[a], *Daniela Meroni*[a], *Luigi Falciola*[a], *Valentina Pifferi*[a], *Guido Soliveri*[a], *Giuseppe Cappelletti* [a], *Chiara D. Aieta*[a], *Robert G. Acres*[d], *Silvia Ardizzone*[a]

a Dipartimento di Chimica, Università degli Studi di Milano, via Golgi 19, 20133 Milan, Italy
b Istituto di Scienze e Tecnologie Molecolari, Italian CNR, Via Golgi 19, 20133 Milan
c Centre for Materials Crystallography, Århus University, Langelandsgade 140, 8000 Århus, Denmark
d Elettra - Sincrotrone Trieste S.C.p.A. S.S, 14 - km 163, 5 in AREA Science Park, 34149 Basovizza, Trieste, Italy

michele.ceotto@unimi.it

Doping with metal and non-metal species represents a promising strategy to tailor the optical and electronic properties of semiconducting oxides, such as TiO_2. N-doped TiO_2 photocatalysts represents a paradigm for such complex systems, where the lattice location of the dopant host and its complex interplay with the material's crystal structure crucially determine the resulting optical and electronic properties of the material [1-3]. In this study, we investigate the structure-property relationships of N-doped and N,metal-codoped nanocrystalline TiO_2 thanks to a combined theoretical and experimental approach. Powder and thin film samples were characterized at synchrotron radiation light facilities to determine their local and long-range structure (EXAFS, XANES, HR-XRD) as well as their composition and electronic properties (XPS, RESPES). The observed experimental results are rationalized on the grounds of DFT calculations aimed at reproducing experimental geometries and electronic structure. In this way, a complete picture of the complex interplay between dopant addition and material properties is provided.

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CHF-O33

Hybrid material based on pyrene functionalized PbS NCs photoactivating CVD monolayer graphene

C. Ingrosso[§a], *G. V. Bianco*[§b], *M. Corricelli*[a,c], *R. Comparelli*[a], *A. Agostiano*[a,b], *M. Striccoli*[a], *M. Losurdo*[b], *M. L. Curri*[a], *G. Bruno*[b]

[a]*CNR-IPCF, c/o Dip. di Chimica, Universita`di Bari, via Orabona 4,70126, Bari, Italy,*
[b]*Dip. di Chimica, Università di Bari, via Orabona 4,70126 Bari, Italy*
[c]*CNR-IMIP, c/o Dip. di Chimica, Università di Bari, via Orabona 4, 70126 Bari, Italy*
[§]*C. Ingrosso and G. V. Bianco equally contributed to the work*

c.ingrosso@ba.ipcf.cnr.it

Graphene is an extraordinarily attractive material for technological applications.[1] Its decoration with colloidal inorganic nanocrystals (NCs) allows the preparation of hybrid materials with original properties.[2] Here, a simple and facile solution-based procedure has been implemented for decorating a large area, monolayer graphene film, grown by CVD, with size-tunable light absorbing colloidal PbS NCs. The hybrid is obtained by exposing a graphene film in a solution of 1-pyrene butyric acid surface coated PbS NCs. The NCs anchor on the graphene platform by means of π-π stacking interactions promoted by the pyrene ligand coordinating directly the NC surface and organizing in a highly interconnected nanostructured multilayer coating. The hybrid absorbs in the visible and near-infrared spectral region and exhibits a sheet resistance (blue dots) decreased of ca. 3% with respect that of graphene. Such an hybrid can be an interesting component for optoelectronics, sensors and for optical communication and information technology.

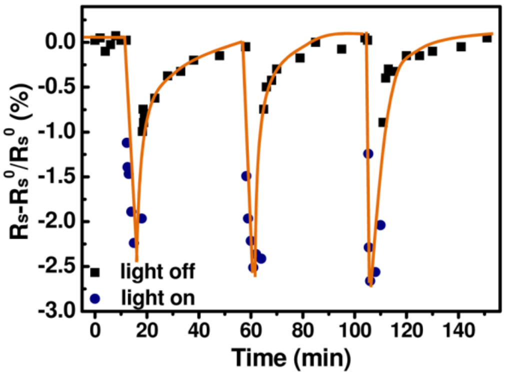

Figure. Monitoring of the change of the sheet resistance of graphene decorated with PBA-capped PbS NCs under three cycles of light irradiation with Rs^0 = 1000 Ohm×sq^{-1} the sheet resistance in the dark

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CHF-O34

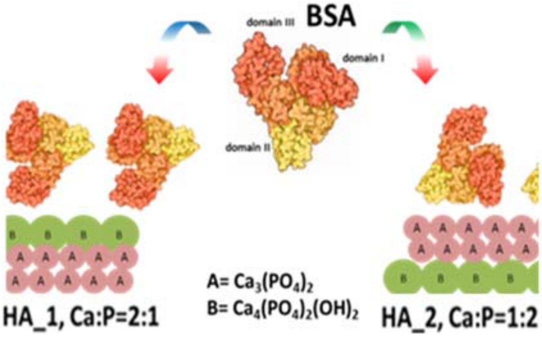
Proteins adsorbed on hydroxyapatite nanoparticles; factors determining a material new biological identity

F. Catalano, P. Ivanchenko, Y. Sakhno, V. Aina, G. Martra*

Department of Chemistry and NIS Interdepartmental Centre, University of Torino, via P. Giuria 7, 10125 Torino, Italy

federico.catalano@unito.it

From the early stages of contact with the biological environment, the material surfaces are covered by a “corona” of endogenous proteins. Understanding of the subsequent cells response, therefore, is the study of the new “epitopes”, formed by material surface termination and amount /orientation of adsorbed proteins [1]. Nanosized hydroxyapatite particles (HA), are among materials of interest as biomimetic counterpart of inorganic phase of bones and teeth [2]. The HA lattice can be described as sequence of $Ca_3(PO_4)_2$ (A) and $Ca_4(PO_4)_2(OH)_2$ (B) layers parallel to {010} crystal planes. Depending on their sequence (A-B-A, A-A-B or B-A-A), they give rise to stoichiometric HA(010) and nonstoichiometric HA(010)_Ca-rich and HA(010)_P-rich surfaces, respectively, having different preferential adsorption of acidic and basic proteins [3]. The use of a theoretical-experimental model based on IR of CO adsorbed as probe molecule allowed to establish that two types of HA nanoparticles exposed Ca-rich and P-rich surfaces. The two materials exhibited ζ-potentials different in value and sign when suspended in HEPES buffer. Moreover an inverse trend of ζ-potentials is observed once a monolayer of adsorbed BSA was attained by incubation in a buffered BSA solution (surface coverage also monitored by effects on CD-UV spectra of adsorbed BSA). Since a complete protein coverage prevents the contribution of HA surfaces to the ζ-potential, these should therefore stem from differences in “surfaces” exposed to the liquid medium by adsorbed proteins oriented in different ways on the two HA (Scheme 1).



Scheme 1. Orientation of BSA exposing different domains onto different types of HA surfaces.

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CHF-O35

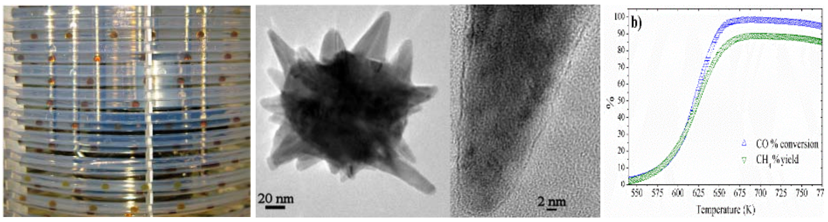
Continuous synthesis of Ni nanopowders: complete characterization and catalytic opportunities

Mattia A. Lucchini[a,b], *Paola Riani*[a], *Andrea Testino*[b], *Fabio Canepa*[a]

a. Università degli Studi di Genova, Dipartimento di Chimica e Chimica Industriale (DCCI),
Via Dodecaneso, 31 16146 Genova, Italy
b. PSI – Paul Scherrer Institut, ENE-LBK-CPM, Villigen 5232, Switzerland

mattia.lucchini@unige.it

The production of nanoparticles in 10-100 g range prepared with laboratory-scale equipment is a target of great interest. In this study, Ni nanoparticles with different sizes, surface morphologies, and magnetic properties were obtained from $NiCl_2$, N_2H_4, NaOH, and ethylene glycol as solvent by tuning the synthesis parameters [1]. Finally, the product has been tested as catalyst in a reaction of CO methanation. The presented work mainly focuses on the continuous synthesis carried out in the Segmented Flow Tubular Reactor (SFTR), used for the first time for a non-aqueous system. By combining SEM, HRTEM, XRD, TGA, XPS, specific surface area, SQUID, and catalytic tests, the complete structural, morphological, and functional characterization of the produced nanoparticles were performed. The continuous production of 2.1 g h^{-1} of Ni nanoparticles was carried out up to 6h without product properties deterioration. The results allow estimating a production >300 g d^{-1} in an ad-hoc low-cost single-tube SFTR system. Catalytic tests of CO methanation showed good activity at 769 K with stable methane yield of 83%. The results presented in this study demonstrate that reliable and reproducible synthesis of relatively high amounts of metal nanoparticles, with very well defined characteristic, can be achieved using a lab-scale equipment. This approach opens new opportunities for reliable and controlled preparation of advanced materials in quantities suitable for a full functional characterization.



Synthesis Characterization Catalysis

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CHF-O36

Cisplatin derivative loaded in mesoporous MCM-41: preparation and characterization

Maria Luisa Saladino[a], *Simona Rubino*[a], *Paola Colomba*[a], *Eugenio Caponetti*[a,b]

[a] *Dipartimento Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche - STEBICEF, Università di Palermo, Viale delle Scienze pad.17, Palermo I-90128, Italy.*
[b] *Centro Grandi Apparecchiature- UniNetLab, Università degli Studi di Palermo, Via F. Marini 14, I-90128 Palermo, Italy*

marialuisa.saladino@unipa.it

The aim of this study is to design and investigate a new material constituted by mesoporous silica MCM-41 and a new cisplatin derivative, cis-$PtCl_2$(DMSO)HL]·2DMSO, where HL = 7-amino-2-(methylthio)[1,2,4]triazolo[1,5-a]pyrimidine-6-carboxylic acid, having biological activity.[1] The high surface area and the tunable pore size of MCM-41 allow it for loading vast amounts of bioactive molecules, including biocides and drugs.

Mesoporous silica MCM-41 was prepared in alkaline environment from tetraethoxysilane as Si source and cetyltrimethylammonium bromide (CTAB) as template. [2] Amino groups have been successfully grafted onto the pore surface with 3-aminopropyl triethoxysilane (APTES) in order to create favorable surface-drug interactions. The encapsulation of the drug was performed adding the MCM-41-NH_2 in a $PtCl_2$(DMSO)HL]·2DMSO chloroform solution.

The characterization of materials was performed by X-ray diffraction, N_2 adsorption and solid state NMR (^{29}Si and ^{13}C). Results showed that the amino groups serve as effective ligands for the linking of Pt atoms to the mesoporous.

The controlled release of the $PtCl_2$(DMSO)HL]·2DMSO in water was investigated.

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CHF-O37

Effect of the Electric Field on the Structure of a Chiral Conductive Polymer Thin Film

Tassinari F.[1], *Mathew S.P.*[2], *Fontanesi C.*[1], *Schenetti L.*[3], *Mucci A.*[1],
Naaman R.[2]

[1] *Department of Chemical and Geological Sciences, University of Modena and Reggio Emilia, Via Campi 183, 41125 Modena (MO)*

[2] *Department of Chemical Physics, Weizmann Institute of Science, Rehovot 76110, Israel*

[3] *Department of Life Sciences, University of Modena and Reggio Emilia, Via Campi 183, 41125 Modena (MO)*

francesco.tassinari@unimore.it

The chemical-physical properties of conductive polymer thin films are strictly related to the structure and conformations of the chains in the polymer lattice. Crystallinity, chain length, substituents, doping level are just some of the many variables that play a role in the final properties of the polymer films.

Another key factor is the orientation of the chains inside the thin film. A polymer chain is anisotropic, and so are its properties. However, a lattice where the chains are randomly arranged will have the same properties no matter which direction we measure them, whereas an oriented lattice will show different properties related to the preferential order of the macromolecular structure.

We used different electric fields to align the macromolecules of a chiral conductive polymer (CCP), capable of self-organizing in chiral helixes in the solid state, and we studied its effect on the anisotropy of the obtained thin films, on the structure of the aggregates and on the conductive properties of the polymer by means of different instrumental techniques.

All the measurements showed a preferential alignment of the polymer chains after the process under applied electric field. Circular dichroism was used to probe the chirality of the polymer aggregates, and it was found that the field strongly influences the helical superstructures of the CCP. The use of the electric field to fine tune the helical structures of this chiral polymer stands out as an interesting possibility which we are currently investigating.

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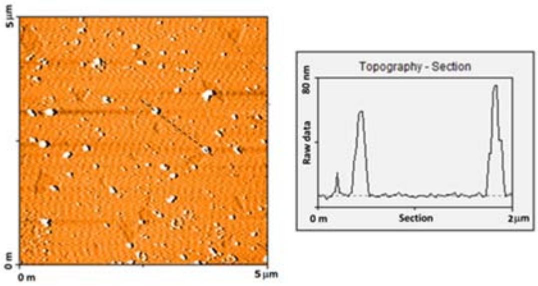
CHF-O38

Nickel Removal From Aqueous Solutions By Curcumin Capped Ag Nanoparticles

S. Bettini,[a] *R. Pagano*,[b] *L. Valli*,[a] *G. Giancane* [c]

a Department of Biological and Environmental Sciences and Technologies, DISTEBA, University of Salento, Via per Arnesano, I-73100 Lecce, Italy.
b Department of Engineering of Innovation, University of Salento, Via Monteroni, I-73100 Lecce, Italy.
c Department of Cultural Heritage, University of Salento, Via Birago 64, I-73100 Lecce, Italy.

simona.bettini@unisalento.it



A totally green synthesis protocol has been proposed to obtain silver nanoparticles capped with the natural compound (1E, 6E)-1,7-Bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-diene), known as curcumin. Synthesis process has been monitored by means of infrared, Raman, visible and fluorescence spectroscopies. The spectroscopic characterization has confirmed that curcumin acts both as reducing and capping agent. Furthermore the obtained colloidal suspension allowed to solubilize curcumin in water and to drastically increase its chemical stability. Curcumin low water solubility and chemical stability are the principal hurdles for its real use in different kinds of biotechnological applications [1]. Nickel chelation by curcuminoids is a well-known process [2], and it needs an alkaline pH to induce the formation of nickel square planar complexes with two curcumin molecules. In this contribution, the silver nanoparticles (AgNPs)/curcumin complex has been dispersed in a water solution containing a known nickel ions concentration. After few days a grey precipitate is observed and the nickel concentration in the solution is reduced of about 70%, without increasing the pH of the solution.

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Chimica Fisica

Poster

CHF-P1

Solid state NMR characterization of the waterlogged wooden part of Acqualadrone roman rostrum

Stella Bastone[a], *Alberto Spinella*[b], *Delia F. Chillura Martino* [a], *Eugenio Caponetti*[a,b]

a Dipartimento Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche - STEBICEF, Università degli Studi di Palermo, Parco d'Orleans II, Viale delle Scienze pad. 17, I-90128, Palermo, Italy
b Centro Grandi Apparecchiature-UniNetLab, Università degli Studi di Palermo, Via F. 14 , I-90128, Palermo, Italy

stella.bastone@unipa.it

The roman rostrum found in the sea of Acqualadrone (ME) was characterized in our previous papers [1,2]. In the present work solid state NMR spectroscopy was applied on a wooden sample of the same artefact collected by coring and divided in four parts in order to correlate the conservation state to the depth. Results were compared with those obtained for a modern wood of the same species.

A structural study was performed by the acquisition of ^{13}C Cross Polarization Magic Angle Spinning (^{13}C CP MAS NMR) spectra. These spectra were acquired to assign the chemical shifts of the species that are present in the wooden matrix. In addition the spectra analysis allowed us to determine the cellulose crystallinity degree and the lignin condensation degree.

The holocellulose-lignin ratio and the cellulose-lignin residual interactions were evaluated through variable contact time (VCT) experiments and through the relaxation times determination respectively. Furthermore these latter experiments allowed us to evaluate the dynamic modifications occurring in the lignin and in the cellulose during the degradation process.

Solid state NMR results showed a decrease of carbohydrates with a complete cleavage of hemicelluloses. The crystallinity degree decreases in depth while the lignin condensation was not modified. Dynamic relaxation times studies demonstrated cellulose and lignin are still interacting to each other in the deepest samples of the wood.

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CHF-P2

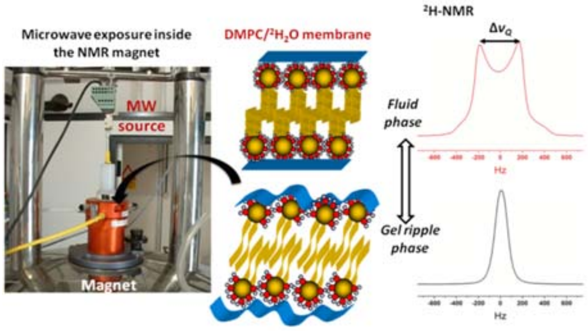
Nonthermal biological effects of millimeter waves: a ^{2}H-NMR study on deuterium-labelled model membranes

Amerigo Beneduci[a], *Katia Cosentino*[a], *and Giuseppe Chidichimo*[a]

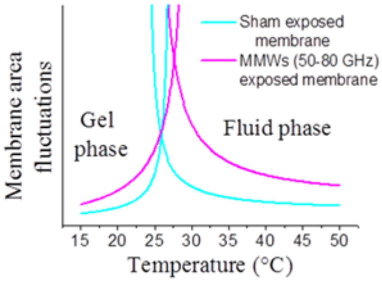
[a] *Department of Chemistry and Chemical Technologies, University of Calabria, Arcavacata di Rende (CS),Italy.*

amerigo.beneduci@unical.it

The nonthermal biological effects of millimeter waves (MMWs; 30-300 GHz) have been mainly attributed to the interaction with biological membranes.[1-4] Several studies on biomimetic membranes, support this conclusion.[6-9] Here we report a theoretical model based on experimental NMR data on deuterium-labeled phospholipid vesicles, in order to explain such interaction.[10] Notably, MMWs induce a time- and a hydration-dependent reduction of the water ordering around the phosphocholine headgroups, leading to an upward shift of the fluid-to-gel membrane phase transition point.[8-10] Microscopically, this effect is interpreted as a change in membrane bound water partitioning, resulting in a measurable relocation of water molecules from the inner to the outer binding sites.



Macroscopically, this unique sensitivity may be explained by the universal dynamic behaviour of the membranes in the vicinity of the transition point, where a pretransitional increase of membrane area fluctuations is observed. MMW exposure increases the above fluctuations and enhances the second order character of the transition.



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CHF-P3

Cs_2O/BEA for CO_2 and alcohol activation

M. Botavina, G.Martra

Department of Chemistry and Interdepartmental Centre “Nanostructured Interfaces and Surfaces – NIS” via P. Giuria 7, 10125 Torino,Italy

maria.botavina@unito.it

Zeolites BEA are characterized by three-dimensional 12-membered ring channel system and their large pores allow an easy diffusion of the various reactants into the zeolite structure. Modifying BEA zeolites with both Cs+ exchanged ions and Cs-oxide like nanospecies it is possible to increase their basic properties [1].

Cs/BEA catalysts were prepared by ion exchange of acidic BEA zeolites (ENI and RIPP). Obtained materials were impregnated with an additional amount of Cs [2]. At the end two series of BEA zeolites with different Cs contents (0.92 after ion exchange and 1.6 after impregnation) were obtained.

BET data shows that the increase of cesia content was accompanied by some decrease in a specific surface area and increase of the average pore diameter.

Introduction of Cs significantly increased catalyst basicity. FTIR analysis verifies that after ion exchange the presence of Brønsted acidic framework-bridged OH groups on the zeolite surface were not observed. The following impregnation with CsOH and subsequent Cs_2O formation resulted in the almost complete disappearance also of nonacidic terminal silanols. On the surface of the impregnated samples CO_2 adsorbtion with the formation of carbonates (interacting with basic centers) was observed. Butanol was adsorbed on Cs/BEA surfaces with the formation of alcolates. Other types of alcohols, such as phenol and catecol should be tested. Spectra of the corresponding alcohols were registered in water (at different pH) and tetraclorometan solutions that should help to identify carefully the type of species formed on the catalyst surface.

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CHF-P4

Self-discharge in $LiCoPO_4$ electrodes

S.Brutti[a]*, J.Manzi*[a]*, F.Vitucci*[b]*, A.Paolone*[b]*, F.Trequattrini*[b]*, D.Di Lecce*[c]*,*
S.Panero[c]

a Dip. di Scienze, Università della Basilicata, V.le Ateneo Lucano 10 85100 Potenza
b ISC-CNR UOS Sapienza, V.dei Taurini 00185 Roma
c Dip. di Chimica, Università di Roma Sapienza, P.le Aldo Moro 5 00185 Roma

sergio.brutti@unibas.it

Polyanalion-type materials, like lithium iron phosphate, are one of the recent great success in the Li-ion cells R&D. Within this family the olivine $LiFePO_4$ (LFP) is now a mature material and its properties have been largely optimized thus opening the door to its commercial exploitation. In recent years the attention of the scientific community is focusing the great advantage of the substitution in the olivine lattice of Fe with Mn, Co and Ni that work at increasing redox potentials. Among them $LiCoPO_4$ (LCP) is currently the best compromise: it shows in lithium cells a constant redox potential above 4.7V vs Li but still within the stability window of the carbonate-based electrolytes.

The aim of this communication is to present our recent results about the study of self-discharge of charged LCP electrodes. Self-discharge is the spontaneous reduction of de-lithiated cathode materials and in the case of LCP it is the major detrimental effect that limits its use in real devices. We have studied self-discharge by a multi-technique approach by coupling electrochemical tests in lithium cells with ex-situ analysis of the self-discharged electrodes by synchrotron diffraction, transmission electron microscopy, Infra-Red and X-ray photoemission spectroscopy.

Self-discharge occurs by the following spontaneous reactions in open circuit conditions on charged electrodes:

$CoPO_4$ + 0.7 Li^+ + electrolyte (reduced form) = $Li_{0.7}CoPO_4$ + electrolyte(oxidized form)

$Li_{0.7}CoPO_4$ + 0.3 Li^+ + electrolyte (reducted form) = $LiCoPO_4$ + electrolyte (oxidized form)

Apparently the electrode/electrolyte interphase is electrochemically active thus allowing a spontaneous transfer of electrons from the electrolyte components to the Co^{3+} redox centers in the de-lithiated electrode. This phenomenon is accompanied by the accumulation of electrolyte decomposition by-products on the electrode surfaces.

CHF-P5

Phase transitions in a CTAB quaternary microemulsion on increasing water amount

Delia F. Chillura Martino [a], Francesco Armetta[a], Renato Lombardo[a], Eugenio Caponetti[a,b]

a Dipartimento Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche - STEBICEF, Università degli Studi di Palermo, Parco d'Orleans II, Viale delle Scienze pad. 17, I-90128, Palermo, Italy
b Centro Grandi Apparecchiature-UniNetLab, Università degli Studi di Palermo, Via F. 14 , I-90128, Palermo, Italy

delia.chilluramartino@unipa.it

In a previously work, nanopowder of yttrium aluminum garnet was prepared in a CTAB quaternary microemulsion as confined environment [1].

By considering the relationship between the structure of the reaction medium and the shape and size of the synthesized nanoparticles [2], the water/CTAB/butanol/n-heptane microemulsion has been investigated on increasing water content in the range $4.1 < x_w < 70.0$.

Phase transition has been identified by means of viscosimetric, conductometric and SAXS data analysis.

Results show that at low water content the system is a W/O microemulsion. By increasing the water content, the structure gradually evolves to a bicontinuous microemulsion, followed by a sudden transition to a lamellar structure and finally a return to the bicontinuous one.

By considering the obtained results [1], to account for the effect of reagents on the microemulsion, the investigation has been extended to the microemulsion containing as aqueous phase an aluminum and yttrium nitrate solution.

The salts exert an effect at high water content by stabilizing the bicontinuous structure. No formation of lamellar structure was observed.

The obtained results could be useful for the YAG nanoparticles synthesis. The synthesis of nanoparticles in the different media structures is currently under investigation.

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CHF-P6

Computational and experimental studies of novel 3',4'-dihydroxy-7-(N,N-diphenylamino) flavylium as sensitizers in dye-sensitized solar cells

Ilaria Citro[a], *Giuseppe Calogero*[a], *Gaetano Di Marco*[a], *Stefano Caramori*[c],
Carlo Alberto Bignozzi[c], João Avó [d] *A. Jorge Parola*[d], *Fernando Pina*[d],

a CNR-IPCF, viale F. Stagno D'Alcontres 37, 98158, MESSINA, IT
b Dipartimento di Chimica, Università di Ferrara, Via L. Borsari 46, 44100 Ferrara, IT
c REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia,
Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

E-mail citro@ipcf.cnr.it

We present a complete study on four synthetic flavylium salts employed as sensitizers for dye-sensitized solar cells (DSSCs). The effect of several donor groups in the flavylium molecular structure was investigated (1). The theoretical evaluation of the electron density in the HOMO and LUMO of the dye molecules and the vertical electronic excitations were calculated using the time-dependent density functional theory (TDDFT) with B3LYP functional and the same basis set above-mentioned (2). The computation indicated that these molecules can interact strongly with the TiO_2 surface by a single OH group of the catechol, and can inject efficiently into the TiO_2. The Electron Density Difference Maps (EDDM) maps of the four dyes confirm the substantial π-π* character of the lowest singlet excited states, with the first, and most intense lowest energy transition exhibiting a stronger charge transfer (CT) character, involving a substantial shift from the dihydroxybenzene unit to the benzopyrylium ring. Calculations indicated that JAD90 (F4) displays an higher exciton binding energy which may be responsible for a lower charge injection quantum yield.

CHF-P7

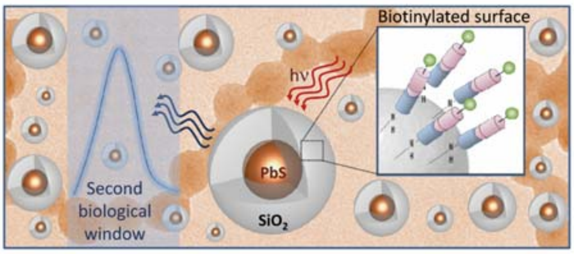
Biotinylation of Silica Coated Near-Infrared Emitting PbS Nanocrystals for Bioimaging

M. Corricelli,[a,b] *N. Depalo,*[b] *E. Di Carlo,*[a] *E. Fanizza,*[a,b] *V. Laquintana,*[c] *N. Denora,*[c] *A. Agostiano,*[a,b] *M. Striccoli,*[b] *M. L. Curri,*[b]

a Dipartimento di Chimica, Università degli Studi di Bari, Via Orabona 4, I-70126, Bari, Italy
b CNR-IPCF c/o Dipartimento di Chimica, Università degli Studi di Bari, Via Orabona 4, I-70126, Bari, Italy
c Dipartimento di Farmacia - Scienze del farmaco, Università degli Studi di Bari, Via Orabona 4, I-70126, Bari, Italy

lucia.curri@ba.ipcf.cnr.it

Nanoparticles (NPs) emitting in the second biological near infrared (NIR) window of the electromagnetic spectrum were successfully synthesized by growing a silica shell onto the hydrophobic surface of OLEA/TOP PbS nanocrystals (NCs), by means of reverse microemulsion approach, and subsequently decorated with biotin molecules.[1] This system represents attractive receptor-targeted NIR fluorescent probes for in vivo tumour imaging.[2] The fabrication of very uniform and monodisperse NPs was demonstrated by means of a set of complementary optical and structural techniques that highlighted how PbS NC and silica precursor concentration, are crucial to direct morphology and optical properties of particles. Subsequently, the silica surface of the core shell NPs was grafted with amino groups, in order to achieve covalent binding of biotin to $PbS@SiO_2$ NPs. Finally the successful reaction with a green-fluorescent labelled streptavidin verified the molecular recognition response of the biotin molecules on the $PbS@SiO_2$ NP surface. Dynamic light scattering and ζ-potential were used to monitor hydrodynamic diameter and colloidal stability of biotin decorated NPs, showing their high colloidal stability in physiological media, as needed for biomedical applications.



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CHF-P8

4-Thiothymidine and water soluble cyclodextrins inclusion complex in aqueous medium

V. Rizzi[a], *S. Matera* [a], *P. Fini*[,b], *A. Ventrella* [a], *P. Semeraro* [a], *A. Agostiano* [a,b], *F. Longobardi* [a], *P. Cosma* [a,b]

a Università degli Studi "Aldo Moro" di Bari, Dip. Chimica, Via Orabona, 4- 70126 Bari, Italy

b Consiglio Nazionale delle Ricerche CNR-IPCF, UOS Bari, Via Orabona, 4- 70126 Bari, Italy

pinalysa.cosma@uniba.it

Thiobase/UVA treatment may offer a novel therapeutic approach for the clinical management of nonmalignant conditions like psoriasis or for superficial tumors that are accessible to phototherapy [1]. Replacement of the oxygen in the carbonyl group by a sulfur atom results in the ultrafast population of the triplet state in high yield due to enhanced spin-orbit and vibronic coupling between the singlet and triplet manifold. [2] Studies have shown that irradiation of thiobase with UVA light results in the formation of reactive oxygen species (ROS) in cells[3]. The inclusion of organic compounds within the Cyclodextrins (CDs) hydrophobic cavity and its effect on the properties of the these molecules have been the subject of many recent investigation[4]. The influence of a delivery system could be a method to improve the thiobase photochemical behavior. The main results of this study will be discussed in the present communication. Cyclodextrin (CD) inclusion complexes containing 4-Thiothymidine (S^4TdR) as a guest were prepared and characterized by means of UV-Visible methods, Fourier Transform Infrared (FTIR), ^1H Nuclear Magnetic Resonance (^1H NMR) and Cyclic Voltammetry (CV) which proved the formation of the inclusion complexes where the pyrimidine ring of S^4TdR was encapsulated by the hydrophobic cavity of CDs.

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CHF-P9

Phospholipid Functionalization of Near Infrared Emitting PbS Nanocrystals for Bioimaging Applications

V. De Leo[a], N. Depalo[b], M. Corricelli[a,b], R. Comparelli[b], R. Gristina[c], L. Catucci[a], L. Curri[b], A. Agostiano[a,b]

a University of Bari, Department of Chemistry, Via Orabona 4, 70126 Bari, Italy
b CNR-IPCF Istituto per i Processi Chimici e Fisici, Bari, Via Orabona 4, 70126 Bari, Italy
c CNR-IMIP Institute of Inorganic Methodologies and Plasmas, Bari, Via Orabona 4, 7016 Bari, Italy

v.deleo@ba.ipcf.cnr.it

Near infrared (NIR) fluorescent probes are highly suitable for imaging of biological tissues, that show very low absorption and auto-fluorescence in the first (650-950 nm) and second (1000-1350 nm) biological NIR windows where, therefore, a maximum penetration of radiation in the tissues can be achieved [1]. Here, NIR emitting hydrophobic PbS nanocrystals (NCs) have been incapsulated in the core of phospholipid micelles or, alternatively, in the bilayer of phospholipid liposomes. Both strategies have demonstrated suitable to i) disperse PbS NCs in aqueous media, preserving their original optical properties, ii) obtain a biocompatible shell around the PbS NCs and iii) achieve a reliable scaffold suitable for their prompt conjugation with biomolecules [3]. The functionalization process of PbS NC surface by phospholipids has been demonstrated successfull only on thiol capped PbS NCs. Remarkably, the ligand exchange procedure implemented to replace the original capping ligand (oleic acid) onto NCs, with a thiol molecule has concomitantly resulted in a NC ripening, likely ascribable to an oriented attachement mechanism, and, hence, in the shift of the emission signal from 800 nm to 1100 nm. In vitro investigation has been also performed by using Saos-2 cells to assess cytotoxicity of PbS NCs after incorporation in micelles or in liposomes. The proposed phospholipid functionalized PbS NCs offer a significant potential for in vitro and in vivo imaging.

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CHF-P10

Liposomes-modified Titanium Implant Surface: a Possible Strategy to Local Delivery of Bioactive Molecules

V. De Leo[a], E. De Giglio[a], M.T. Cimmarusti[a], F. Milano[b], A. Panniello[b], M. Dicarlo[c], M. Mattioli-Belmonte[c], A. Agostiano[a,b], L. Catucci[a,b]

a University of Bari, Department of Chemistry, Via Orabona 4, 70126 Bari, Italy
b CNR-IPCF Istituto per i Processi Chimici e Fisici, Via Orabona 4, 70126 Bari, Italy
c DISCLIMO, Università Politecnica delle Marche, Via Tronto10/A, 60126 Ancona, Italy

v.deleo@ba.ipcf.cnr.it

Different treatments have been performed to improve bone-to-titanium response, thus stimulating implant osseointegration [1]. The opportunity of engineering the surface of implantable materials in order to increase the compatibility to host tissues, providing at the same time a surface-mediated drug delivery, is a very attractive solution to limit inflammation and to promote new bone formation. Here we report for the first time on the assembly of stable supported vesicular layer (SVL) and covalently bound liposomes (CBL) on Ti surface for orthopedic implants applications. SVLs were realized by physical liposome adsorption, instead CBLs were covalently bound on Ti surface by a three-step process that involved the deposition of 3-aminopropyltriethoxysilane (APTES), followed by a reaction between the amine end of APTES with gluteraldehyde, and finally a reaction between the aldehyde end of gluteraldehyde and Phosphatidylethanolamine (PE), a phospholipid component of liposome bilayer. Both systems thus prepared were structurally characterized and the response of cells adhering to these surfaces was evaluated. Specifically, we: (i) demonstrated the effective binding of liposomes onto Ti surface, (ii) verified the biocompatibility of the system by the human osteosarcoma MG-63 cell adhesion and viability, (iii) assessed the uptake of a fluorescent probe from these liposomes by cells, and (iv) showed the delivery of active molecule from the liposome to adherent MG-63 cell.

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CHF-P11

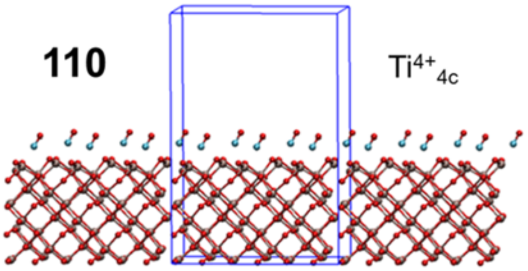
Surface defects on TiO_2 anatase NPs

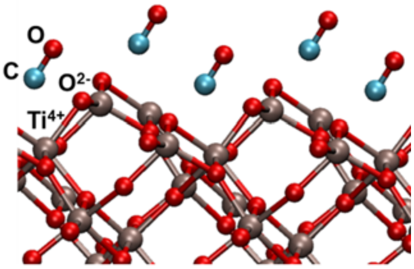
C. Deiana[1]*, G. Tabacchi*[2]*, E. Fois*[2]*, G. Martra*[1]

[1] *Department of Chemistry and Interdepartmental Centre ''Nanostructured Interfaces and Surfaces-NIS'', University of Torino, via P. Giuria 7, 10125 Torino, Italy*
[2] *Department of Science and High Technology, University of Insubria and INSTM*
via Lucini 3, 22100 Como, Italy

chiara.deiana@unito.it

The disclosure of the structure of defective sites exposed at the surface of TiO_2 anatase nanoparticles (NPs) has deserved increasing interest due to the possible role of these sites in the TiO_2 performances [1]. Recently, a pivotal role in the H_2O_2 photocatalytic decomposition has been recognised to α-sites (Ti^{4+} surface defective sites [2] with high Lewis acidity) and to Ti^{4+} centres exposed at the (110) surfaces [3].The presence of surface coordinative defective sites can be identified by *in-situ* IR spectroscopy of adsorbed CO, and, as in the case of the commercial TiO_2 P25 (by Evonik), the stretching frequency of CO adsorbed on α-sites is located at ca. 2006 cm^{-1}. Here, we present some preliminary results of a combined experimental and theoretical study aimed to the structural assignment of α-sites, obtained by comparing several TiO_2 materials characterized by different morphological properties. These findings could contribute to the elucidation of the structure-reactivity relationships of titania, a key material for sustainable processes.





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CHF-P12

Block copolymer-templated assembly of colloidal metal nanoparticles

A. E. Di Mauro[a], C. Ingrosso[a], M. Striccoli[a], V. Villone[a,b], N. Depalo[a], M Corricelli[b], E. Fanizza[b], A. Agostiano[a,b], L. Cano[c], L. Oria[d], A. Tercjak[c], F. Perez-Murano[d], M. L. Curri[a]

a CNR-IPCF, c/o Dip. Chimica, Via Orabona 4, 70126 Bari, Italy
b Dipartimento di Chimica, Università di Bari, Via Orabona, 4, 70126 Bari, Italy
c Escuela Politécnica-UPV, P.za Europa 1, 20018, San Sebastián, Spain
d IMB-CNM, CSIC, Bellaterra, 08913, Barcelona, Spain

e.dimauro@ba.ipcf.cnr.it

Block copolymer (BCP)-driven strategies are particularly promising to achieve nanoparticle (NP)-based pattern in hybrid functional materials, which can be effectively integrated in system and devices.

Here two different approaches for the formation of patterns of colloidal Au NPs, have been followed, by exploiting the self-assembly of a polystyrene-*block*-polyethylene oxide (PS-*b*-PEO) BCP. In particular, the first method, based on the formation of a blend with the NPs and the BCP, has been used for hydrophobic Au NPs and the second technique, based on the decoration of pre-fabricated BC films with NPs, for hydrophilic Au NPs. In first approach high Au NP amount have been selectively incorporated in the PS domain and the conductive properties of the obtained nanocomposite films have been demonstrated by means of the electrostatic force microscopy[1]. Secondly, the selective deposition of hydrophilic Au NPs onto the PEO domains has been achieved, as demonstrated by means of atomic force and scanning electron microscopies[2].

In both approaches the main driving force exploited for the assembly has been the chemical affinity between the organic ligands at the NP surface and the BCP phases. The successful PS-*b*-PEO-templated NP organization opens up venues for different applications in fields that range from optics to sensor technology.

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CHF-P13

Graphene–Derivatives Prepared By Chemical And Physical Approaches For Investigation At The Biointerfaces With Artificial Membranes

Patrizia Di Pietro,[a] *Luisa D'Urso,*[a] *Giusepe Forte*[b] *and Cristina Satriano*[a]

[a] *Dipartimento di Chimica, Università degli Studi di Catania, viale Andrea Doria, 6, 95125 Catania, Italia*
[b] *Dipartimento di Scienze del Farmaco, Università degli Studi di Catania, viale Andrea Doria, 6, 95125 Catania, Italia*

pdipietro@unict.it

Bidimensional carbon materials such as graphene (G), graphene oxide (GO), and reduced graphene oxides (r-GO) combine interesting structural and optical functionalities for developing new materials for nano-bio applications. GO, generally produced from graphite in presence of oxidizing agents, is easily processable in liquid environment, possessing an excellent solubility in water and in some organic solvents. A variety of chemical and physical modifications of GO have been achieved, including the reduction to graphene-like sheets or surface functionalization (e.g., nitrogen-doping, metal doping, …). Induced chemical modifications in GO are generally mediated by the presence of atomic defects and of different types of covalent C-O groups, like carboxyl, epoxy and hydroxyl functionalities.

In this work we prepared GO (aqueous) and G (solid) samples, by the modified Hummers method and exfoliation method, respectively. Successively, several functionalization approaches were tested, including nanosecond pulsed laser irradiation, UV ozone treatment, chemical wet reduction methods and the reaction with amines. The linear and nonlinear optical properties at the interface with water, as well as the bio-interface with lipid vesicles and supported lipid bilayers were scrutinized through both experimental (Raman, dynamic light scattering and zeta potential, confocal microscopy, atomic force microscopy) and theoretical (molecular dynamics and density functional theory) studies.

CHF-P14

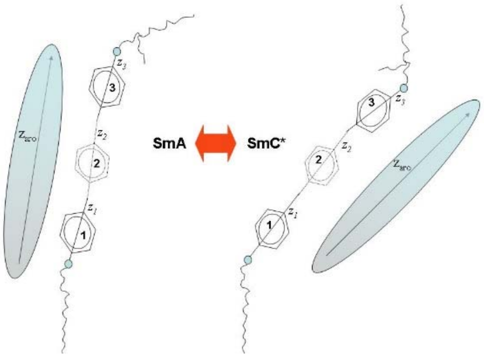
Conformational Properties and Orientational Order of a de Vries Liquid Crystal by NMR Spectroscopy

Valentina Domenici[a]*, *Moreno Lelli*[b], *Mario Cifelli*[a], *Vera Hamplova*[c], *Alessandro Marchetti*[b] *and Carlo Alberto Veracini*[a]

[a]*Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, 56126 Pisa, Italy.*
[b]*Université de Lyon 1, CNRS/ENS Lyon, Centre de RMN à Très Hauts Champs, 5 rue de la Doua, 69100 Villeurbanne, France.*
[c]*Liquid Crystal Group, Department of Dielectrics, Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, 182 21 Prague, Czech Republic.*

valentina.domenici@unipi.it

Solid-state and liquid-state NMR spectroscopic techniques are used to describe at molecular level the behaviour of a de Vries liquid crystal (9HL) at the SmA–SmC* transition, which is characterized by the absence of the layer shrinkage, typical of non-de Vries smectogens. Previous ^{2}H NMR studies [1] on the same smectogen, performed at a different magnetic field provided evidence of the occurrence of a tilt of one of the three phenyl rings, constituting the aromatic core of 9HL, at the SmA–SmC* phase transition. In this work, the study is extended to the whole rigid aromatic core of the 9HL. In particular, the variable temperature behavior of the mesogen studied by ^{1}D ^{13}C NMR cross-polarization (CP) and 2D ^{1}H–^{13}C PDLF (proton-encoded ^{13}C-detected, local field) NMR experiments made possible the characterization of the conformational and orientational properties in the two smectic phases [2].



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CHF-P15

Photoinduced charge transfer, negative solvatochromism and hyperpolarizability of push-pull compounds

F. Elisei[a], *V. Barone*[b], *E. Benassi*[b], *B. Carlotti*[a], *C.G. Fortuna*[c], *A. Spalletti*[a]

a Dipartiment of Chemistry, Biology and Biotechnology, University di Perugia, Via Elce di Sotto 8 , 06125, Perugia, Italy
b Scuola Normale Superiore, P.za dei Cavalieri 7, 56126, Pisa, Italy
c Dipartiment of Chemical Sciences, University of Catania, Catania, Italy

fausto.elisei@unipg.it

Some stilbene and butadiene derivatives bearing an electron deficient pyridinium or quinolinium group and an electron donor aromatic portion have been investigated through a combined experimental and theoretical approach, by using steady-state and femtosecond resolved spectroscopies and DFT calculations.[1,2]
The spectra resulted significantly affected by the solvent polarity: a large blue shift of the absorption band was observed in the polar solvents implying a clear change in the solution colour. The negative solvatochromism was comprehended thanks to the help of the calculations considering the variation of the dipole moment under excitation. The photobehaviour was interpreted considering the ground and excited state optimized geometries as a function of the solvent. The ultrafast measurements allowed an insight into the excited state dynamics revealing an interesting competition among solvent relaxation and photoinduced intramolecular charge transfer (ICT), whose efficiency was modulated by the solvent and the molecular structure. The hyperpolarizability was estimated by the solvatochromic method from the collected experimental data and compared with that predicted by the QM calculations.The findings for the investigated compounds (interesting molecular structure/ICT/NLO properties relationships) indicate their potential application in optoelectronics and photonics as NLO materials.

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CHF-P16

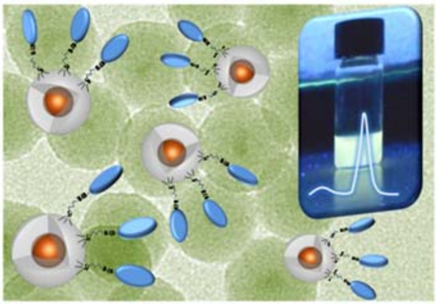
Single White Light Emitting Hybrid Nanoarchitectures Based on Functionalized Quantum Dots

Elisabetta Fanizza,[a-c] *Carmine Urso,*[a-c] *Vita Pinto,*[a] *Antonio Cardone,*[b] *Roberta Ragni,*[a] *Nicoletta Depalo,*[c] *M. Lucia Curri,*[c] *Angela Agostiano,*[a-c] *Gianluca M. Farinola*[a] *and Marinella Striccoli*[c]

[a] *Dipartimento di Chimica, Università degli Studi di Bari, Via Orabona 4, 70126 Bari, Italy*
[b] *Istituto di Chimica dei Composti OrganoMetallici ICCOM-Consiglio Nazionale delle Ricerche CNR, Via Orabona 4, 70126 Bari, Italy*
[c] *Istituto per i Processi Chimico Fisici IPCF Consiglio Nazionale delle Ricerche CNR, Via Orabona 4, 70126 Bari, Italy*

e.fanizza@ba.ipcf.cnr.it

White light emitting materials at the nanoscale represent a research field of both fundamental interest as well as industrial relevance for lighting, display technologies and biomedical imaging. In this work, single white emitting hybrid nanoarchitectures are successfully obtained covalently binding a blue emitting oligofluorene at the surface of silica beads, that embed orange luminescent colloidal CdSe@ZnS quantum dots (QDs). White light is achieved by carefully tuning the size of the QDs to complementarily match the emission color of the blue fluorophore and taking into account the delicate balance between the emission of QDs in the core of the silica beads and the amount of the organic dye bounded to the silica surface. The proposed approach is highly versatile and can be extended to the fabrication of a variety of luminescent hybrid nano-objects.



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CHF-P17

Solid state characterization of chlorophyll *a* supported on modified chitosan biofilm

P.Cosma[a],V.Rizzi[a], F.Fanelli[a,c], T.Placido[a],P.Semeraro[a], A.Agostiano[a], P.Fini[b]

a Università degli Studi "Aldo Moro" di Bari, Dip. Chimica, Via Orabona, 4- 70126 Bari, Italy
b Consiglio Nazionale delle Ricerche CNR-IPCF, UOS Bari, Via Orabona, 4- 70126 Bari, Italy
c Consiglio Nazionale delle Ricerche CNR-IMIP, UOS Bari, Via Orabona, 4- 70126 Bari, Italy
p.cosma@chimica.uniba.it

PDT appears to be suitable also for the treatment of infections originated by microbial pathogens. Recent findings suggest that this technique can be also exploited for addressing a number of environmental problems of high scientific and social impact as, i.e. food safety, in which a significant number of man-made activities can cause the deterioration of the environment promoting the proliferationof potentially dangerous microbial strain contaminating food products [1].In this regard the concept of Active Packaging is an interesting and most innovative alternative to the traditional use of the package[2]. In this work the attention has been focused on Chitosan (CH) an inexpensive, biodegradable, biocompatible, nontoxic and environmentally friendly linear amino polysaccharide. In this study we present the incorporation of antimicrobial substances into packagingmaterials as active packaging agents could be a way for controlling microbial contamination by reducing the growth rate or by inactivating microorganisms bycontact [3].Among all classes of compounds proposed as sensitizers in PDT,our research group has focused the attention on chlorophyll a (Chl a). In this view novel photosensitizing films based on the natural polymer Ch/(2-HP-β-CD) were purpose-synthesized and studied. Chl *a* was incorporated physically in the modified Ch polymer with the support of 2-HP-β-CD.A comprehensive investigation concerning the modified films has been thus undertaken in our laboratory using several techniques.

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CHF-P18

Perovskiti a base $SrTiO_3$: Preparazione, caratterizzazione ed attività fotocatalitica in regime gas-solido

E. García-López[a], Giuseppe Marcì[a], M. Boaro[b], F. Marazzi[b], L. Palmisano[a]

a Schiavello-Grillone" Photocatalysis Group. Dipartimento di Energia, Ingegneria dell'informazione e modelli Matematici (DEIM), Università di Palermo, Viale delle Scienze, 90128 Palermo, Italy.
b Group of Catalysis. Università di Udine, via cotonificio 108, 33100 Udine, Italia

elisaisabel.garcialopez@unipa.it

Le perovskiti a base di titanato di stronzio ($SrTiO_3$) sono materiali conduttori ionici ed elettronici che si utilizzano in elettrodi per celle a combustibile ad ossido solido [1]. Le caratteristiche chimico-fisiche di questi materiali soddisfano inoltre i requisiti per il loro uso come fotocatalizzatori [2,3]. Nel presente lavoro sono stati preparati materiali a base di titanato di stronzio ($SrTiO_3$) in presenza di Y e Co che sostituiscono rispettivamente Sr e Ti nella rete cristallina. Le polveri ottenute sono state caratterizzate e testate come fotocatalizzatori in regime gas-solido, utilizzando un sistema che simula la luce solare, per due reazioni: i) ossidazione completa del 2-propanolo e ii) ossidazione parziale del propene. Tutte le perovskiti sono attive fotocataliticamente. La presenza di Y migliora l'attività nella reazione di mineralizzazione del 2-propanolo, mentre al contrario la presenza di Co la riduce significativamente. Nell'ossidazione parziale di propene per ottenere ossido di propilene la presenza di Co si rivela essenziale mentre che la reazione non avviene utilizzando il $SrTiO_3$ o il materiale in presenza di solo Y.

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CHF-P19

Preparazione, caratterizzazione e attività fotocatalitica sotto luce solare naturale di perovskiti $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$

E. García-López[a], *Giuseppe Marcì*[a], *F. Puleo*[b], *V. La Parola*[b], *L.F. Liotta*[b]

a Schiavello-Grillone" Photocatalysis Group. Dipartimento di Energia, Ingegneria dell'informazione e modelli Matematici (DEIM), Università di Palermo, Viale delle Scienze, 90128 Palermo, Italia.

b [2]Istituto per Lo Studio dei Materiali Nanostrutturati (ISMN)-CNR, via Ugo La Malfa, 153, 90146 Palermo, Italia

elisaisabel.garcialopez@unipa.it

Nel presente lavoro sono state preparate con il metodo del citrato [1] perovskiti nanostrutturate del tipo ($La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$) che presentano una struttura cristallina pura di tipo romboedrico. Questi materiali sono semiconduttori con valori di "band gap" di 2,8-1,5 eV e mostrano attività fotocatalitica per la degradazione del 2-propanolo in regime gas-solido sotto irradiazione da luce solare naturale.

Le perovskiti $LaCoO_3$ e $La_{0.6}Sr_{0.4}CoO_3$ sono i materiali più attivi fotocataliticamente per la completa degradazione del 2-propanolo. I sistemi $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3$ e $La_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ sono risultati leggermente meno attivi rispetto alle lantanio-(stronzio) cobaltiti. La reattività del campione $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ è risultata, invece, molto scarsa. Questi risultati suggeriscono che le perovskiti contenenti Fe sono meno attive e l'attività diminuisce aumentando il contenuto di Fe.

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CHF-P20

A Fluorescence Study of the Interaction between Thymidine Phosphorilase and 5-Fluorouracil Derivatives

Emanuela Gatto[a], *Francesca Giannini*[a], *Francesca Leonelli*[b], *Raffaella Lettieri*[a], *Stephany Rea*[a], *Lorenzo Stella*[a], *Mariano Venanzi*[a]

a Dipartimento di Scienze e Tecnologie Chimiche, Università degli Studi di Roma Tor Vergata, Via della Ricerca Scientifica, 00133, Roma, Italia
b Dipartimento di Chimica, Università degli Studi di Roma La Sapienza, piazzale Aldo Moro, 00185, Roma, Italia

emanuela.gatto@uniroma2.it

Thymidine phosphorylase (TP), also known as "platelet-derived endothelial cell growth factor", is an enzyme, which is upregulated in a wide variety of solid tumors including breast and colorectal cancers.[1] TP promotes tumor growth and metastasis by preventing apoptosis and inducing angiogenesis. Elevated levels of TP are associated with tumor aggressiveness and poor prognosis. Therefore, TP inhibitors are synthesized in an attempt to prevent tumor proliferation. 5-Fluorouracil (5-FU) is one of these drugs used in the treatment of cancer.[2] It is a pyrimidine analog which works through irreversible inhibition of thymidylate synthase and thymidine phosphorylase. It belongs to the family of drugs called antimetabolites.

In this work the interaction between TP and 5-FU derivatives has been evaluated by steady state and time-resolved fluorescence measurements,[3] and compared to the same results obtained with the unsubstituted 5-FU molecule. The derivatives were developed in order to be inserted into phospholipids liposomes: they were synthesized functionalizing the nitrogen with a chain consisting of six or seven units of glicol, linked to an alkyl moiety of 12 carbon atoms.

Our results suggest that the derivatives have a higher affinity than the parent 5-fluorouracil molecule, even when they are inserted into liposomes, suggesting that they might be very promising drugs in cancer therapy.

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CHF-P21

Dynamic Phase Diagram of a Nonionic Surfactant Lamellar Phase

Luigi Gentile[a,b], *Manja A. Behrens*[b], *Kell Mortensen*[c], *Giuseppe A. Ranieri*[a], *Ulf Olsson*[b]

a Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Pietro Bucci 12C, 87036, Arcavacata di Rende (CS), Italia
b Department of Chemistry, Division of Physical Chemistry, Lund University, Getingevägen 60, 87036, SE-221 00 Lund, Sweden
c Niels Bohr Institutet, Strukturel biofysik / Structural Biophysics Universitetsparken 5 2100 København, Denmark

luigi.gentile@unical.it

Systems prone to shear-induced structural changes can have significant impact on industrial pipeline processing. Dramatic changes in the viscosity, which is often associated with structural rearrangement of the system, can give rise to shear thinning or shear thickening behavior [1-3]. For these reasons, the equilibrium phase diagram is not sufficient to describe these types of chemical systems; in fact, the non equilibrium state are also relevant. Thus dynamic phase diagrams should be investigated.

The dynamic phase diagram of a nonionic polyoxyethylene alkyl ether surfactant in D_2O was determined for some surfactant concentration [3]. The shear flow effect on the nonionic lamellar phase was investigated as a function of temperature and concentration. The transition from planar lamellae (Lα)-to-multilamellar vesicles (MLVs) was characterized by means of rheology, rheo-small-angle neutron and light scattering (SANS and SALS). New insight into the nature of the transition region between Lα and the MLVs state is provided. A disorder−order transition was also observed by SANS. This is attributed to a transition from disordered MLVs to a close-packed array of MLV's with slightly higher order than before. Moreover flow instability was observed in the shear thickening regime at 40 °C.

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CHF-P22

A structural analysis of olive oil/Myverol systems

Francesca Lupi[b], *Luigi Gentile*[a,b], *Luigi Filippelli*[a,b], *Cesare Oliviero Rossi*[a], *Domenico Gabriele*[a],, *Bruno De Cindio*[b]

a Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Pietro Bucci 12C, 87036, Arcavacata di Rende (CS), Italia
b Dipartimento di ingegneria Informatica, Modellistica, Elettronica e Sistemistica, Università della Calabria, Pietro Bucci, 87036, Arcavacata di Rende (CS), Italia

luigi.gentile@unical.it

The properties of organogels are particularly interesting in different fields, and among the potential different applications, the rheological modification of vegetable oil-based shortenings and the stabilization of food emulsions are promising techniques adopted to replace, as texturing agents, saturated and trans fats in edible oils or food systems [1,2].

Nuclear Magnetic Resonance (NMR) and rheology were used to evidence the crystallization phenomena and material structure change due to formulation and operating conditions of olive oil/monoglycerides (Myverol^{TM}) systems. Dynamic rheological tests evidenced the onset temperature of the crystallization (T_{CO}), as a sharp increase in storage modulus, and the gelation temperature (T_G), as the dynamic moduli crossover. By means of NMR technique the spin-spin relaxation time (T_2) distributions were estimated by applying the Inverse Laplace Transform to the echo-day of the Carr-Purcell pulse sequence at several temperatures. The obtained NMR and rheological results can be combined to better understand the crystallization phenomena in edible oil gels and the relative production process conditions. This is the first step of a more complex study on the effect of organo-gelators on ternary systems that includes cocoa butter.

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CHF-P23

Meat aging assessment using Magnetic Resonance Imaging

Noemi Baldino[a], *Luigi Gentile*[a,b], *Francesca R. Lupi*[a], *Cesare Oliviero Rossi*[b], *Domenico Gabriele*[a], *Bruno De Cindio*[a]

a Dipartimento di ingegneria Informatica, Modellistica, Elettronica e Sistemistica, Università della Calabria, Pietro Bucci, 87036, Arcavacata di Rende (CS), Italia
b Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Pietro Bucci 12C, 87036, Arcavacata di Rende (CS), Italia

luigi.gentile@unical.it

One challenge of the meat industry is to obtain reliable information on meat quality throughout the curing process, which would ultimately provide a guaranteed quality of meat products for consumers. Meat curing involves biochemical and physicochemical processes. These processes include the action of endogenous proteases on muscle fibre structure, a progressive increase in membrane water permeability, and the weakening of connective tissues.

Magnetic Resonance Imaging (MRI) was used to map out the curing process. This technique can solve many product control problems during production. NMR sequences run on white and black pork samples can produce images where the water and lipid signals are selected to identify the various components of the connective network. NMR micro-imaging on meat samples can be used to quantitatively characterize lipids. Fat content analysis by NMR requires to choosing pulse sequences to be applied to the product. The results highlight the versatility and reliability of the technique, that can be equally well deployed for controlling food composition as for checking food quality. In this study the spin-spin relaxation time and water self-diffusion were monitored along time through the MRI technique to provide quantitative parameters related to the meat properties and quality.

CHF-P24

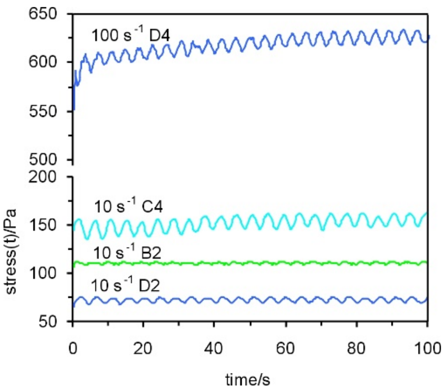
Rheological and NMR Investigations on Branched Micelles of DDAB-Sodium Taurodeoxycholate-D_2O Systems

Luigi Coppola[a], *Luigi Gentile*[a], *Fioretta Asaro*[b]

a Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria., Via Pietro Bucci 14D, 87036, Rende, Italy
b Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Trieste, Via L. Giorgieri 1, 34127, Trieste, Italia

luigi.gentile@unical.it

The extremely extended isotropic micellar region, L_1, is the most prominent feature of the 25 °C dodecyldimethylammonium bromide (DDAB)-sodium taurodeoxycholate (STDC)-water ternary diagram [1]. Here systems at DDAB/STDC molar ratios > 1 and total surfactant concentration in the range 65-85% wt/wt are reported. Notably, in spite of the high concentration, the samples display surprisingly small elastic contribute and viscosity. The rheological measurements carried out at 6°C reveal a clear shear thinning behavior and shear banding [2]. Moreover, the step rate experiments are characterized by periodic oscillations, with frequency independent of shear rate. The flow instabilities can affect both shear-thinning and shear thickening behavior. A number of models have been proposed to explain these instability phenomena. Olmsted [3], used the Johnson–Segalman (JS) model, which continues to be used as a simple and tractable model to describe shear band phenomena; moreover, it can be used to explain the viscosity or stress oscillations. In this case the oscillation signal, it might reside in a flow-microstructure coupling. The results of rheology, diffusivity of water and DDAB [4], and ^{14}N and ^{23}Na relaxation times concur in indicating an intriguing, not very common microstructure of somewhat connected, branched micelles, rather small, specially at room temperature.



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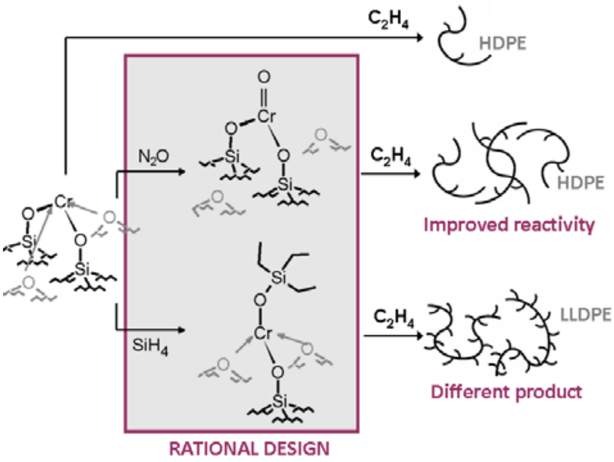
CHF-P25

Rational design of active sites in Phillips catalyst: influence on activity & selectivity

Elena Groppo[a], *Caterina Barzan*[a], *Alessandro Damin*[a], *Carlo Lamberti*[a],
Alessandra Quadrelli,[b] *Adriano Zecchina*[a], *Silvia Bordiga*[a]

a Dipartimento di Chimica, Università diTorino, Via Quarello 15, 10125 Torino, Italia
b Laboratoire Chimie, Catalyse, Polymeres et Procedes C2P2, UMR 5265 Universite Claude Bernard Lyon 1 - CPE Lyon – CNRS

elena.groppo@unito.it



A dominant share of polyethylene market is based on the silica-supported chromium-based Phillips catalyst (Cr/SiO_2), whose largest industrial application is HDPE production. In addition, modified versions of the same catalyst account for the production of LLDPE without the use of external α-olefins as co-monomers.[1] In most of the cases, industrial modifications were the result of empirical observation, more than of a rational design aimed to tune the structure of active sites. We report two examples to show that it is indeed possible to design the structure of the Cr active sites in order to tune their reactivity towards ethylene. The properties of the modified actives sites were finely characterized at a molecular level with a multi-technique approach. The first example describes an easy active-site engineering of the Cr(II)/SiO_2 Phillips catalyst through a controlled thermal treatment with N_2O. The method overcomes some of the structural problems limiting ethylene polymerisation activity and leads to a large increase in the initial rate of polymerisation at room temperature.[2] The second example shows why modification of Cr(II)/SiO_2 with hydrosilanes leads to production of LLDPE. Two types of Cr sites are simultaneously present: a modified site with an homogeneous behavior able to oligomerize ethylene and a classical heterogeneous one which co-polymerizes ethylene and the olefins produced from the former.[3,4]

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CHF-P26

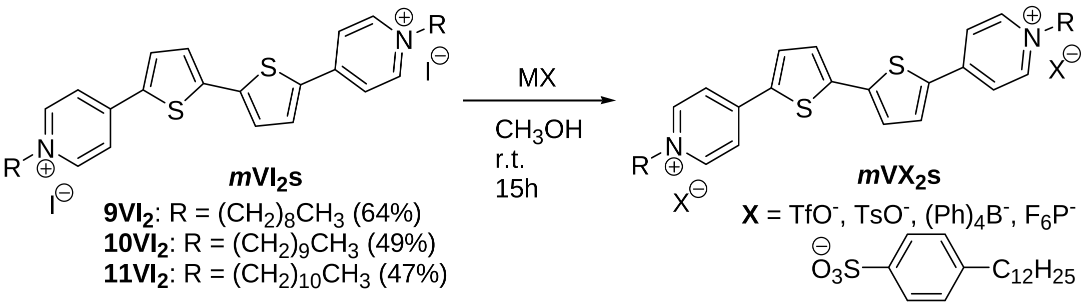
Effect of the anion on the mesomorphism of thienoviologen derivatives

<u>Vito Maltese</u>[a], Lucia Veltri[a], Sante Cospito[a], Amerigo Beneduci[a], Finizia Auriemma[b], Giuseppe Chidichimo[a]

a Department of Chemistry and Chemical Technologies (CTC), University of Calabria, Via P. Bucci Cubo 17/D, 87036 Arcavacata di Rende (CS), Italy.[b] Department of Chemical Sciences, Complesso Monte Sant' Angelo, via Cintia, 80126 Napoli, Italy.

vito.maltese@unical.it

Viologens are salts of the dication with the general formula 1,1'-disubstituent-4,4'-bipyridinium. Extended viologens incorporating π-conjugated bridging units have recently received much attention due to their enhanced electron-acceptor features and are of current interest for organic electronics. Liquid crystal viologens consisting of a bithiophene conducting spacer between the pyridinium rings (thienoviologens) have been recently synthesized with the aim to obtain electron-transport semiconductor materials.[1] They exhibit very interesting multifunctional bulk properties such as electrochromism and electrofluorochromism that can be exploited in several electro-optical devices.[2] Herein we present the synthesis of the viologen dications 4,4'-(2,2'-bithiophene-5,5'-diyl)bis(1-alkylpyridinium)$^{++}$ (mV^{++}s) with alkyl-chains of different lengths (m = 9-11), coupled with different anions in order to investigate their effect on the mesomorphic as well as on the bulk electro-optical properties. The liquid-crystalline phases were studied via polarizing optical microscopy, differential scanning calorimetry and powder X-ray diffraction analysis.



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CHF-P27

Solid State NMR study of hybrid active fillers for PEMFCs

Chiara Ferrara[a], *Alice Silvia Cattaneo*[a], *Simone Angioni*[a], *Davide Carlo Villa*[a],
Eliana Quartarone[a], *Piercarlo Mustarelli*[a]

*a - Dipartimento di Chimica, Università degli Studi di Pavia, Via Taramelli 12 , 27100,
Pavia, Italy*

piercarlo.mustarelli@unipv.it

Proton Exchange Membrane Fuel Cells (PEMFCs) are receiving great attention as energy sources for portable, stationary and transportation applications. The polymer proton conductor electrolyte membrane has a central role in the determination of the functional properties of the fuel cell. Polybenzimidazole (PBI) is a heterocyclic thermoplastic polymer considered one of the principal candidates for cells operating at HT (120-200° C), it needs to be activated with strong acids, *e.g.* H_3PO_4, to obtain high proton conductivity. The main challenge is to enhance the transport properties of PBI membranes, while maintaining its thermal and mechanical properties. One strategy is the use of passive/active inorganic fillers. SBA15 mesoporous silica, thanks to the open structure with hexagonal arrays of pores and high surface area, allows high degree of functionalization with organic chains. A detailed structural characterization of the hybrid organic/inorganic filler is mandatory for the comprehension of the role of the filler under working conditions.

Here we present the one-pot synthesis route for the functionalized SBA15 with propyl sulfonic units. Samples with 10, 20, 50 and 70 % w/w have been prepared for the first time and fully characterized by the means of ^{13}C and ^{29}Si solid state NMR. The analysis of the ^{29}Si data confirms the actual degree of functionalization together with the retention of the mesoporosity; the presence of the SO_3H units and side products is revealed by the ^{13}C measurements. Results on the nature of the interaction between silica and organic parts are presented.

CHF-P28

Dion-Jacobson type organic-inorganic hybrids: a structural study

Chiara Ferrara[a], *Alice Silvia Cattaneo*[a], *Cristina Tealdi*[a], *Piercarlo Mustarelli*[a], *Adriana Mossuto Marculescu*[b], *Antonino Martorana*[b], *Francesco Giannici*[b]

a - Dipartimento di Chimica, Università degli Studi di Pavia, Via Taramelli 12 , 27100, Pavia, Italy

b - Dipartimento di Fisica e Chimica, Università degli Studi di Palermo, Viale delle Scienze, 90128, Palermo, Italy

piercarlo.mustarelli@unipv.it

Organic-inorganic hybrid materials are receiving growing attention as a class of promising compounds with tunable properties, including proton conductivity and photocatalytic activity, that can be modulated thanks to an accurate combination of the host layered structure, the organic moieties and synthetic conditions. Between the variety of inorganic host materials, the protonated form of layered oxides belonging to the Ruddlesden-Popper and Dion-Jacobson families are found to be particularly suitable for organic functionalization. This is due to the possibility to tune the interlayer spacing by accommodating several organic units according to different reaction mechanisms (acid/base interaction or covalent grafting). In particular, the intercalation synthesis approach allows to obtain nano-scaled hybrid materials with well-defined interlayer structure and a good distribution of the organic units between the layers.

In this study we present the synthesis via intercalation of a series of functionalized $HLaNb_2O_7$ samples with different organic molecules, including amines, alcohols, acids and organosilanes. The samples have been investigated through the combined use of XRD and ^1H, ^{13}C solid state NMR in order to characterize both the organic and inorganic components of the system, and to highlight the nature of the interaction, the conformations and the degree of order of the organic chains.

CHF-P29

Physicochemical study of the interaction between an octapeptide derived from glycoprotein gp36 of FIV and model membrane systems

Rosario Oliva[a], Luigi Petraccone[a], Marco Ignazio Stellato[a], Gerardino D'Errico[a], Luigi Paduano[a], Anna Maria D'Ursi[b] and Pompea Del Vecchio[a]

a Dipartimento di Scienze Chimiche, Università di Napoli "Federico II", Via Cintia 21, 80126, Napoli, Italia
b Dipartimento di Farmacia, Università di Salerno, Via Giovanni Paolo II 132 , 84084, Salerno, Italia

rosario.oliva11@gmail.com

The interactions between peptides and lipid bilayers are fundamental in a variety of key biological processes and among these the fusion process by viral proteins is one of the most important. It is known that the glycoprotein gp 36 of the feline immunodeficiency virus (FIV) has a key role in the fusion process. Particularly, it was found that a small region of the membrane proximal external region (MPER) is of fundamental importance[1,2]. In this study, we report a physicochemical characterization of the interaction process between an octapeptide of that region, named C8, and some biological membrane models (liposomes) by using calorimetric and circular dichroism measurements. CD studies have shown that the peptide conformation changes upon binding to the liposomes. ITC measurements have shown that the interaction between C8 and liposomes strongly depends on the lipid composition. DSC studies with liposomes of DPPC, DPPC/Chol and POPC/SM indicated that the peptide interacts preferentially with zwitterionic polar headgroups affecting dramatically the thermotropic properties of the liposomes. In conclusion, this study can provide interesting insights into the role of this short fragment in the infection process.

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CHF-P30

Photochromism of chiral chromenes

Fausto Ortica[a,b], *Michel Frigoli*[c], *Pier Luigi Gentili*[a], *Loredana Latterini*[a], *Francesco Nucera*[a], *Danilo Pannacci*[a], *Roccaldo Sardella*[d], *Stefania Scorzoni*[d]

a Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia, Via Elce di Sotto 8, 06123, Perugia, Italia
b Istituto Nazionale di Fisica Nucleare (INFN), Via Pascoli, 06123, Perugia, Italia
c Institut Lavoisier de Versailles, UMR CNRS 8180, Université de Versailles Saint-Quentin-en-Yvelines, 45 av des Etats-Unis, 78035 Versailles, France
d Dipartimento di Scienze Farmaceutiche, Università di Perugia, Via Fabretti 48, 06123, Perugia, Italia

fausto.ortica@unipg.it

Chromenes are a well-known category of photochromic compounds which generally exhibit T-type behaviour [1,2]. However, the possibility to turn them into P-type molecules constitutes an interesting and challenging opportunity [3], and might offer a possible alternative to other extensively studied P-type molecules, such as diarylethenes [4].

Herein we report on the photochromic behavior of some new helical chromenes, where the helical scaffold has the interesting effect of increasing the thermal stability of the transoid-trans (TT) isomer formed upon UV irradiation of the starting molecule, thus pushing these systems towards a P-type photochromism. These chromenes possess either one or two chiral elements, therefore our efforts have been first addressed to their chromatographic stereoisomeric separation, carried out by two polysaccharide-based chiral stationary phases. The photochromism of the racemic mixtures and the different enantiopure solutions has been investigated by both non-polarized and circularly polarized light. The quantum yields of the photochemical processes and the rate constants of the thermal pathways involved were determined.

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CHF-P31

Identification of two LRET pathways in the *A. Auricula-Judae* Dye-decolorizing Peroxidase: an EPR and QM/MM study

Rebecca Pogni[a], *Maria Camilla Baratto*[a], *Adalgisa Sinicropi*[a], *Francisco Javier Ruiz-Dueñas*[b], *Verónica Sáez-Jiménez*[b], *Dolores Linde*[b], *Angel T. Martínez*[b], *Riccardo Basosi*[a]

a Dipartimento di Biotecnologie, Chimica e Farmacia, Università di Siena, Via A. Moro 2, 53100, Siena, Italia
b Centro de Investigaciones Biológicas, CSIC, Ramiro de Maeztu 9, E-28040 Madrid, Spain

rebecca.pogni@unisi.it

Amino acid radicals are found as redox active reaction intermediates in an increasing number of enzymes [1]. Versatile peroxidases are ligninolytic enzymes capable of oxidizing large molecular size aromatic compounds. The proposed catalytic mechanism involves formation of the Fe^{4+}=O-porphyrin radical (Cpd I), and a long range electron transfer to form a tryptophan radical at the protein surface. High-Field EPR and ENDOR studies, on a freeze-trapped radical intermediate in the reaction of VP from *P.eryngii* with hydrogen peroxide, clearly identified a neutral tryptophan radical [2]. Quantum-mechanics/molecular-mechanics (QM/MM) calculations have allowed a detailed characterization of the tryptophan radical within the protein matrix of VP [3]. In some members of the peroxidase superfamilies, like the more recently discovered, dye-decolorizing peroxidases (DyPs), the catalytic mechanism is still to be defined. Starting from the EPR data of *P. eryngii* VP and its variants, newly collected EPR data combined with a QM/MM investigation on AauDyPI (native and variants) will be presented to shed light on the catalytic mechanism through the identification of surface-exposed protein radical sites for the oxidation of large molecular size substrates.

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CHF-P32

Gold nanoparticles as a novel delivery system for chlorophyll a in aqueous medium

V.Rizzi[a], *T.Placido*[a],*P.Fini*[b],*P.Semeraro*[a], *R.Comparelli*[a], *A.Agostiano*[a], *P.Cosma*[a]

[a]*Università degli Studi "Aldo Moro" di Bari, Dip. Chimica, Via Orabona, 4- 70126 Bari, Italy*

[b]*Consiglio Nazionale delle Ricerche CNR-IPCF, UOS Bari, Via Orabona, 4- 70126 Bari, Italy*

vito.rizzi@uniba.it

The application of biomolecules in a variety of fields of materials science such as biomedical engineering [1] is potentially one of the most important emerging new technologies. Among biomolecules, chlorophylls (Chl) are by far the most abundant on the earth [2] and Chl a could be used as photosentizer (PS) in photodynamic therapy(PDT) to treating malignant tumours and hyperproliferative diseases [3].Yet the drawback of using Chl a, with such a property, is that it has a high tendency to aggregate giving rise to photoinactive forms of the PS, powerless to produce Reactive Oxygen Species(ROS). Subsequently a suitable delivery system is required in order to keep the PS as monomer in solution. Moreover Chl a high photodegradation is another major limitation. This is unfortunate since chlorophylls are the best photoreceptors in nature. Thus, if the photostability of chlorophylls could be changed significantly, their application would be enormously improved since the long-stability of the molecules is the prerequisite for their commercialization.With regard to this, we have employed gold nanoparticles (AuNPs) to develop a novel delivery system able to control the photoprotection of Chla. A comprehensive investigation of the system Chl a/AuNPs has been carried out in our laboratory using several techniques, as UV-VIS, FTIR, XPS spectroscopies and TEM analysis.

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CHF-P33

Rose Bengal-sensitized photooxidation of 4-thiotymidine in aqueous medium

V.Rizzi[a], *I.Losito*[a,c],*P.Fini*[b], *P.Semeraro*[a], *A.Agostiano*[a,b], *P.Cosma*[a,b]

a Università degli Studi "Aldo Moro" di Bari, Dip. Chimica, Via Orabona, 4- 70126 Bari, Italy
b Consiglio Nazionale delle Ricerche CNR-IPCF, UOS Bari, Via Orabona, 4- 70126 Bari, Italy
c Centro Interdipartimentale SMART, Via Orabona, 4- 70126 Bari, Italy

vito.rizzi@uniba.it

Light has played a therapeutic role for humans for centuries. Indeed, ancient Egyptian, Indian and Chinese populations used the exposure to sun to treat a variety of diseases, including vitiligo, psoriasis, cancer and even psychosis [1]. Among modern versions of such a therapeutic approach, the Photo Dynamic Therapy (PDT), i.e. the combination of a light source with a photosensitizing agent and endogenous molecular oxygen, has emerged as a therapy for cancer and for hyperproliferative, ophthalmic and dermatologic diseases in the last 30 years and is currently feasible in several medical institutions around the world [2]. The study of the generation and reactivity of ROS during a PDT process is thus extremely important [3].The most studied ROS, considered the major responsible of the peroxidation of proteins within a cell, is the $^1O_2$ [4]. Although further reactive species can be present during a PDT treatment, they can be difficult to detect, due to the *in vivo* capture by a variety of antioxidants, making their lifetime very short. It is thus essential to develop appropriate methodologies for their detection. Fluorescent probes are excellent sensors of ROS due to their high sensitivity, simplicity in data collection and high spatial resolution in microscopic imaging techniques, but their major drawback is the risk of interference. Consequently, an investigation on a novel probe, potentially able to detect ROS, i.e. 4-Thiothymidine (S^4TdR), has been recently undertaken in our laboratories. The identification of the main photo-oxidation products by means of Electrospray-Ionization Mass Spectrometry (ESI-MS) will be described.

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CHF-P34

Effect of methaacrylic acid on the structure of Eu:YAG-PMMA composites

Maria Luisa Saladino[a], *Delia Chillura Martino*[a], *Francesco Armetta*[a], *Alberto Spinella*[b], *Eugenio Caponetti*[a,b]

[a] *Dipartimento Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche - STEBICEF, Università di Palermo, Parco d'Orleans II, Viale delle Scienze pad.17, Palermo I-90128, Italy.*
[b] *Centro Grandi Apparecchiature- UniNetLab, Università degli Studi di Palermo, Via F. Marini 14, I-90128 Palermo, Italy.*

marialuisa.saladino@unipa.it

Polymeric composites of lanthanide-doped materials were recently considered as potential candidates for the development of light emitting diodes, lasers and luminescent concentrators for solar cells. In particular, nanoparticles of yttrium aluminum garnet (YAG) doped with cerium ions embedded in polymetylmethacrylate (PMMA) have been valuable for white LED devices [1,2].

Different structures and micromechanical properties have been observed when the methacrylic acid (MAA) is present in the composite.

With the aim to understand the effect of MAA on the composite structure, a series of Eu:YAG composites prepared by in situ polymerization starting from mixtures of MAA and methylmethacrylate (MMA) were investigate.

The structure were investigated by using Small Angle X-ray Scattering, X-ray Diffraction, and ^{13}C Cross-Polarization Magic-Angle Spinning NMR. The last technique gave information also about the interactions between the components. Results will be presented and discussed.

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CHF-P35

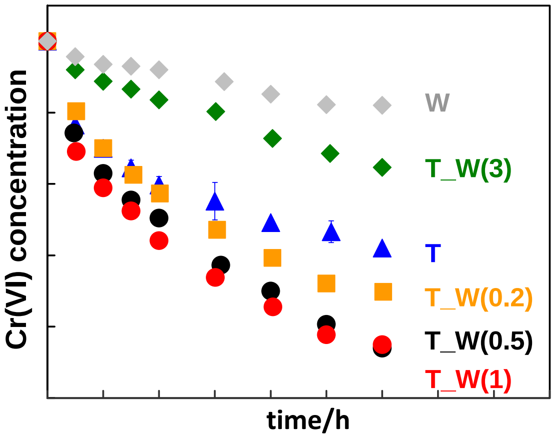
Effect of WO_3 coupling on the Photocatalytic Activity of TiO_2

M. V. Dozzi, F. Riboni, S. Marzorati, M. Longhi, E. Selli

Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milano, Italy

elena.selli@unimi.it

In order to minimize the fast and undesired recombination rate of photoproduced e^-/h^+ pairs on the TiO_2 surface, the effect induced by coupling TiO_2 with different amount of WO_3 [1], according to an alkaline-catalyzed sol-gel method followed by an incipient wetting procedure, has been investigated in both an oxidation and a reduction photocatalytic process, *i.e.* in formic acid (FA) mineralization and in Cr(VI) reduction. A different photo-activity trend of TiO_2-WO_3 materials in the two investigated test reactions was observed. While the progressive increase of W/Ti content limited the surface properties of titanium dioxide in FA oxidation, the coupling of TiO_2 with relatively small amount of WO_3 (0.2-1.0 mol.%) was beneficial in increasing the rate of Cr(VI) photocatalytic reduction, pointing to an essential role of WO_3 domains, acting as electron acceptors, in increasing the efficiency of photoproduced charge carriers separation and of photopromoted electron transfer to the substrate. The correlation between the local distribution of WO_3 regions and the photocatalytic activity of our home-made mixed oxides is discussed in terms of their bulk (XRPD) and surface (BET, DRS, STEM) characterization.



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CHF-P36

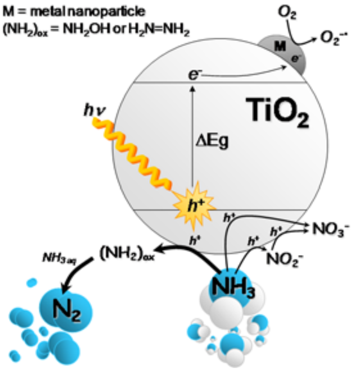
Effects of the TiO_2 phase in the photocatalytic oxidation of aqueous NH_3

M. Altomare[a], M.V. Dozzi[a], G.L. Chiarello[a], A. Di Paola[b], L. Palmisano[b], E. Selli[a]

[a] *Dipartimento di Chimica, Università di Milano, Via Golgi 19, 20133 Milano, Italy*
[b] *Dipartimento di Energia, Ingegneria dell'Informazione, e Modelli Matematici, Università di Palermo, Viale delle Scienze, 90128 Palermo, Italy*

elena.selli@unimi.it

Pure brookite, anatase and rutile TiO_2 nanopowders, synthesized through thermo-hydrolysis of $TiCl_4$ and modified by the deposition of Pt nanoparticles, were tested in the photocatalytic oxidation of aqueous NH_3. Ammonia conversion and the selectivity toward mildly oxidized N_2 and highly oxidized nitrite and nitrate anions were monitored during the runs [1,2], employing both naked and Pt-modified semi-conductor particles as photocatalysts. Pt addition largely increased the rate of ammonia conversion. Pure brookite powders modified with Pt nanoparticles, which already proved to be efficient photocatalysts in thermodynamically up-hill H_2 production through photo-steam reforming of methanol [3], were found to be most efficient also in down-hill aqueous ammonia abatement, with the highest selectivity (*ca.* 30 %) toward innocuous N_2, this parameter being pretty important in view of a large scale photo-abatement of NH_3, where the amount of noxious nitrite and nitrate ions must be kept as low as possible. Furthermore, intriguing effects concerning the mechanism of NH_3 degradation where observed upon Pt nanoparticles deposition on pure brookite powders.



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CHF-P37

Chlorophyll/Alginate microparticles for Photodynamic Therapy applications

Paola Semeraro[a], *Paola Fini*[b], *Guglielmina Alessandra Chimienti*[c], *Tiziana Placido*[a], *Vito Rizzi*[a], *Angela Agostiano*[a,b], *Pinalysa Cosma*[a,b]

a Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro", Via Orabona 4,70126, Bari, Italia
b Dipartimento di Chimica, Consiglio Nazionale delle Ricerche CNR-IPCF, UOS Bari, Via Orabona 4, 70126 Bari, Italia
c Dipartimento di Bioscienze, Biotecnologie e Biofarmaceutica, *Università degli Studi di Bari "Aldo Moro", Via Orabona 4,70126, Bari, Italia*

paola.semeraro@uniba.it

The goal of this study is the chemical-physical characterization of a drug delivery system for Photodynamic Therapy (PDT) [1]: Chlorophyll *a* (Chl *a*) entrapped in a water-soluble matrix made of Ca^{2+} cross-linked alginic acid [2]. Chl *a*, a lipophilic natural pigments, is a molecule with characteristic photosensitising properties usable in PDT. In PDT the photosensitizer, selectively accumulated in malignant tissues, produces, upon light irradiation, reactive oxygen species (ROS) which are responsible for cytotoxicity of neoplastic cells and tumor regression since induce cellular damage via apoptosis, necrosis, or both. The Chl *a*/alginate microspheres produced were characterized by means of different techniques as UV-Vis absorption and emission spectroscopy, FT-IR spectroscopy, Atomic Force Microscopy, Dynamic Light Scattering and Differential Scanning Calorimetry. Moreover, it was estimated the ROS production, mainly singlet oxygen ($^1O_2$) by means of a selective luminescent probe, Singlet Oxygen Sensor Green [3] and *in vitro* tests were carried out on human adenocarcinoma cells (HT29).

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CHF-P38

Computational Spectroscopy of Protein Radicals in Cytochrome c Peroxidase

C. Bernini[a], E. Arezzini[a], R. Basosi[a], A. Sinicropi[a]

a Dipartimento di Biotecnologie, Chimica e Farmacia, Università degli Studi di Siena, Via A. Moro, 2, 53100, Siena, Italia

adalgisa.sinicropi@unisi.it

Cytochrome c peroxidase (CcP) is a heme-containing enzyme involved in the mitochondria electron transport chain. Similar to other heme peroxidases, the ferric resting form of CcP is first oxidized by H_2O_2 to a two-electron oxidized intermediate (Cp-I), in which one oxidizing equivalent is stored as an oxoferryl species, while the second one as a protein radical. Cp-I is then reduced by two molecules of Cytochrome c to cycle back to the resting enzyme [1]. Electron paramagnetic resonance (EPR) and electronic and nuclear double resonance (ENDOR) measurements indicated that both a tryptophan and a tyrosine radical contributed to Cp-I [2]. Despite this, no definitive answer on the assignment of the radical species to a specific tryptophan and tyrosine residue has yet been provided. Moreover, so far, the neutral or charged nature of the tryptophan radical has not been clearly indicated.

Here we employ a computational strategy [3] based on density functional theory (DFT) and multiconfigurational (CASSCF, CASPT2) methods to build quantum-mechanics/molecular-mechanics (QM/MM) models of tryptophan and tyrosine radicals within the protein matrix of CcP. The results show that the models correctly predict the magnetic, electronic and vibrational properties of the observed amino acid radicals of Cp-I and demonstrate that a tryptophan cationic radical (Trp191$^{\bullet+}$) and three tyrosine residues (Tyr203, Tyr236 and Tyr251), located along two possible ET pathways involving Trp191$^{\bullet+}$, are possible candidates to host the Cp-I radical species.

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CHF-P39

Polymer Solar Cells based on Benzodithiophene Copolymers

Parenti F.[1], Diana R.[2], Fontanesi C.[1], Minarini C.[2], Morvillo P.[2], Ricciardi R.[2], Schenetti L.[3], Tassinari F.[1], Mucci A.[1]

[1] Department of Chemical and Geological Sciences, University of Modena and Reggio Emilia,
Via G. Campi 183, 41125 Modena (MO)
[2] ENEA National Research Center, Piazzale E. Fermi 1, 80055 Portici (NA)
[3] Department of Life Sciences, University of Modena and Reggio Emilia,
Via G. Campi 183, 41125 Modena (MO)

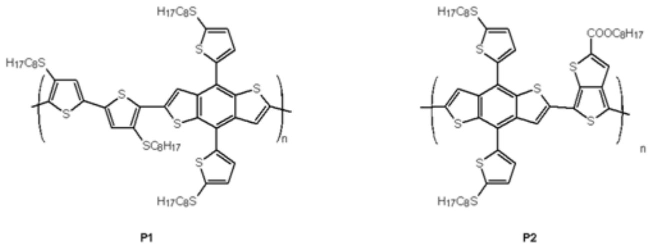
adele.mucci@unimore.it

Polymer solar cells are widely seen as the promise of a cheap alternative to the silicon-based ones. In addition to their low costs, they also have other advantages such as light weight, easy processability and compatibility with large scale flexible substrates, which make them suitable for a wide range of applications.

However, the efficiency of photovoltaic energy conversion for these plastic devices is still low and this is limiting their commercial use. The efficiency of these polymeric photovoltaic cells got a significative increase when the bulk heterojunction (BHJ) configuration was introduced: it consists in an interpenetrating network of electron donor and acceptor materials that largely increases the active area and diminishes the distance that charge carriers have to travel.

Recently, benzodithiophene (BDT) based polymers have been used as electron donors in polymer solar cells showing very promising properties such as an increased charge transport and a red shift on the absorption spectra.

In this work, the synthesis of different regioregular copolymers having substituted BDT as one of the monomers (Fig.1) are described. The obtained polymers are characterized by spectroscopic and electrochemical techniques. Energy conversion measurements of BHJ solar cells produced with these polymers were conducted, and the electrical performances were compared in order to study the influence of the different comonomers on the overall efficiency of the devices.



P1 P2

Figure 1 Structure of P1 and P2. The second copolymer block in P1 is 4-4'-bis(octysulfanyl)-2,2'-bithiophene, while in P2 is octyl thieno[3,4-b]thiophene-2-carboxylate.

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CHF-P40

Synthesis and chemical-physical study of USPION's nanoparticles

Sara Dolci[a], Valentina Domenici[a], Celia Duce[a], Guido Pampaloni[a], Maria Rosaria Tinè[a], Vincenzo Ierardi[b], Ugo Valbusa[b], Zvonco Jaglicic[c], Adriano Boni[d], Mauro Gemmi[d]

[a]Dipartimento di Chimica e Chimica Industriale, Università di Pisa,Via Risorgimento 35, 56126-PISA, Italy, [b]NanoMed Labs, Dipartimento di Fisica, Università di Genova, Largo R. Benzi 10, 16132-GENOVA, Italy, [c]Institute of Mathematics, Physics and Mechanics & Faculty of Civil and Geodetic Engineering, University of Ljubljana, Jadranska 19, 1000 LJUBLJANA, Slovenia. [d]Center for Nanotechnology Innovation @NEST, Istituto Italiano di Tecnologia, Piazza San Silvestro 12, 56127 PISA, Italy.

mrt@dcci.unipi.it

In this research project [1] we deal with the preparation and physical-chemical characterization of new ultrasmall iron oxide superparamagnetic nanoparticles (USPIONs), functionalized with titanium-N,N-dialkylcarbamato, to be used in biomedical and biotechnological applications, as MRI contrast agents, and as MRI probes. The surface and coating structure of both the starting USPIONs, covered by oleic acid, and the new USPIONs functionalized by titanium-N,N-dialkylcarbamato, was characterized by FT-IR spectroscopy on the solid powders and thermo-gravimetric analysis (TGA) coupled with an FT-IR detector in order to investigate the self-assembling properties of the coating. A detailed dimensional and morphological study was carried out by TEM and AFM. Zero-field-cooled (ZFC) and field-cooled (FC) magnetic susceptibility curves as well as the magnetization behavior as a function of temperature were investigated. These results confirmed the superparamagnetic properties of the new nanoparticles functionalized by titanium-N,N-dialkylcarbamato, highlighting the quite high saturation value of the magnetization. A model of the coating structure and ligand organization around the magnetic core is proposed.

[1] PRIN 2010-2011 n. 2010C4R8M8 "Nanoscale Functional Organization of (Bio)Molecules and Hybrids for Targeted Application in Sensing, Medicine and Biotechnology"

CHF-P41

Large scale DFT calculations of ibuprofen adsorbed in MCM-41 mesopores

Piero Ugliengo[a], *Massimo Delle Piane*[a], *Marta Corno*[a], *Alfonso Pedone*[b]

[a]*Dipartimento di Chimica and NIS (Nanostructured Interfaces and Surfaces Centre),*
Università degli Studi di Torino, Via P. Giuria 7, 10125 Torino - Italia
[b]*Università di Modena e Reggio Emilia, Dipartimento di Chimica, Via Campi 183, 41100*
Modena - Italia

piero.ugliengo@unito.it

Mesoporous materials are characterized by an ordered pore network with high homogeneity in size and very high pore volume and surface area. Among silica-based mesoporous materials, MCM-41 is one of the most studied since it was proposed as a drug delivery system. Notwithstanding the relevance of this topic, the atomistic details about the specific interactions between the surfaces of the above materials and drugs and the energetic of adsorption are almost unknown.

We resort to a computational ab-initio approach, based on periodic Density Functional Theory (DFT), to simulate the features of the MCM-41 mesoporous silica material with respect to adsorption of ibuprofen, starting from our previous models of a silica-drug system. [1] We sampled the potential energy surface of the drug-silica system by docking the drug on different spots on the pore walls of a realistic MCM model. [2] The drug loading was then gradually increased resulting in an almost complete surface coverage. Furthermore, we performed ab-initio molecular dynamics simulations to check the stability of the interaction and to investigate the drug mobility.

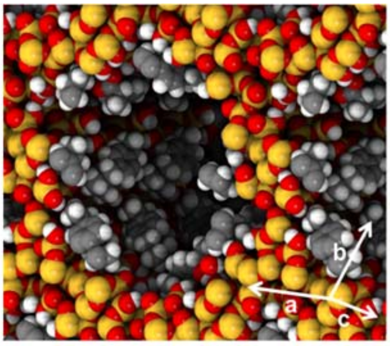

Figure 1. View of multiple ibuprofen molecules adsorbed into the pore of the MCM-41 model.

Through our simulations we demonstrated that ibuprofen adsorption seems to follow a quasi-Langmuirian model. Particularly, we revealed that dispersion (vdW) interactions play a crucial role in dictating the features of this drug/silica system. Finally, simulations of IR and NMR spectra provided useful information to interpret ambiguous experimental data.

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CHF-P42

Nanocrystalline semiconducting-magnetic heterostructures decorated with cyclic RGD peptide for Integrin targeting

G. Valente[1], N. Depalo[2], I. de Paola[3], R. Comparelli[2], E. Fanizza[1], M. Striccoli[2], A. Agostiano[1,2], N. Denora[4], V. Laquintana[4], R. M. Iacobazzi[4], M. Saviano[5], A. Del Gatto[3], L. Zaccaro[3], M. L. Curri[2]

1 Università di Bari, Dip. di Chimica, Via Orabona 4, 70125 - Bari, Italy
2 CNR-IPCF Bari, Via Orabona 4, 70125 - Bari, Italy
3 CNR IBB Napoli,Via Mezzocannone, 16, Napoli 80134, Italy
4 Università di Bari, Dip. di Farmacia , Via Orabona 4, 70125 - Bari, Italy
5 CNR IC Bari,Via Amendola 122/O, 70126 Bari

gianpiero.valente@uniba.it

Multifunctional nanoparticles based on inorganic heterostructures, able to integrate different features within a single construct, can be conjugated with targeting ligands to achieve nanoplatforms potentially useful as theranostic nanosystems.[1,2] Here, asymmetric binary nanocrystals (BNCs), composed of a semiconductor TiO_2 nanorod joined to a magnetic γ-Fe_2O_3 spherical domain, have been embedded in polyethylene glycol (PEG) modified phospholipid micelles. A purposely designed peptide containing the RGD motif for targeting of $\alpha_v\beta_3$, expressed on several types of cancer cells, has been successfully conjugated with the BNC incorporated in lipid micelles. The BNC bioconjugation process has been optically and structurally investigated, and the obtained bioconjugates (with a hydrodynamic diameter <100 nm) have been found homogeneously dispersible and stable in aqueous solutions. In vitro assessement have demonstrated that the peptide/BNC conjugates are not cytotoxic in the range of tested concentrations. These systems have a large potential for cancer diagnostic and treatment, as RGD motif can drive the nanostructures toward tumor area, where magnetically induced hyperthermia can be combined with TiO_2-based photodynamic therapy.

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CHF-P43

The rich morphology of nano- and mesoscopic aggregates of glucosteroid porphyrin derivatives

R. Lettieri,[a] *C. Mazzuca,*[a] *R. Cimino,*[a] *D. Monti,*[a] *L. Cardová,*[b] *P. Drašar,*[b] *G. Bocchinfuso,*[a] *A. Palleschi,*[a] *M. Venanzi*[a]

a Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Via della Ricerca Scientfica 1, 00133, Roma, Italia
b Institute of Organic Chemistry and Biochemistry, AS CR, Praha, Czech Republik

venanzi@uniroma2.it

Porphyrins are extremely versatile materials that have been proposed as ideal candidates for use in many applications (sensors, nanoarrays, dye sensitized solar cells (DSSCs) photosensitizers in photodynamic therapy of superficial tumours).
In this work some amphiphilic steroid porphiryn derivatives, differing from the number and type of ring substitutions, were taken in consideration (Figure 1). The aggregation properties in solutions and the formation of porphyrin films on hydrophilic solid surfaces have been investigated by optical spectroscopy (UV-Vis absorption, steady-state fluorescence, circular dichroism), and atomic force (AFM) and scanning electron microscopy (SEM). Organized porphyrin multilayers were built up through Langmuir-Blodgett (LB) deposition on glass supports and the behavior of each system at the air/water interface has been studied recording compression isotherms.
Transferring the porphyrin LB film on a solid surface under controlled experimental conditions, an array of mesoscopic fibers formed by entwined porphyrin nanowires are obtained. The porphyrin-based architectures were characterized by spectroscopic techniques and their morphology was investigated by AFM and SEM measurements.
The electronic conductive properties of these porphyrin nanorods have been characterized by electrochemical and photocurrent generation experiments.

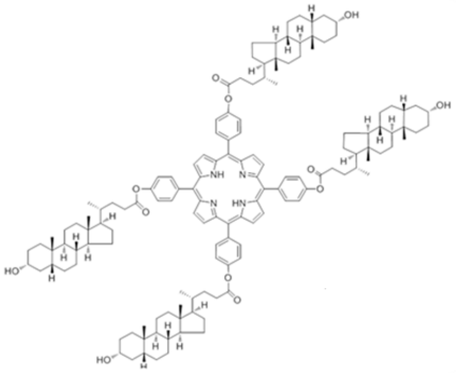

Figure 1. Molecular scheme of a steroid modified porphyrin derivative

CHF-P44

Modelling the carbonate substitution in hydroxyapatite towards bone composition

Marta Corno[a], Massimo Delle Piane[a], Francesca Peccati[b], Gianfranco Ulian[c], Giovanni Valdrè[c], Piero Ugliengo[a]

a Dipartimento di Chimica and NIS (Nanostructured Interfaces and Surfaces Centre), Università di Torino, Via P. Giuria 7, 10125 Torino, Italia
b Departament de Química, Universitat Autònoma de Barcelona, Bellaterra, 08193, Spain
c Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna "Alma Mater Studiorum", Piazza di Porta San Donato 1, 40126 Bologna, Italy

marta.corno@unito.it

Hydroxyapatite [HA, $Ca_{10}(PO_4)_6(OH)_2$] is the main constituent of the inorganic phase of bones and teeth and is studied and applied as a biomaterial for tissues repairing and reconstructing. The biological HA is characterized by the presence of vacancies and defects, the most relevant being the carbonate ion substitution in the lattice (about 6% in weight). The CO_3^{2-} ion can be accommodated either in place of the hydroxyl groups (type A defect) or of the phosphate group (type B) of the unit cell. The detailed knowledge of these possible HA defective structures has recently become fundamental to design improved prosthetic materials, since the carbonate incorporation can influence the adsorption processes at the mineral surface in the biological environment. Theoretical methods can be successfully applied to provide structural information and surface properties and to offer a comparison with experimental measurements.

In the present contribution, some recent results of our computational study on the role of carbonate ion in both fully and partially carbonated hydroxyapatite will be presented. Static calculations at the DFT level have been run to simulate structural, electronic and vibrational bulk properties of the A-, B- and AB-type defects. Moreover, *ab initio* molecular dynamics simulations have been employed to provide insights on the CO_3^{2-} mobility [1]. Work is in progress to model and characterize different surfaces of carbonated apatite, both plain and in interaction with biologically interesting molecules.

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CHF-P45

Sustainable water free cleaning protocol for wax removal from a solid surface

Giuseppe Cavallaro, Giuseppe Lazzara, Stefana Milioto, Filippo Parisi

Dipartimento di Fisica e Chimica, Università di Palermo, Viale delle Scienze Ed. 17, 90128, Palermo, Italia

stefana.milioto@unipa.it

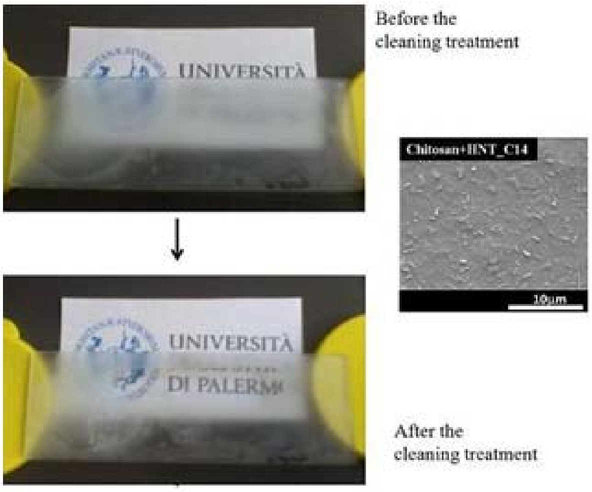

Fig. 1. Example of wax removal and SEM image of chitosan/HNT_C14 composite

In this work we prepared nanocomposite films of chitosan+halloysite by using the casting method. Both components are sustainable and from renewable resources. Beside native halloysite, we investigated the effect of modified halloysite with sodium tetradecanoate (HNT_C14). This modification generates nanotubes with an hydrophobic lumen [1]. This modification generates a "sponge" to incorporate organic solvent (like n-decane) to be used in water free cleaning of solid surfaces. This is a typical case for Cultural Heritage where sustainability of the employed materials is attracting the attention of several operators besides safety concerning the large use of solvents and a controlled cleaning that cannot be obtained by using free solvent or aqueous based mixtures. The results show that chitosan/HNT_C14 is satisfactorily working and a controlled wax removal is achieved (Fig. 1). SEM images on the composites (Fig.1) showed the presence of well dispersed nanotubes at the chitosan/HNT_C14 nanocomposite surface explaining the cleaning performance. The work was financially supported by the University of Palermo, PRIN 2010-2011 (prot. 2010329WPF), FIRB 2012 (prot. RBFR12ETL5) and PON 2007-2013 STI-TAM.

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CHF-P46

Clay Nanotube/PNIPAAM Hybrid Material

Giuseppe Cavallaro, Giuseppe Lazzara, Stefana Milioto, Filippo Parisi

Dipartimento di Fisica e Chimica, Università di Palermo, Viale delle Scienze Ed. 17, 90128, Palermo, Italia

stefana.milioto@unipa.it

Halloysite (HNT) is a naturally occurring nanotube. This two-layered aluminosilicate with empirical formula ($Al_2Si_2O_5(OH)_4$•$2H_2O$) has a polydispersed hollow tubular structure. The HNTs external surface is composed of Si−O−Si groups conferring the negative charge while the internal surface consists of a gibbsite-like array of Al-OH groups conferring the positive charge; such a situation is present in a wide pH range.

We investigated the adsorption of Poly(N-isopropylacrylamide) (PNIPAAM) by TGA, turbidimetry, DLS and ζ-potential measurements onto this material. The PNIPAAMs polymers are stimuli-responsive and undergo rapid changes in their microstructure from a hydrophilic to a hydrophobic state, triggered by changes in the environment including heat, pH, ionic strength, additives, etc. The selectivity towards the inner surface of the HNT lumen was pursued by employing an PNIPAAM amine terminated polymer. The ζ-potential experiments revealed a larger net negative charge for the PNIPAAM/HNT modified (-31±1 mV) with respect to the pristine HNT (-19.4 mV) [1,2]. Turbidimetry measurements show that the obtained hybrid materials can form more stable aqueous dispersion than those obtained for pristine HNTs due to the increased electrostatic repulsions between the functionalized nanoparticles.

We put forward an easy strategy to prepare hybrid materials with PNIPAAM modified hollow cylindrical shape of the nanotube which can be properly used into aqueous phase for external-stimuli triggered solubilization and delivery of hydrophobic compounds. The work was financially supported by the University of Palermo, PRIN 2010-2011 (prot. 2010329WPF), FIRB 2012 (prot. RBFR12ETL5) and PON 2007-2013 STI-TAM.

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CHF-P47

On the photoisomerization of caffeic acid in the presence of nanostructured TiO_2

F. Parrino[a], *E. Garcia-Lopez*[a], *V. Loddo*[a], *I. Pibiri*[b], *A. Di Paola*[a], *L. Palmisano*[a]

a Dipartimento DEIM, Università di Palermo, Viale delle Scienze Ed. 6, 90128, Palermo, Italia

b Dipartimento STEBICEF, Università di Palermo, Viale delle Scienze Ed. 16, 90128, Palermo, Italia

francesco.parrino@unipa.it

Caffeic acid ($C_9H_8O_4$) is a natural compound belonging to the family of hydroxycinnamic acids. The photoisomerization of cinnamic acids may occur through a non-sensitized process by irradiation with light of suitable wavelength [1], but heterogeneous photocatalytic isomerization of cinnamic acids was never reported.

In this work we investigated the photoisomerization of trans-caffeic acid (T) to cis-caffeic acid (C) under UV light irradiation both in homogeneous phase and in the presence of various TiO_2 powders. Two commercial TiO_2 samples (Degussa P25 and Merck) and a home-prepared TiO_2 sample (HP0.5) were used as catalysts. The runs were performed bubbling nitrogen through the reacting mixture at different pH values. The photoisomerization proceeded until a photo-stationary state was reached and a constant value of the C/T ratio was obtained. Increasing pH resulted in higher C/T ratios. In the absence of TiO_2 and at pH = 8, the photostationary state was reached at C/T = 1.8. In the presence of P25 and HP0.5, the C/T ratio reached values of 2 and 2.2, respectively, whereas in the presence of the Merck sample the C/T ratio was ca. 1.6. From these results one can conclude that the P25 and HP0.5 catalysts took part in the photoisomerization process, whereas the Merck sample revealed a weaker interaction with caffeic acid. A similar behaviour was previously found for the Merck sample in the presence of other hydroxycinnamic acids [2]. The isomerization of caffeic acid in the presence of P25 and HP0.5 occurs through two parallel pathways whose effects are synergistic: (i) the known non-sensitized isomerization in homogeneous phase and (ii) the photocatalytic TiO_2-induced isomerization which is, to our best knowledge, hereby reported for the first time.

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Chimica Industriale

Keynote

IND-K1

Medaglia Pino

NO_x storage and reduction over Lean NO_x Traps

Pio Forzatti

Dipartimento di Energia, Politecnico di Milano, P.zza L. da Vinci 32 –Milano (Italy)

pio.forzatti@polimi.it

The development of catalytic technologies for the control of NO_x emissions from vehicles under lean conditions over the past 20 years has been a remarkable technical achievement. Catalytic lean NO_x removal converters are of commercial importance and extensive research has been done on several aspects of their formulation, synthesis and performance.

Presently Selective Catalytic Reduction (SCR) and NO_x Storage Reduction (NSR) represent the top contenders for lean NO_x removal. The NSR, also referred as Lean NO_x Traps (LNT), implies a cyclic operation of the engine by alternating a long lean phase (30-90 s) and a short rich phase (3-5 s). The basic concept is that NO_x are trapped onto the catalyst when the engine is running lean and are reduced to produce N_2 when the engine is running rich. A typical NSR catalyst comprises a noble metal such as Pt (and Rh) to oxidize NO, CO and unburned hydrocarbons and to reduce trapped NO_x, and an alkaline and/or alkaline-earth component such as Barium and/or Potassium to trap the NO_x as nitrites/nitrates.

In this lecture the research carried out at the Laboratory of Catalysis and Catalytic Processes of Politecnico di Milano on Lean NOx Traps is presented. The reaction paths and the mechanism involved in the storage of NO_x are discussed first. Then the release of NO_x, the reaction paths of NO_x reduction and the mechanism involved in the formation of N_2, NH_3 and N_2O are illustrated.

IND-K2

Paolo Chini Memorial Lecture

Supported metal carbonyl clusters and nanoparticles: molecular approach to heterogeneous catalysis

Rinaldo Psaro

CNR Istituto di Scienze e Tecnologie Molecolari, Via C. Golgi 19,20133 Milano, Italia

r.psaro@istm.cnr.it

Molecular metallic clusters constitute a class of organometallic complexes which almost fill the gap between molecular chemistry and surface science. In fact, the family of large molecular clusters developed since the early 1970s by Chini group [1], were excellent good molecular models of metallic particles covered by chemisorbed molecules.

Metal carbonyl clusters have been used as probe molecules on the surface of metal oxides a new field of surface science has been proposed the so-called “surface organometallic chemistry”. The development in the last 30 years of a profound knowledge of surface organometallic chemistry has been a springboard for the preparation and full characterization of single metallic surface sites and tailored supported mono e bimetallic nanoparticles, usually incapsulated into the surface of inorganic oxides [2]. It has become clear that the surface of an inorganic oxide was behaving not only as a ligand but also as an electron donor, whose properties were related to acidic or basic nature of the surface oxygen or hydroxyl groups. Based on this approach, we proposed a mechanism by which molecular rhodium single sites and palladium nanoparticles cooperate with each other in promoting the hydrogenation of arenes. Recently, we report a new focus point on the properties of supported copper oxide nanoparticles: can the particle size induce acidic behaviour?

This presentation is dedicated to the memory of our colleague and friend Laura Sordelli, she has left us too soon.

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IND-K3

Gian Paolo Chiusoli Memorial Lecture

Single-site heterogeneous catalysts: *interior design architecture* at nanometric scale

Matteo Guidotti

CNR Istituto di Scienze e Tecnologie Molecolari, Via C. Golgi 19, Milano, Italia
Accademia delle Scienze dell'Istituto di Bologna

m.guidotti@istm.cnr.it

The search for active and selective single-site heterogeneous catalysts can be properly compared to an "interior-design architecture" at nanometre scale level. Catalyst preparation has been considered for a long time as one of the last strongholds of alchemy. Now the chemist can choose the best combination of parameters in order to design and develop the most suitable catalyst for a specific reaction. With a series of selected examples of nanostructured material-based heterogeneous catalysts for the selective oxidation and transformation of fine and specialty chemicals, it is shown how it is possible to modify and tune finely the nature and the number of catalytically-active sites, their chemical environment, the size and the shape of the pore network around them as well as the hydrophilic-hydrophobic character of the support. These post-synthesis modifications aim at improving the activity or the chemo-, regio- and stereo-selectivity of the catalyst, making the porous inorganic oxide fit around the substrate molecule.

Based on this approach, promising performances were obtained in the oxidation of high-added vale terpenes and substituted phenols [1], in the functionalisation of unsaturated fatty acid derivatives [2] and in the production of aromatic ketones [3].

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IND-K4

ENI research on next generation photovoltaics

Roberto Fusco[a], *Daniele Testa*[a]

a eni S.p.A. Research Center for Non Conventional Energies – Istituto eni donegani, Via Fauser 4, 28100, Novara,

roberto.fusco1@eni.com

Silicon based photovoltaic cells are the most widespread solar cells on the market. The reasons reside in the peculiar properties that make silicon the ideal semiconductor material for this application.1) Their cost dropped dramatically in the last years also for the introduction of new production technologies. However some characteristics like color, opacity, rigidity, weight, make this material not suitable for some applications. Other kinds of PV devices have been developed in the last years, characterized by large color palette, semi-transparency, flexibility, making them more suitable for some applications in Building Integrated PhotoVoltaics and automotive fields. Eni research in photovoltaics is mainly focused on these new technologies, spanning from Organic and Polymeric Solar Cells to Dye Sensitized Solar Cells and Luminescent Solar Concentrators (LSC), as well as on energy storage, an essential complement for an intermittent energy source like sun. New materials, new dyes and new devices have been developed and patented by eni since 2007 and in 2012 the first demo plant based on LSCs, a photovoltaic shelter for recharging electric bicycles, was installed in R&M eni Division site in Rome (see picture). The next years shall play a key role in demonstrating the real applicability of these new technologies.

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IND-K5

Use of macromolecules in tuning self cleaning and amphiphilic properties of multifunctional biohybrid membranes

Lidietta Giorno

Istituto per la Tecnologia delle Membrane, Consiglio Nazionale delle Ricerche,
ITM-CNR, Via P. Bucci 17/c C/o Università della Calabria, 87036 Rende (CS), Italia

l.giorno@itm.cnr.it

Membrane operations performance depends on both material and process parameters. Surface properties are crucial in controlling component-membrane interaction and therefore affecting fouling, selectivity, transport phenomena. Many research efforts aimed at functionalizing membranes in order to avoid/ minimize adsorption phenomena and good results are obtained with tests in static conditions. However, when using membranes under fluid dynamics conditions, the build up of rejected components quickly overcomes the initial advantage of the low adsorption capacity. Therefore, strategies to promote self-cleaning, mimicking natural processes, have been developed. The proof-concept has been promoted by the construction of a biohybrid membrane, containing an enzyme attached on the surface able to decompose the foulant molecules as they accumulate on the membrane during the operation process. Results showed that an increase of steady-state performance higher than 50% could be achieved. Furthermore, to guarantee the preservation of the enzyme during periodical cleaning and maintenance operation, a reversible immobilization on the membrane based on magnetic field was developed. Results confirmed that steady-state performance was significantly increased, as well as the capability of completely restoring initial membrane performance at each maintenance could be achieved.

Similar strategy was used for preparing membranes functionalized with macromolecules having amphiphilic properties, such as lipases. The approach resulted a powerful tool to construct hierarchical structures that can modulate the surface tension of the membrane depending on the solvent flowing along the surface. This functionalization permits to prepare membranes with different wettability between the membrane thickness and its surface.

Chimica Industriale

Oral

IND-O1

A Novel Batch Reactor Coupled with Tubular Membrane to Efficiently Perform Etherification of Glycerol with TBA

C. Cannilla[a], *G. Bonura*[a], *L. Frusteri*[b], *F. Frusteri*[a]

[a]*CNR-ITAE, Via S. Lucia 5, 98126 – Messina, Italy*
[b]*Dip. di Ing. Elet., Chim. ed Ing. Ind., Contrada Di Dio, Messina I-98166, Italy*

catia.cannilla@itae.cnr.it

Recent growth in biodiesel production by transesterification reaction has produced a significant surplus of glycerol, it being the main byproduct of such process [1]. As a result of this increased availability, the market price of glycerol has dropped rapidly and consequently research has been focused on developing new technologies to convert or use the glycerol to improve the biodiesel business and its economic viability. In this work, a novel approach to obtain high yield to poly-*tert*-butylglycerolethers by glycerol etherification reaction with *tert*-butyl alcohol (TBA) is proposed [2]. The limit of this reaction is the production of the water, which inhibits the formation of poly-ethers potentially usable in the blend with conventional diesel. The results herein reported demonstrate that the use of a water permselective membrane offers the possibility to shift the equilibrium toward the formation of poly-ethers since the water formed is continuously and selectively removed from the reaction medium by the recirculation of the gas phase. Using a proper catalyst and optimizing the reaction conditions, in a single experiment, a total glycerol conversion can be reached with a yield to poly-ethers close to 70%, which represents data never before reached using TBA as reactant. The approach here proposed could open up new opportunities for all catalytic reactions affected by water formation

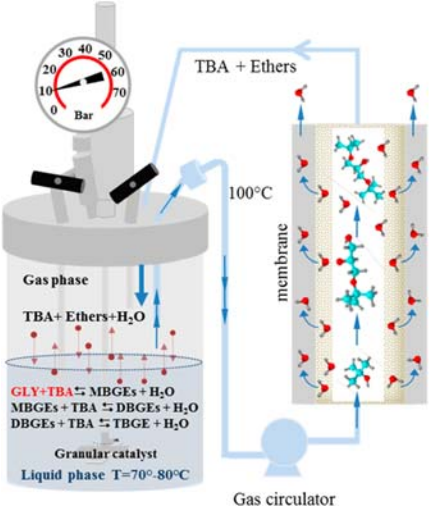

Fig. 1. Reactor-membrane separator configuration for etherification reaction with TBA

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IND-O2

Simultaneous removal of soot and NO_x over silver-based catalytic materials

<u>L. Castoldi</u>[a], E. Aneggi[b], R. Matarrese[a], A. Trovarelli[b], L. Lietti[a]

a Energy Department, Politecnico di Milano, p.za L. da Vinci 32, 20133 Milano, Italy
b DCFA, Università di Udine, via Cotonificio 108, 33100 Udine, Italy

lidia.castoldi@polimi.it

In the present investigation catalytic systems different from PMG-based LNT catalysts have been prepared, which are relevant for the development of improved NO_x abatement systems: Ag(5%wt)/Ba(10%wt)/M_xO_y and Ag(5%wt)/Sr(10%wt)/M_xO_y (M_xO_y = CeO_2, ZrO_2, Al_2O_3) [1,2]. In particular these systems have been tested in the simultaneous removal of NO_x and soot. Soot oxidation experiments show that the presence of Ba, as storage component instead of Sr, decreases the onset temperature of the TPO both in the presence of only O_2 and $NO+O_2$. In Fig. 1 is reported a typical lean-rich cycle carried out over Ba/Ag/Al_2O_3 at 350°C in the absence of soot. As a typical LNT catalyst, this system shows a significant NO_x storage capacity (Fig.1A) but results poorly selective to nitrogen during reduction phase (Fig.1B). When soot is mixed with the catalyst, soot combustion is observed mainly during the lean phase.

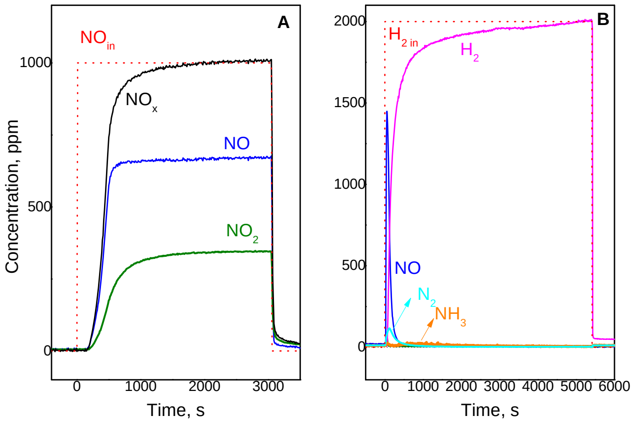

Fig. 1. Lean (A) and rich phase (B) @ 350°C over Ba/Ag/Al_2O_3.

We thank financial support from MIUR (Futuro in ricerca, project SOLYST).

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IND-O3

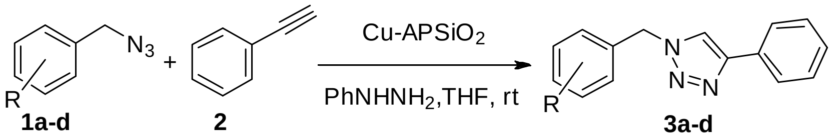
Aminopropyl-silica supported Cu nanoparticles: an efficient catalyst for *continuous-flow* Huisgen azide-alkyne cycloaddtion (CuAAC)

Ravindra P. Jumde,[a] *Claudio Evangelisti,*[a] *Alessandro Mandoli,*[b] *Rinaldo Psaro*[a]

a Istituto di Scienze e Tecnologie Molecolari, CNR, Via Golgi 19, 20133, Milano, Italy.
b Dipartimento di Chimica e Chimica Industriale, Universita di Pisa,Via Risorgimento - 35, 50126, Pisa, Italy

claudio.evangelisti@istm.cnr.it

Here we report the use of Cu nanoparticles obtained by metal vapour synthesis (MVS)[1] supported on commercial aminopropyl-fuctionalized silica (APSiO$_2$) as a novel catalyst for CuAAC reactions under *continuous-flow* conditions.



a = (R = H); **b** = (R = 4-OMe); **c** = (R = 4-NO$_2$); **d** = (R = 3,4-dioxole)

Transmission electron microscopy (TEM) analysis confirmed the presence of Cu nanoparticles highly dispersed on the support, with an average diameter close to 2.8 nm. The immobilized Cu-nanoparticles on APSiO$_2$ in packed-bed reactor were used in continuous-flow CuAAC reactions, which showed remarkable activity and recyclability. Flow-reactions positively compete with the batch reactions, thus affording greater productivity of catalyst and simplified separation procedure. Careful tailoring of reaction conditions allowed exploiting the supported catalyst more effectively and for longer time (productivity = 1689) and also diminished the Cu leaching in the reaction medium (< 9 ppm). The versatility of the flow-system was also proven by sequentially converting different substrates to 1,2,3-triazole products with the same column.

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IND-O4

DRIFTS-HEROS study of CO oxidation on Pt catalysts

Valentina Marchionni[a], *Jakub Szlachetko*[a], *Anastasios Kambolis*[a],

Marteen Nachtegaal[a], *Oliver Kröcher*[a], *Davide Ferri*[a]

a Paul Scherrer Institute,CH-5232 Villigen PSI, Switzerland

valentina.marchionni@psi.ch

The understanding of structure-performance relationships under working conditions is fundamental for catalyst and process development. The combination of complementary spectroscopic techniques in a single experiment is extremely useful to obtain a deeper insight in the catalyst structure under working conditions. Moreover, subjecting the catalyst to fast transient changes is a more suitable approach to selectively access information on active species. In modulation excitation spectroscopy (MES), the catalyst is perturbed by continuous changes of an external parameter with simultaneous acquisition of the spectroscopic signals. To enhance the sensitivity towards structural changes phase sensitive detection (PSD) is applied.

MES was used to investigate CO oxidation over Pt-based three way catalysts combining DRIFTS and high energy resolution off-resonant spectroscopy (HEROS)[1]. The MES-HEROS study allowed characterizing the dissociative adsorption of oxygen followed by partial oxidation of the Pt subsurface that represent the two stages of the slow oxidation step. PSD facilitated the isolation of faint spectroscopic features of Pt-CO and Pt-O species. We identified an intermediate chemisorbed O on Pt that is adsorbed in atop position. Addition of ceria retards Pt reduction and greatly improves the activity of the catalyst in reducing conditions. DRIFTS data of the same experiment shows different sites for CO adsorption and a more important contribution of carbonates species in the presence of Ce.

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IND-O5

W/O microemulsion: a promising synthesis for $Ce_{0.5}Zr_{0.5}O_2$ support for metal catalysts for reforming processes

R. Mafessanti, F. Basile, D. Barbera, G. Fornasari, A. Vaccari

Dipartimento di Chimica Industriale "Toso Montanari", Università di Bologna, V.le Risorgimento 4 , 40136, Bologna, Italy

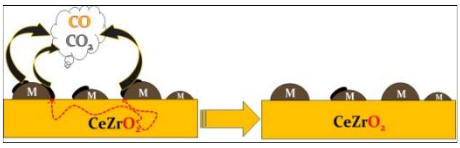
rodolfo.mafessanti2@unibo.it

Steam reforming (SR) is the most utilized process for H_2 production. More than 96% of H_2 derives from the SR of hydrocarbons and more than 50% of the latter amount comes from the steam reforming of methane (SRM – Eq. (1)).

$$CH_4 + H_2O \leftrightarrows CO + 3H_2 \qquad \Delta H^0_{298} = +206\ kJ/mol \qquad (1)$$

This process is affected by two principal problems: the high operative temperature involved (900–1000°C), that require high costs; and the formation of carbonaceous deposits on the active phase, that lead to a sudden deactivation of the catalyst. Thus, the development of new catalytic systems able to avoid carbon formation and stable at high temperatures, is a topic of great interest.

CeO_2-ZrO_2 mixed oxides (CZO) could be good candidates for the formulation of new supported Rh-based catalysts. ZrO_2 gives an high thermal stability while CeO_2 peculiar redox properties (high oxygen mobility), further improved by ZrO_2 insertion, can be exploited in order to eliminate possible carbonaceous deposits formed on the active phase through a "self-regeneration" mechanism (see figure). The oxygen mobility of CZO oxides varies in function of the Ce/Zr ratio, reaching a maximum value for the specific metastable phase $Ce_{0.5}Zr_{0.5}O_2$, not easy to obtain through classical synthesis method, hence the w/o microemulsion has been compared with the classical co-precipitation method. The wished $Ce_{0.5}Zr_{0.5}O_2$ phase is showed (XRD, Raman, TPRO) only by the microemulsion samples. Furthermore, the catalytic activities of the Rh (1% wt) impregnated systems are compared in the oxy-reforming process carried out at lower temperature (750°C) with respect to the SRM. In all of the conditions tested, the microemulsion catalysts show the best activity together with an high stability for a long time of reaction. The effect of Ce/Zr ratio ($Ce_{0.75}Zr_{0.25}O_2$) has been also studied, obtaining results that confirm the higher stability of $Ce_{0.5}Zr_{0.5}O_2$ phase, probably thanks to its higher homogeneity coming from the w/o microemulsion method.



IND-O6

Lactose: from stables to stars

Matteo Mariani[a,b], *Federica Zaccheria*[a], *Nicoletta Ravasio*[a], *Rinaldo Psaro*[a]

a ISTM-CNR, Via Golgi 19, 20133 Milano, Italia
b Dipartimento di Chimica, Università degli Studi di Milano, Via Venezian 22 , 20133, Milano , Italia

matteo.mariani@unimi.it

Lactose is a disaccharide consisting in one molecule of glucose and one of galactose, linked by a β-1→4 linkage. Whey is the primary source of this sugar, indeed it contain about 60% of lactose. Moreover the unprocessed whey is an environmental problem, due to its high oxygen demand[1]. In some countries, like Italy or France, this problem is amplified because of the high production of cheese. In these cases it becomes important to have some processes in hand to valorize this waste. Starting from our knowledge in the field of cellulose deconstruction[2], we have thought to apply it to the disaccharide lactose, because it contain the same glycosidic bond. With Cu/SiO_2 prepared by chemisorption-hydrolysis method, we are able to break the glycosidic bond and, in the same time, to reduce the two sugars. In fact the products of the reaction are sorbitol and dulcitol. Sorbitol is widely used in industry, for example in sugar-free foods, in medicine as laxative, in cosmetics as humectants and in toothpaste. Dulcitol can have similar fields of employ, although inexplored up to now due to very low availability of this sugar. Reactions were carried out in water under 30 bar of H_2 at 180°C for 8 hours and analyzed by HPLC. We observed conversions up to 90% with all catalysts used, and selectivity to sugar alcohols up to 80% with different types of Cu/SiO_2. Temperature and H_2 pressure are also important. A reaction temperature of 200°C decrease the selectivity in reduced product, as well as a lower temperature while an increase in hydrogen pressure cause an higher yield. In conclusion, we started to study a new method for performing one-pot synthesis of reduced sugars (sorbitol and dulcitol), starting from lactose that is obtainable from whey, the largest waste produced from dairy industry.

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IND-O7

Kinetics of NH_3-oxidation and NH_3-SCR over V-based catalysts: impact on the performance of full scale SCR reactor

N. Usberti[a], *A. Beretta*[a], *L. Lietti*[a], *P. Forzatti*[a]

[a] *Dipartimento di Energia, Politecnico di Milano, piazza L. da Vinci 32, 20133 Milano*

alessandra.beretta@polimi.it

NH_3-SCR full-scale reactors operate at NH_3/NO inlet ratios of 0.8, in order to keep NH_3 slip below 2 ppm. A strategy that has been considered in the literature to enhance the NO_X abatement while maintaining NH_3 slip under this limit consists of increasing the NH_3/NO inlet ratio (*High Efficiency SCR Process*) while adding an extra catalyst layer able to efficiently convert the unreacted NH_3 to N_2.

In previous studies, we have first evaluated to possible contribution of NH_3 oxidation on the kinetics of the NH_3-NO reacting system over traditional SCR catalysts. NH_3-SCR and NH_3-oxidation tests on powders showed that at sufficiently high temperature (>350°C) and NH_3/NO inlet ratios close to 1, the DeNOx process ($4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$) is accompanied by an additional contribution of NH_3 non-selective oxidation to NO ($2NH_3 + 5/2\ O_2 \rightarrow 2NO + 3\ H_2O$). In this work, the kinetics of NH_3-SCR and NH_3-oxidation were incorporated in the model of an SCR reactor with honeycomb catalysts, accounting for inter and intra-phase mass transfer resistances; the model is presently applied to design of the SCR reactor operating at high NH_3/NO ratios.

Although the rate of NH_3 oxidation is significantly lower than that of the NH_3-SCR reaction, the overall catalyst volume of the full scale reactor (which is fully available to NH_3 oxidation, characterized by high efficiency factors, while it is only partially exploited by the SCR reaction due to the mass transfer control) is such that the integral effect of the unselective oxidation to NH_3 conversion is important. In practice, the occurrence of some ammonia oxidation inside the monolith wall tends to minimize the NH_3 slip even at high NH_3/NO ratios; this makes unnecessary the use of a “finishing” catalyst layer for NH_3 abatement. However this occurs at the expense of some NO formation.

This study shows the importance of the correct identification of the kinetic scheme (rate expression and stoichiometry) of the NO-NH_3 system for the design of SCR reactors operating under High efficiency conditions.

IND-O8

Low-T Standard SCR reaction mechanism

Tommaso Selleri, Maria Pia Ruggeri, Massimo Colombo,
*Isabella Nova, Enrico Tronconi**

Dipartimento di Energia, Politecnico di Milano, Piazza Leonardo da Vinci 32,
20133, Milano (Italy)

enrico.tronconi@polimi.it

The catalytic mechanism governing the low-T Standard NH_3-SCR performances over metal promoted zeolites is still a matter of discussion. Uncertainties are mostly related to the nature of reaction intermediates [1]. In the present work we apply chemical trapping techniques to conclusively identify the products of the NO oxidative activation over Fe- and Cu-zeolites catalysts. The collected evidence enables us to propose a coherent mechanism that accounts for all the experimental results collected so far [2]. Experiments are performed on a mechanical mixture of Fe- or Cu-zeolite (active phases) + BaO/Al_2O_3 (NOx trap) powders. Intermediates trapped on BaO were then identified by i) analyzing their thermal decomposition products by TPD runs; ii) probing their reactivity with NH_3; iii) ex situ FTIR analysis of the BaO/Al_2O_3 phase unloaded and separated from the test reactor mixture. Three major results are obtained: i) HONO/nitrites (not NO_2) are the primary products of the NO oxidative activation over Fe- and Cu- zeolites, ii) nitrites/HONO and nitrates/HNO_3 exist in mutual equilibrium and are responsible for the observed reaction dynamics, iii) the preferred pathway for the Standard SCR at low temperature is the reaction of HONO in gaseous phase (in equilibrium with Fe- of Cu-nitrites) with adsorbed ammonia. The following mechanism, accounting for both the Standard SCR reactivity and the NO oxidation to NO_2 over Fe-zeolite catalysts, is proposed:

$Fe^{3+}OH + NO \leftrightarrow Fe^{2+} + HONO$ R.1
$Fe^{3+}OH + HONO \leftrightarrow Fe^{3+}ONO + H_2O$ R.2
$Fe^{3+}ONO \rightarrow Fe^{2+} + NO_2$ rds for NO → NO_2 R.3
$HONO + Z - ONH_4 \rightarrow N_2 + 2H_2O + Z - OH$ R.4
$2Fe^{2+} + \frac{1}{2}O_2 + H_2O \rightarrow 2Fe^{3+}OH$ **rds for Std SCR** R.5

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IND-O9

On the process for furfural and HMF oxidative esterification over gold catalysts

F. Menegazzo[a], *M. Signoretto*[a], *F. Pinna*[a], *M. Manzoli*[b], *F. Boccuzzi*[b]

a Department of Molecular Sciences and Nanosystems, Ca' Foscari University Venice and INSTM-RU Ve, Dorsoduro 2137, 30123 Venezia, Italy
b Department of Chemistry & NIS Centre of Excellence, University of Turin, Via P. Giuria 7, 10125 Turin, Italy

fmenegaz@unive.it

The upgrading of lignocellulosic biomass wastes into higher added-value chemicals is one the most researched topics in the forthcoming concept of bio-refinery. The present work concerns the oxidative esterification of furfural (a C5 compound) to alkyl furoate and of 5-hydroxymethylfurfural (HMF, a C6 compound) to 2,5 dimethylfuroate. The latter is a monomer for the replacement of terephtalic acid in plastics, while alkyl furoates find applications as flavor and fragrance component in the fine chemical industry. Gold nanoparticles supported on sulphated zirconia are efficient catalytic systems for these processes even without the use of a base such as sodium methoxide, which makes the process less green and less advantageous from an economic point of view [1, 2]. Many variables of the process, such as reaction time, temperature, pressure, nature of the oxidant, have been optimized. For both processes, a considerable effect of the reaction temperature has been evidenced in the range here investigated (60-140 °C). As regard as furfural, oxygen pressure can be lowered from 6 to 1 bar without significant changes in the catalytic performances. Molecular oxygen can be replaced by the more economic air, still at very low relative pressure (0.5 bar). In the case of HMF, oxygen pressure can be lowered from 6 to 1 bar without significant changes in the catalytic performances.

Data on the reaction mechanism have been also verified by FTIR spectroscopy measurements performed in the same experimental conditions.

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IND-O10

Premio Adolfo Parmaliana

Some Features of Anodic TiO_2 Nanotubes

M. Altomare,[a,b] E. Selli,[b] P. Schmuki[a]

[a] Department of Material Science and Engineering, WW4–LKO, University of Erlangen-Nuremberg, Martensstrasse 7, D-91058, Germany.
[b] Department of Chemistry, University of Milan, via Golgi 19, I-20133, Italy

m.altomare85@gmail.com

One-dimensional nanostructured oxides are efficient materials for solar-into-chemical energy conversion due to preferential percolation pathway for charge carriers and enhanced electron-hole separation [1]. In particular, TiO_2 nanotubes (NTs) grown by electrochemical anodization are receiving large attention because of their versatile fabrication allowing for the growth of tubes that exhibit advanced properties and functional structures [2].

The anodization of Ti-based alloys couples the advantage of nanostructuring with those of doping, heterojunction formation and noble metal decoration. For instance, the anodization of Ti-Ta alloys leads to Ta-doped TiO_2 NTs that show higher conductivity and enhanced water splitting ability. On the other hand, tubes decorated with Au (or Pt) nanoclusters can be grown on Ti alloys containing small amounts of noble metals. This strategy results in NTs showing better charge carrier separation and efficient photocatalytic production of H_2 [3].

Yet, tubes with functional structures can be grown in specific conditions. Anodization in hot HF/H_3PO_4 electrolytes gives highly ordered TiO_2 NTs with optimized morphology for hosting photocatalytic reactions, that is, these tubes have structural features fulfilling the requirements for efficient light absorption, hydroxyl radical diffusion and solid-state diffusion of charge carriers [4].

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IND-O11

Dimethyl ether synthesis via methanol dehydration: effect of zeolite structure

E. Catizzone, A. Aloise, M. Migliori, G. Giordano

Dipartimento di Ingegneria per l'Ambiente e il Territorio e Ingegneria Chimica, Università della Calabria, Via P. bucci Cubo 45a, 87036, Rende (CS), Italia

massimo.migliori@unical.it

Due to good performance as catalysts in chemical and petrochemical processes, zeolites properties have bee deeply investigated in the last decades. The possibility to modulate the catalyst acidity suggests the zeolites as reliable option to improve selectivity for reactions sensitive to this parameter. This is the case of Dimethyl ether (DME) synthesis through methanol dehydration. Due to good performances in the diesel engines, with low emission of NOx and absence of particulate matter and SOx in exhaust gases, DME may represent a reliable fuel alternative [1]. DME can be synthesized following either the indirect or direct way. Indirect synthesis is a two-steps process: the methanol synthesis from syngas over ACZ ($Cu/ZnO/Al_2O_3$) redox catalyst, followed by methanol dehydration over acid catalyst. In the direct synthesis the two steps occur in the same reactor over bi-functional catalyst and this way is more economic than the other one [2]. Methanol dehydration can be catalyzed by γ-Al_2O_3 but this catalyst is deactivated by water [3]. Zeolites, due its high versatility of both acidity and selectivity can be used as catalyst in methanol dehydration in both direct or indirect synthesis. In this work effect of structure on methanol dehydration is investigated, by comparing different of acid zeolites. Zeolites exhibiting different channel configurations and acidity, H-MFI, H-BEA and H-FER, where prepared and characterized in terms of physical (XRD, DSC/TGA, BET surface area, SEM and TPD) and chemical (ICP) properties. Aiming at understand the effect of different structures on catalytic activity, reaction test where performed and activity, selectivity and durability where evaluated. Data revealed a different behaviour either for performance or durability, depending upon catalyst structure.

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IND-O12

Steam reforming of bioethanol, effect of substrate concentration and purity

José Lasso F.[a], *Matteo Compagnoni*[a], *Ilenia Rossetti*[a]

[a] *Dip. Chimica, Università degli Studi di Milano, Via C. Golgi, 19, 1-20133 Milano, Italia*

ilenia.rossetti@unimi.it

H_2 production from bioethanol is attractive, given the fact that it is the most available biofuel worldwide. One of the efficient ways of using bioethanol as a power source it's steam reforming to synthesis gas and the production of electric power from the hydrogen contained in the synthesis gas by fuel cells. Therefore, low concentration solutions are acceptable for steam reforming, whereas they are unsuitable for combustion, and are characterized by much lower purification cost. Therefore, they may be attractive from an economical point of view, provided that they do not contain poisons depressing catalytic activity. This work was aimed to present the effect of bioethanol concentration and purity on the activity performance of different catalyst formulations.

We tested the activity for H_2 production of Ni-based catalyst supported over ZrO_2 and La_2O_3 prepared by different methods and activated at 500ºC. The steam reforming reaction was carried out at low temperature (300, 400 and 500ºC) and high temperature (625, 750°C) on a continuous micropilot plant using a solution of bioethanol at two different concentration, 90 and 50% (supplied by Mossi & Ghisolfi) mixed with water in order to have an overall ethanol/water molar ratio 1:3.

Bioethanol 90% showed the highest activity irrespectively of catalyst formulation. By contrast, bioethanol with lower concentration (50%) induced different performance for the steam reforming reaction, mainly depending on the control of the acidity of the support. Regardless of the bioethanol concentration, the high temperature testing allowed to reach complete ethanol conversion and satisfactory durability, whereas for low temperature testing there was a correlation between bioethanol purity/concentration and catalyst formulation.

IND-O13

Nano dispersioni di silicato idrato per la Solidificazione/Stabilizzazione dei rifiuti

Vincenzo Russo[a], *Giorgio Ferrari*[a], *Marco Squinzi,*[a] *Gilberto Artioli*[b]

a Laboratorio Ricerca e Sviluppo, Mapei S.p.A., Via Cafiero 22 , 20158, Milano, Italia
b Dipartimento di Geoscienze, Università di Padova, Via Gradenigo , 35100, Padova, Italia

hpss.lab@mapei.it

La tecnologia di solidificazione/stabilizzazione ha lo scopo di ridurre la mobilità e la tossicità dei contaminanti inorganici contenuti nei materiali di scarto, per mezzo del loro incapsulamento in una matrice solida, tipicamente di tipo cementizio, dotata di integrità strutturale. Uno degli inconvenienti principali del processo è l'effetto di inibizione dell'idratazione del cemento esercitato da molti contaminanti inorganici, con la conseguente riduzione della loro capacità di immobilizzazione. Le nano dispersioni di un nuovo silicato idrato sono state utilizzate per migliorare il potenziale legante del cemento portland nei processi di solidificazione/stabilizzazione delle ceneri volanti derivanti dalla combustione del coke petrolifero. L'aggiunta di una nano dispersione del nuovo silicato idrato alla miscela fresca di ceneri, cemento ed acqua promuove l'idratazione del legante e modifica la struttura delle fasi idrate producendo un conglomerato più denso e meno poroso, come risulta da test di resistenza meccanica ed analisi al microscopio elettronico. Di conseguenza, la cessione dei contaminanti è ridotta e la compatibilità ambientale del prodotto di solidificazione/stabilizzazione è notevolmente migliorata. Il meccanismo di funzionamento delle nuove dispersioni di silicati idrati è discusso in termini di nucleazione auto-catalitica e crescita del silicato di calcio idrato nei pori capillari della miscela cementizia idratata.

IND-O14

New synthetic approach to hydroxytyrosol

P. Ziosi, F. Cavani, F. Santarelli, P. Righi

Dipartimento di Chimica Industriale « T. Montanari » Università di Bologna, Viale Risorgimento 4, 40136, Bologna, Italia

paolo.ziosi@unibo.it

Currently, hydroxytyrosol (commercial name, DOPET) is obtained by hydrolysis of olueropein, a phenolic compound extracted with large amounts of ethylacetate from olive waste water.[1] Synthethic organic routes start from relatively expensive compounds, like tyrosol,[2] or make use of halogenated reactants.[3] Our purpose was to develop a new, cheap and halogen-free synthesis, using water as solvent and heterogeneous catalysts. We carried out the reaction in two steps: the first one is the synthesis of mandelic derivatives of cathecol using oxygenated C2 reactants, such as glyoxylic acid, glyoxal and derivatives. In this step we obtained a nearly complete conversion of catechol, with a selectivity to the desired product in the range 67-78%. Initially, sodium hydroxide was used as the catalyst; at a later stage, NaOH was replaced by tetrabutylammonium hydroxide, with the outlook of using an ammonium quaternary resin. The second step is the one-pot reduction of the mandelic intermediate to hydroxytyrosol. We tested various catalysts supported on carbon (platinum, palladium and rhodium), with and without different amounts of acetic acid. All these reactions were carried out in an autoclave at different hydrogen pressures (up to 6 bar) and temperature (up to 150°C); the solvent was water. Kinetic studies showed the formation of different reaction intermediates, that lead to hydroxytyrosol in few hours reaction time (5-10 h), with selectivity around 70%. The reduction showed the formation of two side-products: 4-ethyl cathecol and 4-methyl cathecol. Concluding, we have found a new synthetic procedure which allows the production of hydroxytyrosol with good yields starting from a cheap and widely available reactant.

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IND-O15

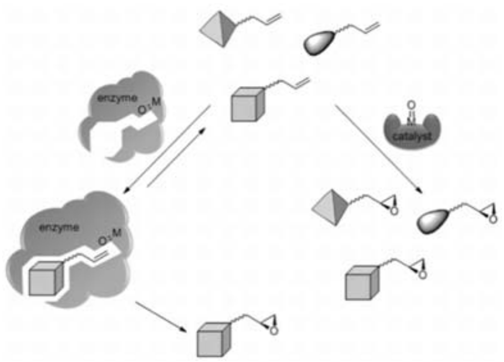
Supramolecular Approaches to Substrate Selectivity in Homogeneous Catalysis

Alessandro Scarso[a]

a) Dipartimento di Scienze Molecolari e Nanosistemi,
Università Ca' Foscari di Venezia, Calle Larga S Marta 2137,
0123, Venezia ITALIA

alesca@unive.it

Enzymes are superb examples of both product and substrate selective catalysts thanks to their ability to recognize reagents before the catalytic event. Heterogeneous catalysts are intrinsically more easily tunable to provide substrate selectivity because of their porosity properties, while homogeneous catalysts are limited mainly to kinetic resolution of racemates or other examples of substrate selectivity limited to mixtures of substrates characterized by large differences in their structures. Homogeneous catalysts that discriminates between substrates differing only to a small extent in positions remote from the reactive center and lacking extra interaction with the catalyst are indeed rare. To overcome this issue and provide a general solution to it, it is possible to wrap the homogeneous catalyst within a supramolecular self-assembled host to impart extra steric or attractive selection rules. In this contribution examples of significant substrate selectivity achived through a supramolecular approach are presented working both in organic media for the alkyne hydration within a hexameric resorcinarene capsule[1] or in water for Heck[2] and hydrogenation reactions[3] within micelles.



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IND-O16

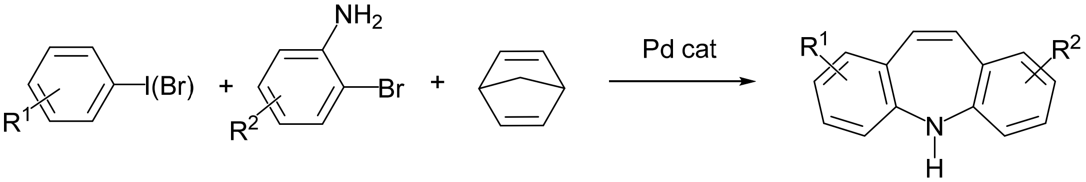
A new catalytic way to dibenzo[b,f]azepines

N. Della Ca', E. Motti, M. Fontana, M. Cremaschi, G. Coruzzi,
M. Catellani

Dipartimento di Chimica, Università di Parma and CIRCC, Parco Area delle Scienze 17/A, 43124, Parma, Italy

nicola.dellaca@unipr.it

We have previously reported the one-pot palladium-catalyzed synthesis of dibenzo[b,f]azepine derivatives starting from aryl iodides, 2-bromoanilines and norbornene or norbornadiene.[1] Further work in this area has allowed us to enlarge the scope of the reaction. Commercial dibenzoazepines can be obtained in good yield following this simple procedure.



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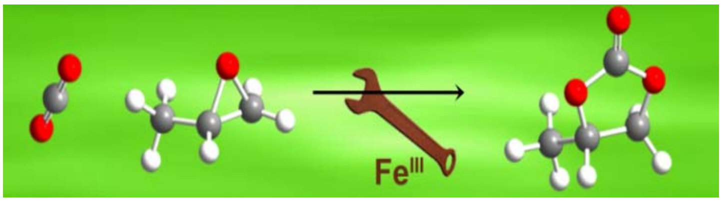
IND-O17

Novel Highly Effective Iron(III) Catalyst for the Synthesis of Cyclic Carbonates from CO_2 and Epoxides

Assunta De Nisi[a], *Antonio Buonerba*[a], *Carmine Capacchione*[a], *Bernhard Rieger*[b], *Alfonso Grassi*[a]

[a] *Dipartimento di Chimica e Biologia, Università degli Studi di Salerno, Via Giovanni Paolo II - 84084 Fisciano (SA), Italy*
[b] *WACKER Lehrstuhl für Makromolekulare Chemie, Technische Universität München, Lichtenbergstrasse 4, 85748 Garching, Germany*

assunta.denisi@gmail.it



Carbon dioxide is a cheap, non-toxic, abundant and biorenewable resource. The chemical fixation of CO_2 by means of its incorporation into chemicals is in the focus of interest of the scientific research. In this area, an important process is the synthesis of cyclic carbonates via the coupling of CO_2 and epoxides. Cyclic Carbonates find application as high boiling and polar aprotic solvents, as intermediates in the manufacture of fine chemicals, *i.e.* as alkylating agents and, through ring opening polymerization, for the synthesis of polycarbonates and polyurethanes. Industrially are obtained from phosgene and diols or by coupling of the CO_2 and epoxides under harsh conditions. Homogeneous metal complex catalysts have been introduced effectively for the CO_2/epoxide coupling, typically bearing Co(II), Cr(III) or Al(III) as active sites.[1] Recently, iron is emerging as a cost-effective, abundant and non-toxic metal catalyst. In this work, we reported a novel Fe(III)-based catalyst with a *di*(thioether)-*tris*(phenolate) ligand, highly effective and selective for the production of cyclic carbonate. Several substrates as propylene oxide, cyclohexene oxide, styrene oxide, epichlorohydrin, allyl glycidyl ether, glycidyl phenyl ether have been tested. To the best of our knowledge, this catalytic system shows the highest TOFs reported among the iron-based catalysts.

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IND-O18

Vanadium catalyzed oxidative cleavage of lignin model substrates

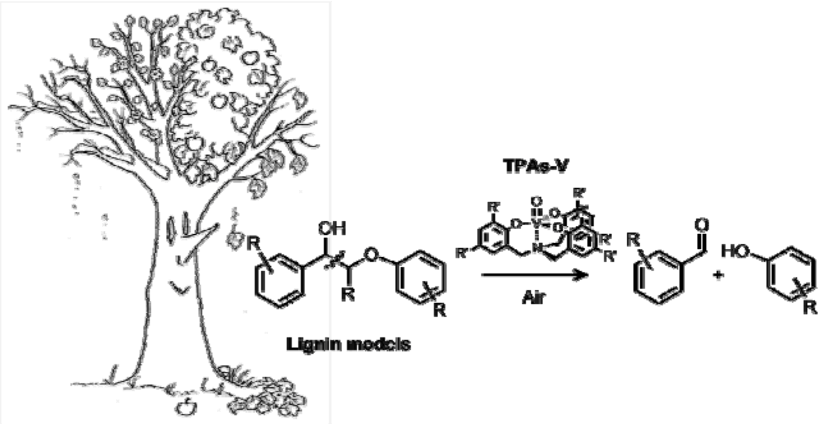
E. Amadio[a]*, B. Gjoka*[b]*, C. Zonta*[b]*, G. Licini*[b]***

a Istituto per la Tecnologia delle Membrane (ITM-CNR), Via Marzolo 1 , 35131, Padova, Italy.
b Department of Chemical Sciences, Università di Padova, Via Marzolo 1,35131, Padova, Italy.

emanuele.amadio@unipd.it

Lignocellulosic biomass is an important feedstock for the renewable production of chemicals, fuels and energy. With its unique structure lignin can be regarded as the major aromatic resource of the bio-based economy and, therefore, a wide variety of aromatic compounds may result from its efficient valorization However, due to its complex nature and inert resistance to chemical reactivity and the lack of suitable conversion technologies, selective lignin depolymerization to value-added products is a challenge. [1]

Here we show that vanadium(V)-amino triphenolate complexes (TPAs-V) are good candidates to achieve such ambitious goals in a very active and selective manner under mild reaction conditions. Specifically, the reactivity of **TPAs-V** under catalytic aerobic conditions with different classes of lignin model substrates will be presented.



We thank Fondazione CARIPARO Progetti di Eccellenza 2011 (Nano-Mode) (E.A. fellowship) and COST Action CM1005.

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IND-O19

Influence of NAC ligands on the anion position and in Gold (I) catalysis

Luca Biasiolo,[a,b] *Leonardo Belpassi,*[a]* *Giovanni Bistoni,*[a,c] *Gianluca Ciancaleoni,*[a] *Alceo Macchioni,*[c] *Francesco Tarantelli,*[a,c] *Daniele Zuccaccia.*[b]*

[a] CNR-ISTM, Dip. di Chimica, Univ. degli Studi di Perugia, I-06123, Perugia, Italy;
[b] Dip. di Chimica, Fisica e Ambiente, Univ. di Udine, Via Cotonificio 108, I-33100 Udine, Italy;
[c] Dip. di Chimica, Univ. degli Studi di Perugia Via Elce di sotto 8, I-06123, Perugia, Italy

luca.biasiolo@aol.com

N-acyclic carbenes (NAC)[1] Gold (I) complexes are successfully employed as catalysts and the interest around their properties is continuously increasing.[2] A key role in Gold mediated reactions could be played by the counterion,[3] it was also been observed that the anion influences the structure of the catalyst and important intermediates of the catalytic cycle. For this reason, in the last years we have been carrying on a systematic NMR/DFT study on the linear bis-coordinated L-Au(UHC)$^+$ BF_4^- ion pair.[4] In order to understand how this could modify a Gold (I) catalysis, we first studied the ion pair properties (DFT calculations) and the structures (HOESY spectra) of five gold complexes (figure below) and secondly we investigated the alkoxylation of 3-hexyne. We have observed huge differences for what concern the ion pair structure and those differences are reflected in the catalysis. We found that when the anion is far from the reaction centre (trapped close to the NH or OH group) the catalysis rate is lower than when it is close to the substrate. The position of the anion can be tuned building ligands with particular functional groups and that functionality can be switch ON or OFF changing the catalytic conditions.

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IND-O20

Photopolymers for Grätzel's solar cells

Federico Bella[a,b], *Roberta Bongiovanni*[a]

a Dipartimento di Scienza Applicata e Tecnologia - DISAT, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italia
b Center for Space Human Robotics @Polito, Istituto Italiano di Tecnologia, Corso Trento 21, 10129 Torino, Italia

federico.bella@polito.it

The conversion of solar energy by photovoltaic effect is the most quoted reality in the world of renewable resources. As a feasible option for photovoltaic technology to meet the growing energy demand, dye-sensitized solar cells (DSSCs) have attracted much attention due to their low cost, ease of fabrication and good performance. Furthermore, DSSCs are representing an important common ground among synthetic chemistry, polymer science, electrochemistry and industrial scaling-up.

We have recently proposed polymer electrolyte membranes as a promising strategy to solve the poor long-term stability of standard liquid-state DSSCs [1-4]. Membranes were prepared by a rapid, energy-saving and environment friendly technique of light-induced polymerization, that can find an appropriate location also in the nascent industrial production plants of third generation photovoltaic cells.

A light-cured polymer electrolyte membrane for DSSCs

The talk will be focused both on special fillers (MOF and nanocellulose) used to increase the light harvesting, and on the introduction of new redox couples, whose compatibility with polymeric matrix and effects on the light-curing process will be detailed. Lastly, the transfer of these polymer electrolytes in flexible devices (one of the most promising ambitions of DSSCs) will be presented.

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IND-O21

Membrane reactors for innovating hydrogen stream upgrade

Barbieri G.[a], *Drioli E.*[a, b], *Brunetti A*[a]

[a] *National Research Council – Institute on Membrane Technology (ITM-CNR), Via P. Bucci, Cubo 17C , 87036, Rende (CS), Italy*
[b] *Dept. of Environmental and Chemical Engineering, University of Calabria, Via P. Bucci, Cubo 44A , 87036, Rende (CS), Italy*

giuseppe.barbieri@cnr.it; *g.barbieri@itm.cnr.it*

Water gas shift is a key/upgrading stage in the hydrogen production process. This two-steps – high and low temperature - conventional process operates in a temperature range of (200-400°C) on feed streams containing up to 40-50% (on a dry basis) of hydrogen. Pd-based membranes selectively removing hydrogen significantly shift the equilibrium conversion of this new reactor model at a value higher than those imposed by thermodynamics to traditional reactors. This membrane reactor (MR) property offers important benefits in terms of process intensification and innovation.

In this work the advantages offered by MRs operated in the typical high temperature range for (300-450°C), were demonstrated. The values of gas hourly space velocity, temperature, H_2O/CO feed molar ratio, feed composition, etc. used in the simulations are those typical of an industrial application of a WGS upgrading stage. A feed pressure of 15 bar was assumed as reference value, it being the strength limit of the self-supported Pd-Ag current commercial membranes. The pressure demonstrated to be one of the most interesting variables in MR processing. The proposed analysis demonstrated how only one stage based on a Pd-alloy MR can replace the two reactors of the conventional process, arising an intensified process with a smaller reaction volume, higher conversion and GHSV, pure hydrogen recovered.

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IND-O22

New structured catalysts and system for H_2 and syngas production

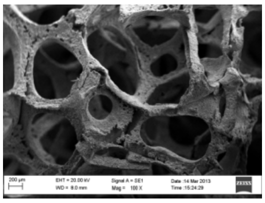
F. Basile, D. Barbera, P. Benito, G. Fornasari, R. Mafessanti, M. Monti, A. Vaccari

a Dip. Chimica Industriale, Univ Bologna, V.le Risorgimento, 4 ,40129, Bologna, Italy

f.basile@unibo.it

Synthesis gas production with intermediate hydrogen membrane separation or integrated in a catalytic membrane reactor is a small scale promising solution. Integration of partial oxidation with steam reforming can further improves heat control and flat thermal profile. Tests with $CH_4/O_2/H_2O$ 52/11/37 v/v mixture at 750°C show lower ΔT than classical CPO and reforming reaction. The reaction conditions allows discrimination among catalysts activity. Rh catalysts have been obtained by bulk coprecipitation and its reducibility optimized as function of composition and thermal treatment improving its activity on CH_4 oxyreforming by increasing four times the metal surface area. The improved catalyst has been than used to produce a monolith. The prepared catalyst compared with a semi-commercial system both as pellets and 1*1 inch monolith shows an higher activity and high stability towards carbon formation during 100h of tests. New structural systems have been also prepared and tested using metallic support. Rh/Mg/Al catalyst on a conducting foam by an innovative method involving precipitation by base electro-generation. Using a 1*1 inch FeCrAl foam as working electrode in a cation nitrate solution, generate a pH increase by nitrate reduction at the electrode interface allowing the precipitation of the hydrotalcite as a thin layer (2-3 μm) on the surface of the foam. The systems shows results similar to the semi-commercial catalyst having 1/10 less noble metal. The preparation method have been used on porous tube plate and fiber showing wide applicability on structured conducting supports. Several oxide (such as Al_2O_3, ZrO2) and mixed oxide have been obtained to be used as coating for metallic support of Pd membrane or even as component for fuel cell.

	commercial Monolith		**Rh1% Monolith**	
H_2	61.1	%	60.8	%
CO	17.8	%	18.8	%
CH_4	15.9	%	12.6	%
CO_2	5.5	%	7.8	%



IND-O23

Kinetic and Raman study in the CPO of C_3H_8, C_3H_6 and n-C_8H_{18}

A Donazzi[a], D. Pagani[a], A. Lucotti[b], M. Tommasini[b], A. Beretta[a], G. Groppi[a], C. Castiglioni[a], P. Forzatti[a]

a Politecnico di Milano, Dipartimento di Energia, Via Lambruschini 4, 20133, Milano
b Politecnico di Milano, Dipartimento di Chimica Materiali e Ingegneria Chimica, Piazza Leonardo da Vinci 32, 20133, Milano, Italy

alessandra.beretta@polimi.it

Fuel flexibility is a major goal of the Catalytic Partial Oxidation (CPO) for small-scale production of H_2: the reformer is required to process fuels ranging from NG and LPG, up to logistic and biomass-derived fuels. The main drawbacks are the high temperatures reached by the catalyst (>1000°C) and the formation of C-deposits. In this work, we analyze the CPO of C_3H_8, C_3H_6 (C_{2+} coke-forming fuel) and n-C_8H_{18} (logistic fuel) performed on Rh/αAl_2O_3 catalysts: the formation of C-species as a function of temperature is analyzed by combining kinetic investigations in an annular reactor with Raman measurements of the catalyst surface. The combined application of these techniques allows to individuate the nature of the catalytic site for the fuel activation (O*-O*, O*-* or *-* pairs) as well as the tendency of the fuel to from C. In C_3H_8 CPO, under oxidative conditions, the results show that the C-H bond breaks on O*-O* pairs, while, in the absence of O_2, the C-H bond breaks on a free Rh site pair *-*. Raman spectra suggest that the Rh surface remains fairly clean [1]. Instead, kinetic analyses on C_3H_6 CPO show that the C_3H_6 activation occurs on a surface only partially saturated by O* and that the dissociative adsorption of C_3H_6 on a O-* pair is the Rate Determining Step. In the absence of O_2, C_3H_6 strongly adsorbs on the surface, forming different C-species and leading to C-poisoning and kinetic inhibition. Kinetic tests on n-C_8H_{18} CPO show an intermediate behavior. The activation of n-C_8H_{18} occurs on O*-O* site pairs, in line with saturated alkanes (e.g. C_3H_8). Inhibition by n-C_8H_{18} adsorption and C-poisoning are supported by Raman spectra, as with unsaturated species (e.g. C_3H_6): in the presence of O_2, the surface is almost C-free, whereas, once O_2 is consumed, amorphous deposits and graphitic-like platelets form, with nanotubes gradually growing at increasing temperature.

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IND-O24

Mixed Matrix Membranes for Gas Separation

Gianni Golemme[a], *Anna Santaniello*[b]

[a]*Department of Environmental and Chemical Engineering, University of Calabria, and INSTM Consortium, Via P. Bucci 45/A, 87036 Rende, Italy*
[b]*Department of Physics, University of Calabria, Via P. Bucci 32/C, 87036 Rende, Italy*

ggolemme@unical.it

The replacement of the energy-intensive separation processes of commodities (*e.g.* distillation) with membrane operations [1] requires new tough and resistant materials able to withstand organic solvents and aggressive environments [1,2]. Highly permeable polymers are not very selective, and very selective polymers are not very permeable [3]; ceramic, carbon and metal membranes with outstanding separation performances, instead, are unfit for most processes because of unfavourable footprints and high costs [1,2,4]. Polymer based membranes containing porous filler particles in the separating layer (hybrid or mixed matrix membranes, MMMs) are a viable option to obtain advanced performances [1,2,4,5] by coupling the outstanding separation properties of non polymeric materials with the low cost of polymeric membranes.

The opportunities and the main hurdles faced today for the industrial application of MMMs (advanced polymers; high aspect ratio fillers; compatibility; thinner membranes; elimination of defects; control and prediction of transport properties) will be highlighted with selected examples of potential applications, mainly in the field of natural gas purification [6-8].

This work has been supported by the European Community FP7 2007-2013, Project MATERIA (PONa3_00370), and by Project MICROPERLA (PON01_01840).

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IND-O25

Mono and bi-metallic Ni-based catalysts over alumina for CH_4 Dry Reforming: benefit of second metal addition

F. Puleo[a], *G. Pantaleo*[a], *V. La Parola*[a], *A.M. Venezia*[a], *H. Wu*[a,b], *A. Martinez-Arias*[c], *L.F. Liotta*[a]

a Institute for Study of Nanostructured Materials (ISMN)-CNR, Palermo, Via Ugo La Malfa , 90146, Palermo, Italy.
b Department of Applied Physics, Northwestern Polytechnical University (NPU), Xi'an 710072, P. R. China.
c Institute of Catalysis and Petrochemical, CSIC, C/Marie Curie 2, Cantoblanco, 28049 Madrid, Spain.

fabrizio.puleo@pa.ismn.cnr.it

In recent years the Dry Reforming of Methane (DRM) has received considerable attention as an attractive route to produce synthesis gas, with H_2/CO molar ratio close to unity, making it an ideal feed for the Fischer Tropsch synthesis [1]. At 1 atm pressure DRM is not spontaneous below 633°C, therefore higher temperatures are needed. Simultaneously other endothermic reactions are favoured, such as CH_4 decomposition and reverse water gas shift (RWGS), that may change the H_2/CO molar ratio and cause catalysts poisoning due to coke deposition. Nickel is the most frequently reported metal in DRM because of its good catalytic activity and its cost-effectiveness as compared with Pt, Ru or Rh-based catalysts [2], but the production of significant amount of carbon and the sintering at the high temperatures limit its applications. Carbon poisoning can be limited by addition of second noble metals, such as Pt, Rh, Au [3,4]. In the present work a series of mono- (Ni) and bi-metallic (Ni/Pd, Pt, Au) catalysts supported over Al_2O_3 have been prepared and characterized in order to investigate the role of the second metal on the DRM activity and stability [4]. A promoting effect of the second metal to the activity and stability of Ni/Al_2O_3 was observed. Bimetallic Pt- and Pd-Ni/Al_2O_3 showed the best catalytic performances catalysing the reaction at temperature as low as 400°C and forming low carbon content. Conversely, over Ni/Al_2O_3 the reaction started at 575°C and the highest coke formation was measured.

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IND-O26

Design of CPO Reformers for Hydrocarbon Fuels: Effect of Pressure

A. Donazzi, A. Carrera, S. Rebughini, M. Maestri, A. Beretta, G. Groppi, P. Forzatti

Dipartimento di Energia, Politecnico di Milano, piazza Leonardo da Vinci 32, Milano

gianpiero.groppi@polimi.it

Operation under pressure is a major requirement for the intensification of the Catalytic Partial Oxidation (CPO) of hydrocarbon fuels. Related issues are the increase of the thermal loads experienced by the catalyst and the promotion of gas phase chemistry, which lead to the formation of coke precursors, the degradation of the catalyst properties, as well as safety hazards. The nature of the fuel and the presence of a diluent (N_2, H_2O or CO_2) strongly influence the design criteria of the reformer, in terms of choice of the catalyst support (spheres, honeycombs, foams), its geometry (aspect ratio) and shape (conical, linear), and internal layout of the elements (position of the radiant heat shields). Gas velocity, heat dissipation and conduction, both radial and axial, influence the severity of the hot spots and the heat management. Spatially resolved temperature and concentration profiles, coupled with detailed models of the reactor and of the chemical kinetics are thus essential requisites for the analysis.

In this work, we investigate the performance and thermal behavior of the autothermal CPO reformer operated under pressure with CH_4, C_3H_8 and i-C_8H_{18}, extending our previous analysis at 1 atm. Spatially resolved experiments up to 4 bar are presented and numerically analyzed. Detailed simulations allow to predict the system behavior up to 15 bar and C/O ratio different than 1.

Experiments and simulations show that the increase of pressure affects the product distribution in line with thermodynamics; notably, it does not increase the severity of the process in terms of catalyst thermal stress. In fact, the mass transfer limitations on the rate of heterogeneous reactions make the surface hot-spot temperature insensitive to pressure, while the onset of homogeneous reactions brings part of the exothermic contribution in the gas-volume.

IND-O27

Nanoporous-Crystalline Polymers

Gaetano Guerra,[a] *Maria Rosaria Acocella,*[a] *Christophe Daniel,*[a] *Concetta D'Aniello,*[a] *Simona Longo,*[a] *Paola Rizzo,*[a] *Vincenzo Venditto,*[a] *Oreste Tarallo*[b]

[a] *Department of Chemistry and Biology, University of Salerno, Italy;*
[b] *Department of Chemistry, University of Naples "Federico II",, Italy*

gguerra@unisa.it

The contribution is devoted to thermoplastic materials including nanoporous-crystalline phases,[1-5] which are obtained from co-crystalline host-guest phases by suitable guest extraction procedures (e.g., by carbon dioxide in supercritical conditions). These nanoporous-crystalline phases are able to absorb guest molecules also from very dilute solutions and have been till now obtained only for two commercial polymers: syndiotactic polystyrene (s-PS) [1,2] and poly(2,6-dimethyl-1,4-phenylene)oxide (PPO)[3,4].

Most studies have been devoted to s-PS, which exhibits two different nanoporous-crystalline phases, δ[1] and ε,[2] whose nanoporosity is organized as isolated cavities and channels, respectively.

It will be shown that suitable processing conditions can lead to the unprecedented formation of films with three different kinds of planar orientations of the co-crystalline and nanoporous-crystalline phases.[5] The availability of s-PS films with three different kinds of uniplanar orientation can be, of course, relevant also for practical purposes. For instance, it allows guest orientation control for co-crystalline phases and guest diffusivity (and hence permeability) control for the nanoporous δ and ε phases.

The final part of the presentation will be devoted to possible advanced applications of materials based on co-crystalline and nanoporous crystalline s-PS phases. In particular, applications of nanoporous films for molecular sensor and for active packaging of fruit and vegetable[6] will be presented.

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IND-O28

Polimeri a base aceto-vinilica in dispersione e sicurezza alimentare

Fabio Chiozza[a], *Fabio Abbà*[b], *Tito Zanetta*[a]

[a] *Vinavil S.p.A., R&D, via Toce, 7 28844 Villadossola VB Italia*
[b] *Vinavil S.p.A., Regulatory Office, via Toce, 7 28844 Villadossola VB Italia*

f.chiozza@vinavil.it

I MOCA (Materiali ed Oggetti destinati al Contatto con Alimenti) rientrano nell'allegato I del Regolamento Quadro 1935/2004 CE che stabilisce che i materiali e gli oggetti non trasferiscano ai prodotti alimentari componenti in quantità tale da compromettere la sicurezza, la composizione, le caratteristiche organolettiche dell'alimento e la salute del consumatore.

L'industria che produce materie prime per la formulazione (da parte di un utilizzatore a valle) di un prodotto impiegato nel campo degli adesivi o dei rivestimenti è pertanto obbligata a chiarire la conformità al Regolamento citato.

Ad oggi, in assenza di una definizione nel Regolamento stesso di misure specifiche per alcuni gruppi di materiali ed oggetti, tra cui adesivi e rivestimenti, è pratica consentita di mantenere o adottare disposizioni nazionali o utilizzare documenti non legislativi (ad esempio FDA o BfR) per la valutazione della conformità al Regolamento medesimo.

Tuttavia, a livello europeo, i MOCA sono oggetto di crescente attenzione in tema di Risk Assessment (Analisi del Rischio): infatti, a livello normativo, tale analisi, nonostante non sia descritta da alcuno strumento operativo o richiesta in alcuna disciplina afferenti i MOCA, è quella che consente di dimostrare meglio la conformità degli stessi alle legislazioni vigenti.

Il presente studio traccia le modalità impiegate da un produttore di materie prime inserito a pieno titolo nella filiera di manifattura di MOCA, per la valutazione dell'idoneità al Regolamento Quadro, in assenza di una disposizione specifica comunitaria o nazionale applicabile. La valutazione dei limiti di migrazione specifica delle sostanze, il concetto di calcolo di pre-screening, la verifica delle sostanze potenzialmente migranti e la loro valutazione da un punto di vista del rischio tossicologico costituiscono linee guida indispensabili al chimico industriale che deve sviluppare polimeri aceto-vinilici in dispersione acquosa conformi alle legislazioni di riferimento dei MOCA.

IND-O29

Tailoring of the porosity in geopolymers

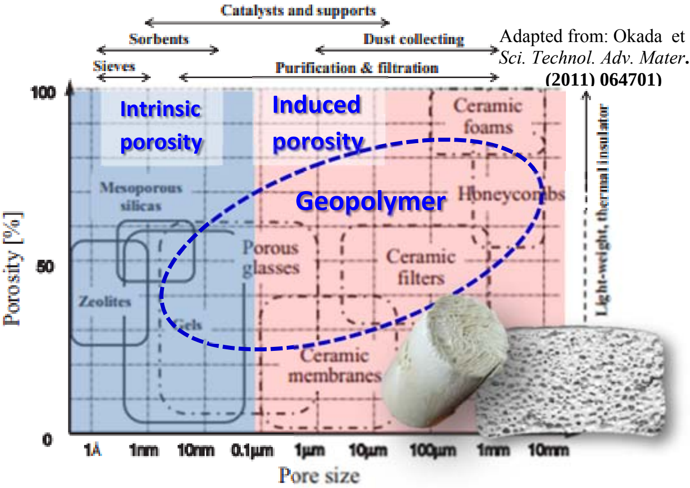
E. Papa[a], *E. Landi*[a], *P. Benito*[b], *A. Vaccari*[b], *V. Medri*[a]

[a]*CNR-ISTEC, National Research Council of Italy, Institute of Science and Technology for Ceramics, Via Granarolo 64, 48018, FAENZA, Italy*
[b]*Dipartimento di Chimica Industriale "Toso Montanari" – ALMA MATER STUDIORUM - Università di Bologna, Viale Risorgimento 4, 40136 BOLOGNA, Italy*

elettra.papa@istec.cnr.it

The production process in aqueous medium of geopolymers allows to tailor the porosity from nanometric to millimetric range. Different techniques have been used in order to fulfill the porosity requirements for many different purposes.

Water content in the starting mixtures affects the intrinsic mesoporosity of the geopolymer matrix, since water acts as pore former during the polycondensation stage. Moreover, ultra-macroporosity is obtained by direct foaming, using the redox reaction of metallic Si powder. Furthermore, porous architectures with main unidirectional anisotropic macropores may be gained by freeze-casting. The ice crystals act as pore network template, forming lamellar morphologies depending on the water amount in the mixture and the mold geometry. It is noteworthy that this is the first time that ice-templating technique is applied to geopolymer slurries, based on a sol/gel reactive system very far from the colloidal suspension of inert ceramic particles normally reported in literature. Geopolymer matrices and foams were deeply investigated in order to optimize the consolidation process and to design the desired porosity. Since the skeletal material is originally mesoporous, a hierarchical pore system in which mesopores are directly connected to macro- and finally to ultra-macro pores may be obtained. For this reason, potential applications may be found in many unforeseen fields, such as catalysis, biomaterials, filtering, insulation, etc.



Adapted from: Okada et al. *Sci. Technol. Adv. Mater*. **12 (2011) 064701)**

Fig.1: Correlation between porosity and applications

IND-O30

Monolithic Polymeric Aerogels with Nanofillers

Simona Longo [a], *Marco Mauro*[a], *Christophe Daniel*[a], *Gaetano Guerra*[a]

[a] *Dipartimento di Chimica e Biologia, Università degli Studi di Salerno, Via Giovanni Paolo II,132,84084 , Salerno, Italia.*

simmylongo@hotmail.it

Aerogels are a unique class of materials results attractive for many applications such as thermal and acoustic insulation, capacitors, or catalysis[1].

In this study monolithic polymeric aerogels based on thermoplastic uncrosslinked polymers, where the knots of the three-dimensional networks are physical, formed by crystallites, are presented [2]. In particular aerogels, where the crystallites that constitute the physical knots exhibit a nanoporous-crystalline form were prepared from polymers that exhibit a nanoporous crystalline phase,.e.g. syndiotactic polystyrene (s-PS).[2][3]The achievement of aerogels with nanofillers such as organically modified montmorillonite (OMMT) [4] and graphene oxide (GO), is described. Aerogels with large amounts of both intercalated and exfoliated OMMT and including the nanoporous-crystalline δ form of s-PS, were prepared. Also for high OMMT content, the aerogel preparation procedures occur without re-aggregation of the exfoliated clay, which is instead observed for other kinds of polymer processing. Analogous aerogels were prepared with GO leading to complete GO exfoliation as well as its substantial reduction.The most important result of the study is that the aerogel preparation allows the inclusion of also large amount of nanofillers, without aggregation, at least up to a content of 20 wt%. This allows to improve mechanical and electrical properties of the nanoporous-crystalline aerogels of s-PS, which are particularly suitable to remove selectively traces of pollutants from water and air.[2]Composite aerogels exhibiting large nanofiller content, can be also used as masterbatches or catalysts for polymer composites.

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IND-O31

Preparation of polyimide mixed matrix membranes containing functionalized multiwalled carbon nanotubes

Valentina Grosso[a,b]*, Enrica Fontananova* [a]*, Danilo Vuono* [b]*, Efrem Curcio* [b] *, Janos B. Nagy* [b]*, Mohammed A. Bahattab* [c]*, Enrico Drioli* [a,b]

[a] Institute on Membrane Technology of the National Research Council (ITM–CNR), Via Pietro BUCCI, c/o The University of Calabria,87036 Rende CS, Italy
[b] Department of Environmental Engineering and Land and Chemical Engineering, University of Calabria, 87036 Rende (CS), Italy
[c] King Abdulaziz City for Science and Technology (KACST), Riyadh, Kingdom of Saudi Arabia

v.grosso@itm.cnr.it

The presence of dyes in textile industrial wastewater is one of the most worrisome ecological problem [1]. There are several conventional methods for treating wastewater containing dyes [2] but the need for more efficient and environmental friendly wastewater treatments has attracted the attention towards membrane technology [3]. In this work porous membranes were prepared and tested for the removal of organic dyes having different charge but similar molecular weight. Three different polyimide type polymers were used to prepared porous asymmetric membrane: an homopolymer (Matrimid) and two co-polymers (P84 and Torlon). Moreover, the co-polyimide P84 was selected for further investigations in the form of mixed matrix membranes (MMMs) containing functionalized multiwalled carbon nanotubes (oxidized or aminated MWCNTs). The presence of the MWCNTs in the membrane matrix improved the performance in the filtration of dyes solutions (enhanced permeance and reduced fouling, with similar or higher rejection), with respect to reference polymeric membranes (without MWCNTs).

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IND-O32

La colla bianca “responsabile” di Vinavil

Ivan Fuso Nerini [a]

Vinavil S.p.A., via Valtellina, 63 – 20159 Milano

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- Un contenuto bassissimo, ai limiti della sensibilità dei metodi analitici, di sostanze volatili e in particolare di monomero acetato di vinile residuo.
  L’assenza di odore, che era una delle caratteristiche del prodotto anni fa presente sul mercato, è rimarcata dagli utenti che addirittura rimpiangono il “buon profumo” di un tempo.
- La presenza di triacetina, un plastificante “food - grade” che ha sostituito il tradizionale plastificante a base di ftalati, candidati nella lista di prodotti “high concern” della normativa *REACH*.

Il lavoro presenta tecnicamente l’attività di ricerca dei laboratori VINAVIL che ha consentito di raggiungere i risultati sopra descritti.

IND-O33

Synthesis and testing of a small eggshell Co/γ-Al_2O_3 Fischer-Tropsch catalyst with thin active shell region

L. Fratalocchi[a], *C.G. Visconti*[a], *L. Lietti*[a], *E. Tronconi*[a], *S. Rossini*[b]

a Politecnico di Milano, Dipartimento di Energia, Piazza Leonardo da Vinci 32, 20133 Milano, Italy
b Eni, Exploration & Production division, Via Felice Maritano 46, 20097 San Donato Milanese (MI), Italy

carlo.visconti@polimi.it; luca.lietti@polimi.it

The low-temperature Fischer-Tropsch synthesis (FTS) over Co-based catalysts is strongly influenced by intra-catalyst mass transport limitations, which decrease both the reaction rate and the C_{5+} selectivity for diffusion lengths over 50 μm [1]. Upon decoupling the pellet diameter and the diffusion length, eggshell catalysts represent an interesting solution for the intensification of the FTS in fixed-bed reactors (FBR) [2-3]. In this work, small Co/γ-Al_2O_3 eggshell catalysts, to be used in compact FBRs, have been prepared by following a new impregnation method, which relies on both the control of the contact time between the impregnating solution and the support, and the protection of the support pores with an organic solvent. In particular, thin active layers have been obtained by filling the pores of γ-Al_2O_3 pellets (D_p= 600 μm) with n-undecane and then contacting the wet pellets with an impregnating solution of $Co(NO_3)_2 \cdot 6H_2O$ in EtOH for 2s. Impregnated pellets have been dried in air at 393K for 2 h and then calcined at 673K in static air for 12 h. In order to achieve the desired cobalt loading, the impregnation procedure has been repeated nine times: the final cobalt weight fraction in the active shell has been found to be 16 wt. % and the average thickness of such layer about 75 μm. The FTS reactivity of the eggshell catalyst has been compared to that of a pelletized catalyst with the same size, but uniformly impregnated. Upon working in a lab-scale FBR at process conditions relevant to industrial operations, the eggshell catalyst has shown a higher CO conversion and a higher C_{5+} selectivity with respect to the uniform sample.

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IND-O34

Pd@CeO_2 core-shell catalysts for methane oxidation: Effect of water

T. Montini,[a] *M. Monai,*[a] *T. Duchon.,*[b] *N. Tsud,*[b] *E. Fonda,*[c] *C. Chen,*[d]
R.J. Gorte,[d] *K. Prince,*[e] *V. Matolin,*[b] *P. Fornasiero*[a]

[a] *Department of Chemical and Pharmaceutical Sciences, University of Trieste, INSTM and ICCOM-CNR Trieste Research Unit, via L. Giorgieri 1, 34127 Trieste, Italy*
[b] *Charles University in Prague, Faculty of Mathematics and Physics, V Holešovičkách 2, 18000 Prague 8, Czech Republic*
[c] *Synchrotron SOLEIL, BP48 Saint Aubin, 91192 Gif sur Yvette CEDEX*
[d] *Department of Chemical and Biomolecular Engineering, University of Pennsylvania, 311A Towne Building, 220 South 33rd Street, Philadelphia, PA 19104, USA*
[e] *Elettra-Sincrotrone and Istituto Officina dei Materiali, Consiglio Nazionale delle Ricerche, Area Science Park, 34149 Trieste, Italy*

tmontini@units.it

Pd@CeO_2/Al_2O_3 catalysts prepared by self-assembled core-shell units demonstrate extraordinary stability and activity in CH_4 combustion with respect to conventional impregnated catalysts [1]. The nanocrystalline CeO_2 shell has a pivotal role in the catalyst's performance: first, it hinders the sintering of Pd-based nanoparticles and, second, it stabilizes the PdO active phase through the donation of oxygen thanks to the optimal contact between the two components. In situ XANES/EXAFS experiments indicates that the presence of an excess water at high temperature favours the reduction of the catalytically active PdO to the less active Pd(0), as a consequence of the formation of stable surface hydroxyls bounds to Ce(III). Consistently, ex situ XPS and SRPES experiments performed on model systems evidence the presence of significant quantities of Ce(III) and stable hydroxyl groups after aging in the presence of water. Therefore, H_2O adsorb on oxygen vacancies of CeO_2, form hydroxyl that hinder the O spillover from CeO_2 to the Pd phase.

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IND-O35

Characterization and modification of Flaxseed Mucilages

Valeria M. Pappalardo[a], *Federica Zaccheria*[a], *Rinaldo Psaro* [a], *Nicoletta Ravasio*[a], *Giovanna Speranza*[a,b]

a ISTM-CNR, via Golgi 19, 20133, Milano, Italia
b Dipartimento di Chimica, Università di Milano, Via Golgi 19, 20133, Milano, Italia

valeria.pappalardo@istm.cnr.it

Mucilages are heterogenic polysaccharides and common bioproducts of metabolism of seed or soft stem plants, i.e. okra, psyllium and tamarind. Besides pectin, chitosan and alginate, mucilages are unique raw materials widely available, non-toxic and inexpensive. These polysaccharides are extensively used in pharmaceutical, food and manufacturing industry as biodegradable and biocompatible starting materials for a large number of applications, such as binding, thickening, emulsifying, and gelling and as controlled release agents [1].

Among vegetable sources, flax seed (*Linum usitatissimum* L.) contains reasonable amount of mucilage that are easily extracted in water. However the extraction procedure and the variety of the starting raw materials affect yield, chemical composition and physicochemical properties of the resulting mucilage [2].

Three different methods of extraction of flaxseed mucilages were developed and the resulting materials compared by NMR, ATR and TGA analyses. Viscosity, solubility as well as foaming ability and stability were also investigated.

The water soaking of the whole seeds followed by ethanol precipitation resulted to be the best method. The mucilages extracted in this way were chemically modified through different routes in order to change the interactions between polymers as well as the physicochemical and functional properties of the starting material and to improve their shelf life.

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IND-O36

New niobium-phosphate-silicate catalysts for lubricants production

Rosa Vitiello[a], *Rosa Turco*[a], *Riccardo Tesser*[a], *Antonella Gervasini*[b], *Paolo Carniti*[b], *Grazia Accardo*[c], *Luciana Minieri*[c], *Antonio Aronne*[c], *Martino Di Serio*[a]

a Universty of Naples Federico II, Dep. of Chemical Sciences, via Cintia I-80126 Napoli, Italy and CIRCC ;
b University of Milan, Dep. of Chemistry
c University of Naples Federico II, Dep. of Chem. and Material Eng. and Ind. Production.

rosa.vitiello@unina.it

Niobium phosphates can be used as catalyst in several acid catalyzed reaction [1]. Different syntheses have been proposed to obtain niobium-phosphorus mixed-oxides with high surface area. Recently, new niobium-phosphate-silicate (NPS) materials, characterized by P/Nb molar ratio equal to one and with Si content ranging from 95 to 80 mol%, have been synthesized by an innovative sol-gel route [2]. The catalytic activity of $2.5Nb_2O_5 \cdot 2.5P_2O_5 \cdot 95SiO_2$ (2.5PNb) has been tested in the esterification of 1,3-propandiol and pentaerythritol with fatty acids. Those reactions can be considered as test reactions to study the acidity of the solid but it has also an important application in the industry for lubricants production. 2.5PNb catalyst was prepared by sol-gel according to the preparation procedure reported by Aronne et al. [2]. The titrations in cyclohexane confirmed the high *intrinsic* acidity of the solid (total acidity 0.60 mequiv/g; strong acidity 0.52 mequiv/g) that is comparable with zeolite materials. More than 20% of the total acidity was maintained in water, confirming the acid-tolerant properties of niobium.- This strong acidity has been confirmed by the activity of the catalyst in the esterification of 1,3-propandiol with oleic acid and of pentaerythritol whit pelargonic. The same results have been obtained with the reused catalyst. 2.5PNb catalyst, belonging to a new class of strong and stable gel-derived acid solids (NPS), exhibits high activity in the esterification reaction. This result opens the possibility to use the NPS catalysts in a wide range of other reactions.

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IND-O37

Membrane engineering for CO_2 recovery from gaseous streams

Brunetti A[a], *Drioli E.*[a, b], *Y. M. Lee*[c], *Barbieri G.*[a]

[a] *National Research Council – Institute on Membrane Technology (ITM-CNR), Via P. Bucci, Cubo 17C , 87036, Rende (CS), Italy*
[b] *Dept. of Environmental and Chemical Engineering, University of Calabria, Via P. Bucci, Cubo 44A , 87036, Rende (CS), Italy*
[c] *WCU Department of Energy Engineering, College of Engineering, Hanyang University, Seongdong-gu, Seoul 133-791, S. Korea*

a.brunetti@itm.cnr.it

The possibility of using a membrane unit in the separation of a gaseous stream is strictly connected to three main factors: the composition of the feed, the available operating conditions, and the separation properties of the membrane chosen for the specific application. Therefore, together with material science, a crucial role for the real application of membrane technology in CO_2 separation is played by membrane engineering, which involves the integrated scheme design and optimization of the operating conditions. In this work the possible application of membranes for CO_2 separation in the treatment of non-valuable streams (e.g., flue gas of a power plant or cement industry) or valuable streams (e.g., biogas) has been analyzed [1] using general "maps" of CO_2 permeate concentration versus CO_2 recovery. They have been developed by means of a simple tool taking into account the influence of the most important parameters affecting the membrane system performance (that is, membrane selectivity and permeation driving force). The maps are reported as function of the feed/permeate pressure ratio and the permeation number. This latter is a determining parameter for the module performance.

The "Ministero degli Affari Esteri, Direzione Generale per la Promozione e la Cooperazione Culturale" of Italy is gratefully acknowledged for the financial support of project "New highly innovative membrane operations for CO2 separation (capture) at medium and high temperature: Experimental preparation and characterization, theoretical study on elementary transport mechanisms and separation design" co-funded in the framework of a bilateral agreement between MAE (Italy) and MOST (South Korea).

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IND-O38

C-N/TiO_2: effect of co-doping for the NO oxidation under visible light

V. Trevisan[a*], *F. Pinna*[a], *M. Signoretto*[a], *A. Olivo*[a], *G. Cerrato*[b], *C.L. Bianchi*[c]

[a]*Dept. of Molecular Sciences and Nanosystems, Ca'Foscari University Venice and INSTM, RU of Venice, Dorsoduro 2137, 30123, Venezia, Italy*
[b]*Dept. of Chemistry & NIS Centre of Excellence and INSTM, RU of Turin, University of Turin,via P. Giuria 7, 10125 Torino, Italy*
[c]*Dept. of Chemistry, Milan University and INSTM, Via Golgi 19, 20133 Milan, Italy*

valentina.trevisan@unive.it

TiO_2 is the most used photocatalyst for solar energy conversion and environmental applications, because of its good photoactivity, high chemical stability in the reaction condition, low cost and non-toxicity. Unfortunately, TiO_2 has two major drawbacks, consisting in its relatively large energy band-gap (3.2 eV), which hampers the exploitation of visible solar light in photocatalytic reactions, and in its relatively low surface area. Considerable efforts have been addressed to expand the optical response of TiO_2 from the UV to the visible light region. It is common knowledge that the introduction of nonmetal atoms, (S, C, N, F, B) [1] into the titanium oxide lattice promotes the decrease of the bad gap energy [2]. In particular, simultaneous doping with two kind of these atoms into TiO_2 has attracted considerable interest as it can result in a higher photoactivity.

In the present work visible-light-active C,N/TiO_2 were prepared through $TiOSO_4$ precipitation using NH_4OH as N source [3] and succinic acid as C source [4].

The photocatalytic abatement of NOx has been used as test reaction.

Through an appropriate synthetic method, we obtained N,C co-doped photocatalysts which preserved morphological properties (high surface areas, good crystallinity and anatase phase) and enhanced physical assets (low band-gap energy). In particular, C,N/TiO_2 samples have shown an improved activity in the visible light region compared to pure or single doped TiO_2.

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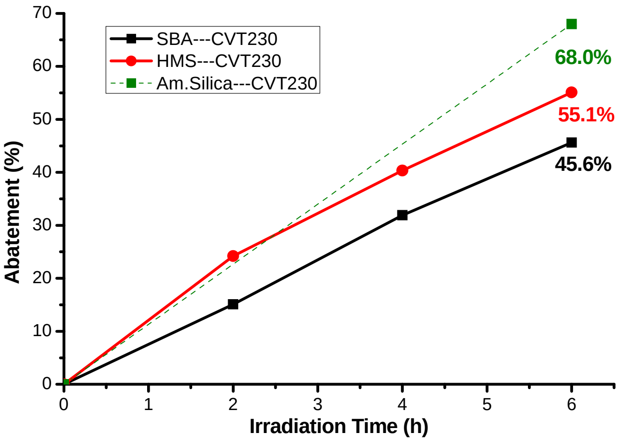
IND-O39

Waste-derived heterogeneous photocatalysts for the degradation of pollutants in aqueous solution

M.L. Tummino[a,b*], *M.L. Testa*[b], *F. Deganello*[b], *G. Magnacca*[a,§], *P. Avetta*[a], *A. Bianco Prevot*[a]

a Università di Torino, Dipartimento di Chimica and §NIS Centre of Excellence, Via P. Giuria, 7 10125 Torino, Italy
b Consiglio Nazionale delle Ricerche (CNR), Istituto per lo Studio dei Materiali Nanostrutturati (ISMN), UOS-PA, via U. La Malfa 153, I-90146 Palermo, Italy

marialaura.tummino@unito.it



In recent years, scientific research has been orienting towards environmental protection. Eco-sustainable syntheses and production of materials for environmental remediation are among the most important challenges. Furthermore, wastes accumulation problems can be solved with recycling and reusing, making refuses a valuable resource. Recently, soluble bio-organic substances (CVT230), derived from urban bio-refuses, were tested as homogenous photocatalysts for the degradation of chlorophenols. [1] In this work CVT230 was grafted on different types of silica [2] both amorphous and with ordered mesopority (HMS and SBA-15). The obtained hybrid organic-inorganic materials were characterized by N_2 adsorption isotherm, FT-InfraRed Spectroscopy and Small Angle X-Ray Scattering. Their photocatalytic activity was tested for the abatement of 4-methylphenol, a representative phenolic compound that could be found in wastewaters. The experiments were performed in aqueous solution irradiated by simulated solar light.

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IND-O40

Modelling of Microreactors for Ethylene Oxide Synthesis

Vincenzo Russo[a,b], *Teuvo Kilpiö*[b], *Riccardo Tesser*[a], *Tapio Salmi*[b], *Martino Di Serio*[a]

a Chemical Sciences Department, University of Naples "Federico II", Via Cintia, 4,80126, Naples, Italy.
b Laboratory of Industrial Chemistry and Reaction Engineering, Åbo Akademi University, Piispankatu, 8, 20500, Turku, Finland.

v.russo@unina.it

Ethylene oxide is one of the most versatile chemical intermediates for the chemical industry, being an extremely reacting molecule. It is used for the production of bulk chemicals, with an annual production of about $15 \cdot 10^6$ tonnes. The classical catalysts for the direct synthesis of ethylene oxide, from oxygen and ethylene, are silver based. These catalysts typically give an initial selectivity of about 80-90%, with total oxidation as side reactions. The reactions are extremely exothermic, so it is necessary to provide an excellent heat exchange to reduce the risk of runaway. An adequate choice of technology would be to carry out the reaction in microreactors. Recently, Salmi et al. [1] and Carucci et al. [2] have used plate microreactors to investigate the kinetics of ethylene oxide direct synthesis in both wash-coated ($Ag/\alpha\text{-}Al_2O_3$) and pure silver plate microreactors. A reaction mechanism was suggested in the previous work [12], but complete data elaboration that would give quantitative information on the reaction kinetics is still needed. The interaction of intrinsic kinetics and diffusion in the porous catalyst layer is a very interesting phenomenon, which can be elucidated by precise mathematical modelling. Two microreactor models are proposed, where the catalyst is either wash-coated on the reactor plates or the microreactor plates themselves. The models take into account the mass transfer phenomena, solving the concentration profiles in both axial, radial and coating direction. The results show that the models are able to describe all the experimental data reported in references [1-2] with a very satisfactory agreement.

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IND-O41

Photocatalytic hydrogenation of acetophenone in membrane reactors under UV and visible light

Pietro Argurio, Cristina Lavorato, Raffaele Molinari

Department of Environmental and Chemical Engineering, Università della Calabria, Via P. Bucci, cubo 44/A, I-87036, Arcavacata di Rende (CS), Italia

pietro.argurio@unical.it

The reduction of acetophenone to phenylethanol, which is used as a building block for the synthesis of bioactive compounds such as agrochemicals, pharmaceuticals, and natural products, is an important reaction due to the limited natural resources of the reduced product. On this regards photocatalytic hydrogenation, using water as solvent and formic acid (which is present as pollutant in some waters) as electron donor, is a green way to limit environment pollution and reduce conventional energy consumption by using a sustainable energy resource such as sunlight. Photocatalytic membrane reactors can be used for this type of reactions because they combine the advantage of classical photoreactors and those of membrane processes with a synergy of both technologies [1]. In the present work the hydrogenation of acetophenone was investigated using commercial titanium dioxide and homemade Pd/TiO_2 in photocatalytic batch and membrane reactors under UV and visible light. The use of a membrane reactor was found to improve the efficiency of the photocatalytic reaction compared to a batch reactor. The most efficient system for photocatalytic hydrogenation of acetophenone in terms of productivity, amount of phenylethanol produced and extraction of desired product was found to be the membrane reactor in which acetophenone was used as both extracting organic phase and substrate reservoir. The presence of palladium on TiO_2 enhances the photocatalytic activity under visible light, while it was negligible by using bare TiO_2. The productivity by using Pd/TiO_2 photocatalyst under visible light increased five times more than using TiO_2 under UV light.

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Chimica Industriale

Poster

IND-P1

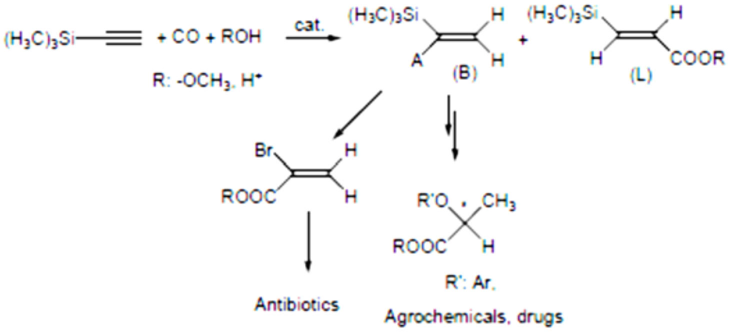
Stereoselective synthesis of 2-substituted acrylic derivatives via carbonylation reaction

M.M. Alam, V. Beghetto, A. Scrivantia, M. Bertoldinia, U. Matteolia, A. Zancanaroa

a Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari Venezia,
S. Marta 2137, 30123 Venezia, Italia

mahbubul.alam@unive.it

The carbonylation of 1-alkynes is a versatile tool for the synthesis of important intermediates such as α,β-unsaturated carboxylic acids [1,2]. In our recent work, we have disclosed the synthesis of the important intermediate 2-(trimethylsilyl)acrylic acid and its methyl ester, starting from commercially available trimethylsilylacetylene, in the presence of the readily available catalytic system obtained *in situ* from $Pd(OCOCH_3)_2/CH_3SO_3H$/2-methyl(diphenylphosphino)pyridine (Scheme 1)[3].



Scheme 1. Methoxy- and hydroxycarbonylation reaction of trimethylsilylacetylene.

Reactions are carried out at 80 ºC; methoxycarbonylation reactions allow to obtain methyl 2-(trimethylsilyl)acrylate in good conversions (ca. 93%) and with a branched/linear ratio 95/5, whereas hydroxycarbonylation reactions give lower conversions and selectivities (ca. 53%, and 93/7 respectively).

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IND-P2

One step phenol synthesis and recovery in membrane contactors

Pietro Argurio[a], *Raffaele Molinari*[a], *Teresa Poerio*[b]

[a] *Department of Environmental and Chemical Engineering, Università della Calabria, Via P. Bucci, cubo 44/A, I-87036, Arcavacata di Rende (CS), Italia*
[b] *Institute on Membrane Technologies ITM-CNR, c/o Università della Calabria Via P. Bucci cubo 17/C, I-87036 Arcavacata di Rende (CS), Italia*

pietro.argurio@unical.it

Phenol is a very important chemical intermediate in industry. It is industrially synthesized by the cumene process, which presents important drawbacks. On these basis, the search for new routes for phenol synthesis, such as the direct hydroxylation of benzene, became more intensive in the past decade. The prompt removal of the produced phenol from the reaction environment plays a key role to develop such a method. On this regard, membranes can play an important role.

In our previous works [1, 2] the direct hydroxylation of benzene to phenol in a biphasic membrane reactor was performed. A flat-sheet hydrophobic membrane separated an acidic aqueous phase (containing a Fe or V based catalyst and H_2O_2) and an organic phase (benzene). Benzene permeates across the membrane and reacts at the aqueous interface, while produced phenol permeates back and it is extracted into the organic phase, where it is protected by subsequent oxidations.

In the present work the use of three phase membrane contactors, where phenol extracted in the organic phase is simultaneously stripped in an alkaline aqueous phase, has been studied [3]. Two different configurations, in which two solid (SMC) or liquid (LMC) membranes separate three compartments, have been tested. Better results (phenol productivity 0.62 $g_{ph}\ g_{cat}^{-1}\ h^{-1}$) were obtained using the SMC containing 0.1 M Na_2SO_4 in the aqueous reacting phase, thanks to the high phenol flux away from the reacting phase which permitted to extract a high amount of phenol in the organic and aqueous (strip) phases.

The results evidenced that use of a third compartment containing an alkaline aqueous stripping phase, permitted to perform the process of phenol synthesis, simultaneous product recovery, purification (100% purity) and concentration.

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IND-P3

Surface properties of nanocrystalline ZnS and $Cu_xZn_{1-x}S$ photocatalysts

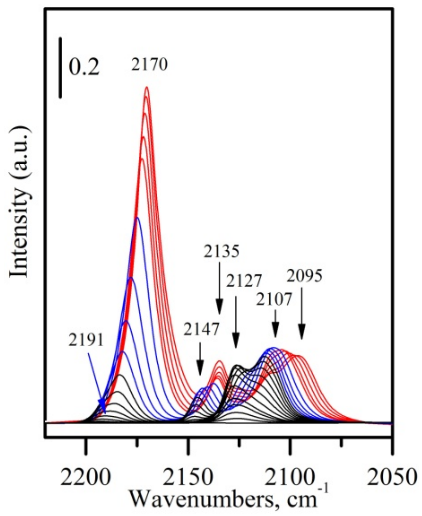
E. Balantseva, _G. Berlier, A. M. Ferrari, S. Coluccia_

Dipartimento di Chimica and NIS Centre of Exellence, Università di Torino, , Via P. Giuria 7, 10125, Torino, Italy

elena.balantseva@unito.it

The engineering of zinc sulfide (ZnS) semiconductor properties by doping with copper or other heteroatoms is a fascinating and promising approach for many applications, including photocatalytic water splitting in the sulfite mediated Sulfur-Ammonia process. This is related to the possibility of tuning the electronic properties of ZnS (band gap Eg = 3.7 eV) for visible solar light harvesting [1]. Nanostructuration is another desirable property for photocatalysts, in order to improve the electron/hole mobility and efficacy in surface redox processes.

ZnS and Cu/ZnS ($Cu_{0.01}Zn_{0.99}S$) nanostructured materials were prepared by a simple and easily scaled up precipitation method. Introduction of small amounts of copper (1 and 5% atomic) in the reaction mixture resulted in materials with sensibly different electronic properties with respect to pure ZnS. This contribution reports on *in situ* spectroscopic studies, to study the electronic and surface properties of ZnS and $Cu_{0.01}Zn_{0.99}S$ samples, by employing Diffuse Reflectance UV-Vis and FTIR spectroscopies, coupled to the adsorption of probe molecules (Figure). The results are supported by DTF calculations and photocatalytic activity results.



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IND-P4

Green catalytic hydrolysis of polycarbonate through microwave heating

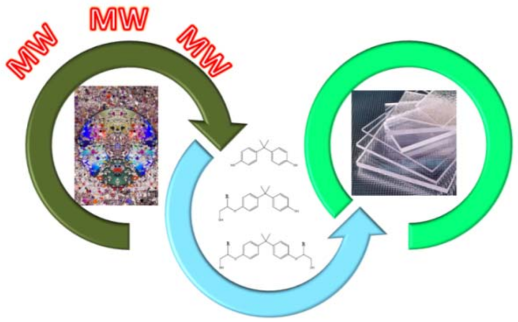
Mattia Bartoli, Andrea Undri, Marta Priori, Luca Rosi, Marco Frediani, and Piero Frediani*

[a] *Chemistry Department "Ugo Schiff", University of Florence,*
Via Lastruccia 3, 50019, Sesto Fiorentino (FI), Italy

**mattia.bartoli@unfi.it*

During the last 20 years polycarbonate (PC) has been largely used to take advantage of its transparency, heat resistance and toughness[1]. In the last few years PC In the last few years management of waste PC has become a significant problem and development of efficient methods for recycling has assumed a great relevance. A lot of processes has been devoted to recovery bis-phenol-A (BFA) from PC[2]. Among these, some processes has been modified to obtain interesting BFA derivatives but they require long reaction[3] time or unfriendly reactants and conditions[4]. A new green way to hydrolyze PC obtaining high value products is here proposed. Recycling was run in two steps with a microwave (MW) heating using green solvents (THF and glycols). An Na_2CO_3 catalyst was used in the first step, and ZnO in the second where urea was a reactant.

A complete hydrolysis of PC was obtained in 10 min with Na_2CO_3 as catalysis. MW heating allowed a drastic decrease of reaction time if compared with the classical thermal heating[5]. Use of different solvent allowed to obtain selected products: THF let to obtain only BFA while glycols (ethylenglycol or 1,2-propylenglycol) gave the corresponding BFA-alkoxylated. Products were obtained with high yields and they may be employed for manufacturing PC, modified PCs or polyurethanes strongly reducing the use of new oil derivatives.



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IND-P5

Nanoscale microfibrillated cellulose for green polymer electrolytes for DSSCs

Federico Bella[a,b], *Annalisa Chiappone*[a], *Jijeesh R. Nair*[b], *Giuseppina Meligrana*[b], *Roberta Bongiovanni*[b], *Claudio Gerbaldi*[b]

a Center for Space Human Robotics @Polito, Istituto Italiano di Tecnologia, Corso Trento 21, 10129 Torino, Italia
b Dipartimento di Scienza Applicata e Tecnologia - DISAT, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italia

federico.bella@polito.it

As a feasible option for photovoltaic technology to meet the growing energy demand, dye-sensitized solar cells (DSSCs) have attracted much attention due to their low cost, ease of fabrication and good performance. At the same time, polymer electrolytes represent the ultimate in terms of desirable properties of energy conversion devices, as they can offer an all-solid-state construction, a suitable interface with device electrodes, a wide variety of shapes and sizes, light-weight, low costs and safety [1,2,3].

In this work, nanoscale microfibrillated cellulose (NMFC) is introduced into a light-cured polymeric matrix, thus resulting in a green, cheap and highly efficient quasi-solid electrolyte for bio-based DSSCs.

The effect of NMFC on the photovoltaic parameters and performance of the resulting photoelectrochemical cells is thoroughly investigated, and a noticeable increase in both the photocurrent (due to optical phenomena) and the photovoltage (through a shielding effect on the recombination reactions) is demonstrated. Upon thorough optimization of the amount of NMFC introduced in the polymeric network, sunlight conversion efficiencies as high as 7.03% and 8.25% are achieved at simulated light intensities of 1.0 and 0.4 sun, respectively. Furthermore and outstandingly, NMFC addition also positively affects the long-term stability of the device, which is able to retain > 95% of the initial efficiency after 500 h of extreme aging conditions.

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IND-P6

Fluoropolymeric luminescent downshifters for organic-dye-sensitized solar cells

Federico Bella[a,b], *Gianmarco Griffini*[c], *Roberta Bongiovanni*[a], *Stefano Turri*[c]

a Dipartimento di Scienza Applicata e Tecnologia - DISAT, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italia
b Center for Space Human Robotics @Polito, Istituto Italiano di Tecnologia, Corso Trento 21, 10129 Torino, Italia
c Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italia

federico.bella@polito.it

As a feasible option for photovoltaic technology to meet the growing energy demand, dye-sensitized solar cells (DSSCs) have attracted much attention due to their low cost, ease of fabrication and good performance [1]. In particular, metal-free organic dyes are currently under investigation because of their low cost and high molar extinction coefficient; thus, they are ideal sensitizer for large-scale applications. However, their absorption range is often narrow, so that an important portion of the solar spectrum is not absorbed [2].

In this context, we think that luminescent materials, which are capable of converting a broad spectrum of light into photons of a particular wavelength, can be used to improve the light harvesting efficiency of the solar-cell-based energy conversion process [3].

In this work, for the first time ever new crosslinked fluoropolymeric systems are employed as luminescent downshifters for organic-dye-sensitized solar cells. The effect of these parameters on the photovoltaic cells and the study of devices aging will be presented.

[1] F. Bella et al., *J. Photochem. Photobiol., C*, 2013, **16**, 1-21.
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IND-P7

Reactivity and surface adsorption sites of Cu-Zn-Zr catalysts for the CO_2-to-MeOH hydrogenation reaction

G. Bonura[a], *M. Cordaro*[a], *C. Cannilla*[a], *F. Frusteri*[a]

[a] *CNR-ITAE, Via S. Lucia 5, 98126 – Messina, Italy*

giuseppe.bonura@itae.cnr.it

Currently, alternative routes aimed at recycling carbon dioxide for the production of chemicals or fuels, like methanol, represents a very challenging research topic to address the main issues on the climate change [1]. In particular, using CO_2 in place of CO for methanol synthesis would represent a decisive technological breakthrough with a remarkable improvement of the overall process economics [2-3]. The present study is focused to assess the efficiency of the synthesis methodologies considered as the most promising in literature (*i.e.*, coprecipitation with sodium bicarbonate, complexation with citric acid, gel-oxalate coprecipitation) along with the optimal catalyst composition of Cu-Zn-Zr systems, suitable to enhance the catalytic pattern in the CO_2-to-MeOH hydrogenation reaction.

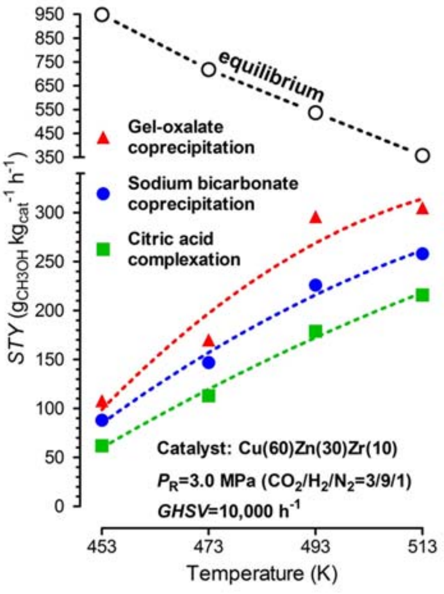

Fig. 1 - Catalyst productivity.

As shown in Fig. 1, the catalyst obtained by the gel-coprecipitation procedure showed a superior functionality, attaining a specific productivity of 305 g_{CH3OH} kg_{cat}^{-1} h^{-1} at 513 K, 3.0 MPa and 10,000 h^{-1}.

Peculiar structure-activity relationships pointed out the factors to be taken into account for the optimization of the catalytic systems, in terms of physico-chemical properties and productivity to MeOH from CO_2/H_2 mixtures. An adequate balance between metal and oxide surface sites, in correspondence of a well defined particle size, was proposed to be crucial to design active and selective catalysts for such reaction.

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IND-P8

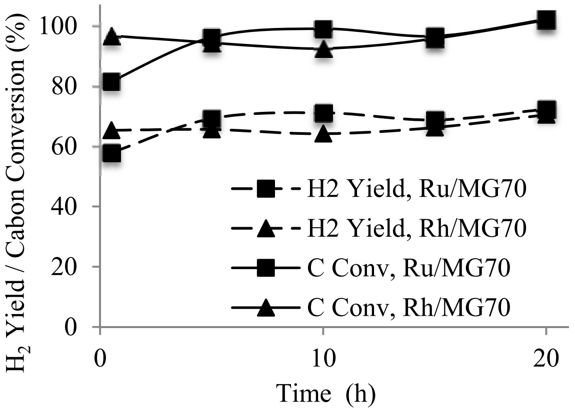
Stable catalysts for acetic acid steam reforming

Filippo Bossola[a], Claudio Evangelisti[b], Marcello Marelli[b], Rinaldo Psaro[b], Sandro Recchia[a], Vladimiro Dal Santo[b].

a Dipartimento di Scienze e Alta Tecnologia, Università dell'Insubria, Via Valleggio 11, 22100, Como, Italia
b CNR-Istituto di Scienze e Tecnologie Molecolari, Via Golgi 19, 20133, Milano, Italia

filippo.bossola@gmail.com

Steam reforming of acetic acid (HAc), as one of the major component of bio-oil derived by pyrolysis of biomass, is considered a promising and economical way for sustainable hydrogen production [1]. Rh and Ru heterogeneous catalysts supported on Hydrotalcite derived materials (MG series, Sasol - Germany) at 0,5 and 2 wt.% metal loading, respectively, were prepared by wet impregnation methods and characterized by BET, TPR, and TGA analysis. Catalytic testes were performed at 700 °C at a steam-to-carbon ration (S/C) of 3. As shown in the figure, both catalysts displayed good performances in terms of hydrogen yield, carbon conversion and stability up to 20 hours of time on stream. The low amount of coke found after the tests (0,0459 and 0,0381 g_{coke}/g_{cat} for Ru and Rh catalysts respectively) do not affect catalysts performances. This can be attributed to the low acidity of the support and/or to the high –O and/or –OH spillover to the metal nanoparticles [2].



H_2 yield and carbon conversion of 2% Ru/MG70 and 0,5% Rh/MG70 at 700 °C and S/C = 3 in steam reforming of HAc.

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IND-P9

Catalytic Partial Oxidation of liquid fuels: experimental study in autothermal reactor

A. Carrera[a], *D. Pagani*[a], *A. Donazzi*[a], *A. Beretta*[a], *G. Groppi*[a], *P. Forzatti*[a]

[a] *Laboratory of Catalysis and Catalytic Processes, Department of Energy, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133, Milano, Italy*

andrea.carrera@polimi.it

Catalytic Partial Oxidation (CPO) of hydrocarbons is interesting for hydrogen production on decentralized and mobile systems. Goal of this work is to investigate the CPO of liquid fuels (e.g. gasoline), extending previous studies on CH_4 CPO [1] and C_3H_8 CPO [2-3]. Since gasoline is a mixture of many different hydrocarbons, the strategy is to study few model compounds, such as i-C_8H_{18}. Experimental tests carried out in a isothermal annular reactor, loaded with a 2% Rh/α-Al_2O_3 catalyst, show a reaction mechanism which consists of a sequence of exothermic combustion reaction followed by endothermic steam reforming and reverse water-gas-shift. In order to better investigate hydrocarbon CPO in more relevant operating conditions, CPO experiments with stoichiometric concentrations (O_2/C=0.56) were carried out in a lab scale autothermal reformer with a honeycomb monolith catalyst (2% Rh/α-Al_2O_3), equipped with probes for temperature and species concentrations spatially resolved measurements. Sharp gradients of temperature and concentration establish at the catalyst inlet. Due to the high heat release for total oxidation reaction, all the hydrocarbons show an hot spot of temperature within the catalyst. High catalyst temperatures may lead to sintering and rapid catalyst deactivation. This issue is crucial with heavier fuels, because of the higher heat of total combustion: solutions may involve modification of the reactor aspect ratio and increasing the catalyst load [2-3]. Moreover, in i-C_8H_{18} CPO, high temperatures activate homogeneous reactions, which compete with surface reaction, modifying the product selectivity.

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IND-P10

Recupero di acqua da correnti gassose inquinate utilizzando condensatori a membrana

Maurizio Cersosimo, Francesca Macedonio, Adele Brunetti, Enrico Drioli, Giuseppe Barbieri

Consiglio Nazionale delle Ricerche, Istituto per la Tecnologia delle Membrane (ITM-CNR), Via P. Bucci, Cubo 17C, 87036 Rende (CS) ITALIA.

m.cersosimo@itm.cnr.it

Membrane idrofobiche microporose in PVDF sono state utilizzate per il recupero di acqua contenuta in correnti gassose simulanti quelli in uscita da processi industriali. Sfruttando l'idrofobicità di queste membrane e applicando una differenza di temperatura (ΔT) tra le fibre di PVDF e la corrente gassosa in ingresso è possibile ottenere la condensazione di acqua sulla superficie delle membrane. I risultati ottenuti sono stati espressi in termini di quantità e purezza di acqua recuperata. In particolare l'acqua recuperata è stata definita in termini di massa di liquido trattenuto nel retentato rispetto a quello totale contenuto nella corrente di gas in ingresso. Le varie prove sono state effettuate variando di volta in volta la temperatura del modulo contenente le fibre e del gas in ingresso e cambiando la portata. È stato osservato che con un ΔT di circa 19°C ed una portata di 222 mL min^{-1} è possibile recuperare il 50% dell'acqua contenuta in una corrente gassosa con umidità relativa del 100%. Sono stati condotti ulteriori studi sulla capacità di tali membrane di ridurre la concentrazione di contaminanti presenti nella corrente di alimentazione. È stato osservato che grazie alla loro elevata volatilità solo il 2% delle specie contaminanti viene condensata ed i risultati ottenuti (50% di acqua recuperata e 98% di contaminanti rimossi) mostrano come questi sistemi possono affrontare le problematiche della condensazione[1]. I condensatori a membrana descritti potrebbero esser usati per il pretrattamento dei gas esausti provenienti dalle centrali elettriche.

Si ringrazia il progetto di ricerca "Capwa – Capture of evaporated water with novel membranes" finanziato dalla Unione Europea EU-FP7.

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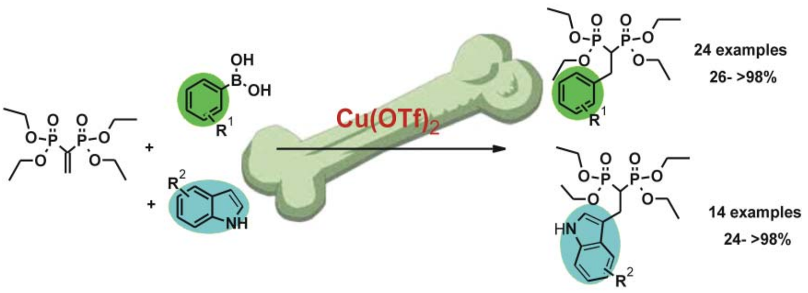
IND-P11

Cu(II) Mediated 1,4-Conjugate Addition of Boronic Acids and Indoles to VBP Leading Bisphosphonates as Potential Anti-Resorption Bone Drugs

A. Chiminazzo[a], *M. Damuzzo*[a], *L. Sperni*[a], *G. Strukul*[a], *A. Scarso*[a]

a Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari di Venezia,
Dorsoduro2137 ,30123,Venezia, Italy

andrea.chiminazzo@unive.it



Thanks to their structural similarity with pyrophosphate, bisphosphonates (BPs) ensure specific bone targeting [1] and are widely employed as drugs for the treatment of bone disorders. New recent studies demonstrated the cellular activity of BP acting as potent inhibitors of specific enzymes [2] thus leading to osteoclast inactivation. Herein we present a straightforward synthesis of gem-BP bearing different alkyl, aryl and indolyl derivatives in the β-position through Cu(II) mediated conjugate addition of alkyl and aryl boronic acids as well as indoles to VBP. While boronic acid addition proceeds much better in the non-coordinating solvent toluene, indole addition can be performed either in DCE as well as in water with SDS under micellar conditions leading to comparable efficiency. This efficient and versatile synthesis of BPs allowed the preparation of several BP tetraethyl esters that were transformed into the corresponding bisphosphonic acids that are currently under investigation to assess their activity in the inhibition of the osteoclast activity.

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IND-P12

Unusual anion effect on the gold(I)-catalyzed hydroalkoxylation of alkynes

G. Ciancaleoni[a]*, P. Belanzoni*[b]*, L. Belpassi*[a]*, L. Biasiolo*[c]*, A. D'Amora*[d]*, A. Macchioni*[b]*, F. Tarantelli*[b]*, M. Trinchillo*[d]*, D. Zuccaccia*[c]*.*

a Istituto di Scienze e Tecnologie Molecolari del CNR (CNR-ISTM), via Elce di sotto 8, 06123, Perugia, Italy
b Dipartimento di Chimica, Biologia e Biotecnologie, Università degli Studi di Perugia, Via Elce di Sotto 8, I-06123, Perugia, Italy
c Dipartimento di Chimica, Fisica e Ambiente, Universita di Udine, Via Cotonificio 108, I-33100 Udine, Italy
d Dipartimento di Scienze Chimiche, Università Federico II di Napoli, Via Cintia - Complesso di Monte S. Angelo, 80126, Napoli, Italy

gciancaleoni@gmail.com

Homogeneous gold catalysis has received considerable attention in recent years and great efforts have been made to optimize known reactions and find new catalytic applications [1]. Among the factors that influence the catalytic performances, the anion demonstrated to be very important in tuning the activity, the regio- and the stereo-selectivity of the process [2]. However, the mechanism by which the anion actually influences the mechanism is still largely unknown, even if useful information can be drawn from the interionic characterization of gold catalysts [3]. In this contribution, we studied the addition of methanol to 3-hexyne catalyzed by [(NHC)AuX] complexes [NHC = N-Heterocyclic Carbene, X = $B(C_6H_3(CF_3)_2)_4^-$, BF_4^-, *p*-toluensolfonate (OTs^-), trifuoroacetate and acetate] by a combined experimental/theoretical approach. Experimental results showed that, surprisingly, OTs^- gives better results than the non-coordinating BF_4^-. DFT studies gives a rationale to this finding, showing that OTs^- is a good compromise between coordination power, which must be moderate to allow the coordination of the 3-hexyne, and basicity, which favors the abstraction of the alcoholic proton from the methanol during the nucleophilic attack.

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IND-P13

Impiego di biocatalizzatori per trasformazioni selettive nella sintesi di molecole farmacologicamente attive

Samuele Ciceri[a], *Paride Grisenti*[b], *Patrizia Ferraboschi*[a]

a Dipartimento di Biotecnologie Mediche e Medicina Traslazionale, Università Statale di Milano, Via Saldini 50, 20133, Milano, Italia
b EUTICALS SpA, Via Volturno 41/43 , 20089, Rozzano (MI), Italia

samuele.ciceri@guest.unimi.it

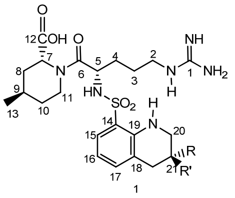
Nel corso della sintesi di composti farmacologicamente attivi che presentano strutture polifunzionali e contengono uno o più centri stereogenici sono richieste trasformazioni chemoselettive, regioselettive, stereoselettive realizzabili attraverso l'impiego di biocatalizzatori (enzimi purificati o microrganismi).

Scopo del nostro lavoro è stato l'ottenimento di alcuni principi farmacologicamente attivi con metodi biocatalitici che avrebbero potuto apportare miglioramenti, rispetto alle preparazioni già note, in termini di rese e di semplificazione della via di sintesi.

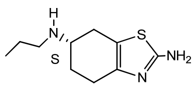
Con l'utilizzo della lipasi da *Pseudomonas fluorescens* sono stati ottenuti i sintoni enantiomericamente puri per l'ottenimento dell'(R) e (S)-argatroban, un antitrombotico sintetico.

L'utilizzo del microorganismo *Saccharomyces cerevisiae* ha consentito la preparazione del sintone otticamente puro per ottenere sia l'(S)-pramipexolo (Mirapex), un ammino tetraidrobenzotiazolo di origine sintetica utilizzato nel trattamento del morbo di Parkinson, sia l'(R)-pramipexolo (Dexpramipexolo), attualmente in fase di studio per il trattamento della SLA (Sclerosi Laterale Amiotrofica).

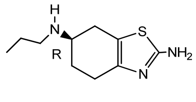
Attraverso una trasformazione regioselettiva, catalizzata dalla proteasi Alcalase CLEA, è stato possibile preparare la capecitabina (Xeloda), un antitumorale a struttura nucleosidica.



R = CH_3 ; R' = H (21R)-argatroban
R = H; R' = CH_3 (21S)-argatroban



(S)-pramipexolo



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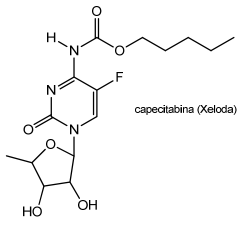


capecitabina (Xeloda)

IND-P14

Ni-ZrO_2 catalysts for the steam reforming of ethanol: influence of the preparation method on the catalytic performance

M.Compagnoni[a], *J.Lasso F*[a], *I.Rossetti*[a], *V. Nichele*[b], *M. Signoretto*[b]

[a] *Dipartimento di Chimica, Università Degli Studi di Milano, Via C. Golgi 19, 20133, Milano, Italia*

[b]*Dip. di Scienze Molecolari e Nanosistemi, Università Cà Foscari Venezia, Calle Larga S. Marta, 2137, Venezia, Italy and INSTM Unit Venezia*

ilenia.rossetti@unimi.it

A set of Ni catalysts supported over ZrO_2 for the steam reforming of ethanol were prepared by two different procedures to evaluate the influence of the preparation method on the catalytic performance. Flame pyrolysis (FP) is a one step high temperature synthesis and usually imparts a strong metal-support interaction, besides high thermal resistance. It was compared with a multistep synthesis, consisting of the precipitation of ZrO_2 from the precursor solution, followed by the addition of active phase by incipient wetness impregnation and calcination at 500°C in flowing air. The samples were thoroughly characterised by AAS, XRD, N_2 adsorption-desorption, TPR, SEM, TEM and FT-IR. Activity testing for the steam reforming of ethanol was performed after activation at 500°C in H_2 flow by means of a continuous micropilot plant, by feeding a 3:1 (mol:mol) mixture of water/ethanol. Testing has been carried out at 500°C, 400°C and 300°C for 8 h-on-stream. Spent catalysts were characterized by TPO, TEM, FE-SEM and Raman analysis.

Very high activity has been observed at high reaction temperature (>600°C), but it would be interesting to operate under milder conditions, in order to lower the energy input to the process and to improve H_2 productivity by favoring the water gas shift reaction. The main issue at low operating temperature is coke accumulation, which leads to fast catalyst deactivation and appearance of by-products. The catalytic performances, in terms of both H_2 productivity and stability towards coking and sintering, were related to the physico-chemical properties, in particular to the metal–support interaction. The stronger the latter parameter, the higher was metal dispersion, leading to small and stable Ni clusters, less active for coking. In addition, acidity was tuned by doping ZrO_2 with alkali and alkali-earth oxides, helping to prevent ethanol dehydration and coking by ethylene polymerization. The FP method allowed to prepare samples very resistant to coking, and alkali doping was a successful strategy to improve catalyst life.

IND-P15

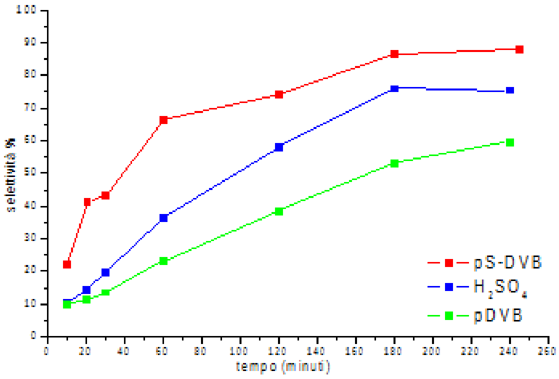
Nuovi processi in bioraffineria: etanolisi di furfuril alcol a etil levulinato

C. Dalla Valle, M. Zecca, P. Centomo

Dipartimento di Scienze Chimiche, Università di Padova, Via Marzolo 1, 35131,Padova

chiara.dallavalle.1@studenti.unipd.it

La produzione di biocarburanti, potenziali sostituti rinnovabili dei carburanti fossili, riveste una grande importanza nell'autotrazione. Attualmente l'interesse è rivolto verso lo sfruttamento di biomasse non edibili il cui impiego non interferisce con la catena alimentare. Particolarmente abbondanti e facilmente reperibili sono le biomasse lignocellulosiche (scarti agricoli e della lavorazione del legno) da cui è possibile ricavare diverse *platform molecule* per la produzione di prodotti chimici. Tra queste interessante risulta essere il furfurale, da cui è possibile ottenere l'etil levulinato (EL), impiegato come additivo per biocarburanti, attraverso un processo a due step: idrogenazione a Furfuryl alcool (FAlc) e etanolisi acido catalizzata a EL [1]. In questo lavoro sono state studiate le prestazioni catalitiche nella reazione di etanolisi del FAlc di resine acide a base stirenica (pS-DVB) con morfologie di tipo gel e macroporosa, preparate in laboratorio a partire da materiali commercialmente disponibili. E' stato inoltre studiato un polimero reticolato (polidivinilbenzene, pDVB) caratterizzato da un sistema di mesopori permanenti, ottenibile mediante sintesi solvotermale. I risultati catalitici mostrano un interessante effetto del supporto polimerico sulla selettività della reazione. Da un lato, i catalizzatori con morfologia mesoporosa mostrano selettività inferiori al catalizzatore omogeneo di riferimento (H_2SO_4), mentre quelli caratterizzati principalmente da porosità di dimensioni nanometriche risultano apprezzabilmente più selettivi. Le evidenze suggeriscono che la promozione della reazione all'interno di un sistema poroso nanostrutturato tende a sfavorire la formazione di sottoprodotti di oligomerizzazione del FAlc, stericamente ingombranti, a beneficio del prodotto ricercato, EL.



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IND-P16

Safety by design strategy on CNT

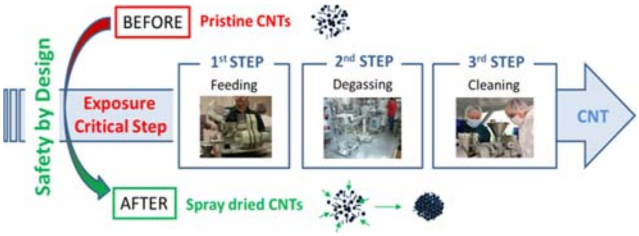
C. Delpivo[a,b], S. Ortelli[a,b], M. Blosi[a], A. L. Costa[a],
S. Albonetti[b], A. Vaccari[a,b]

[a] *Nanotechnologies and Colloidal Processing, CNR-ISTEC, Via Granarolo, 64 - 48018 Faenza RA, Italy*

[b] *Department. of Industrial Chemistry "Toso Moantanari", ALMA MATER STUDIORUM University of Bologna, Viale Risorgimento 4 - 40136, Bologna, Italy*

camilla.delpivo2@unibo.it; camilla.delpivo@istec.cnr.it

"Safety by design" (SbyD) strategies are breakthrough tools that inspire EU research project *Safe Nano Worker Exposure Scenarios*, where they are aimed to prevent workers from exposure and hazards related to nanomaterials (NM). Possible NM are carbon nanotubes (CNT) used as nanofiller in a polypropylene (PP) matrix to enhance mechanical and flame retardant properties. Below are shown the critical steps during the extrusion process of PP charged with CNT (PP-CNT) due to CNT's dust airborne. The strategy applied is the consolidation of CNT in µm-size granules (gCNT) by spray drying to lower their emissivity. CNT and gCNT size, shape, and specific surface area have been determined; their emissivity have been evaluated by "dustiness test" and on-site measurements. Both analyses validate the granulation as SbyD strategy, since the lower level of CNT's dust airborne detected employing gCNT. In further tests, CNT and gCNT were introduced in PP by extrusion obtaining nanocomposites (NC) as pellets, then injected to obtain specimens. The performances of NC have been compared in term of mechanical and flame retardant properties. NC crystallinity decreases when gCNT were used instead of pristine one, although flexural properties were similar in both samples and PP-gCNT tensile modulus was slightly higher than in NC including bare CNT. The introduction of CNT and gCNT in PP contributes to obtain a tensile resistant material, but both NC showed the flammability of bare PP. In conclusion the SbyD strategy applied is useful to lower the NM emissivity and to enhance mechanical properties of PP, but does not provide an improvement of flame retardant property.



IND-P17

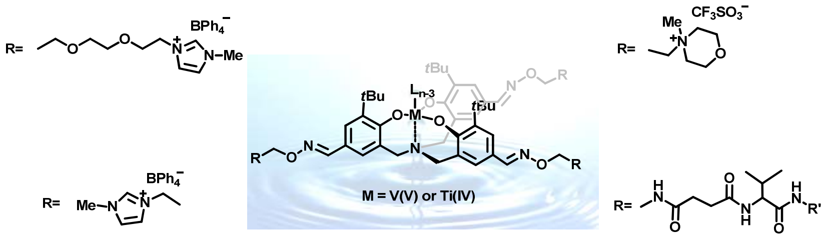
Towards Water Soluble Triphenolamine based Catalysts

R. Di Lorenzo[a], *E. Amadio*[b], *A. Mroczek*[a], *C. A. Angulo-Pachón*[c], *B. Escuder*[c], *C. Zonta*[a], *G. Licini**[a]

a Department of Chemical Sciences, Università di Padova, Via Marzolo 1,35131, Padova, Italy
b Istituto per la Tecnologia delle Membrane (ITM-CNR), Via Marzolo 1 , 35131, Padova, Italy
c Department of Inorganic and Organic Chemistry, Universitat Jaume I, Av. Sos Balnat, s/n, 12071, Castelló de la Plana, Spain

rosalia.dilorenzo@studenti.unipd.it

The development of water soluble catalytic systems represents a great interest nowadays, as it can offer the opportunity to perform organic transformations in a green and cheap solvent.
In this context, we want to exploit our experience in synthesizing amine triphenolate (TPA) complexes [1] for the realization of water soluble and hydrogel-supported catalysts. In particular, the aim of the present work is to address this challenge by developing a robust and efficient TPA functionalization strategy, that includes the TPA skeleton decoration through a three fold-*para* formylation of the phenol moieties and further functionalization *via* oxime bonds in order to introduce ion-tagged moieties or hydro-gelator residues [2].



The formation of metal complexes, e.g. Ti(IV) or V(V), will then give rise to nanostructured systems, whose catalytic activity towards oxidation reaction is currently under study.

We acknowledge COST Action CM1005 (RDL STSM) and University of Padova (PRAT 2012, CPDA123307) for financial support.

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IND-P18

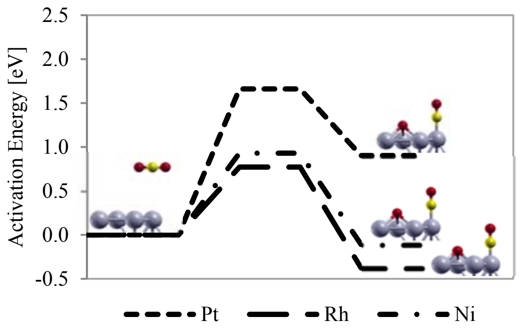
First-Principles Assessment of CO_2 Activation Pathways over Metal Catalysts

Luca Dietz[a], *Simone Piccinin*[b], *Matteo Maestri*[a*]

a Laboratory of Catalysis and Catalytic processes, Dipartimento di Energia- Politecnico di Milano, Italy
b CNR-Democritos c/o SISSA, Trieste, Italy

matteo.maestri@polimi.it

We present a detailed analysis at the atomistic level of the CO_2 activation pathways on Pt, Rh and Ni surfaces [1-3] to gain fundamental insights for the development of a predictive microkinetic model for the CO_2 methanation, Water Gas Shift (WGS) and Reverse Water Gas Shift (RWGS) reactions [4]. In particular, by using periodic PBE-DFT calculations, we illustrate how the different metal catalysts enable different catalytic cycles and thus show specific observed reaction orders. On one hand, CO_2 disproportionation has been identified as the dominant step on those metals which exhibit high affinity towards oxygen. On the other hand, the hydrogenation prevails over the disproportionation mechanism as much as the oxygen binding energy decreases. Such findings provide crucial insights to explain the different observed reaction orders for WGS and RWGS, which are of direct use for the development of detailed microkinetic models [5,6]. Moreover, our analysis clearly points out that the CO_2 activation on metal catalysts cannot be described by a unique catalyst descriptor and local conditions of the surface coverage have to be accounted for.



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IND-P19

Modellazione matematica di SOFC per utilizzo con H_2, CO e CH_4

A. Donazzi, M. Maestri, G. Groppi

Dipartimento di Energia, Politecnico di Milano, Via Lambruschini 4, 20156, Milano

alessandro.donazzi@polimi.it

La diffusione della tecnologia SOFC per la produzione di energia distribuita richiede lo sviluppo di celle funzionanti sia con combustibili tradizionali (CH_4 e GPL) che con combustibili derivati da biomasse (etanolo, biogas) a temperature comprese fra 500 e 700°C. La ricerca sperimentale va accompagnata da modelli numerici in grado di predire le prestazioni di cella e quantificare i contributi dovuti ai diversi fenomeni chimici e fisici aventi luogo negli elettrodi. In questo lavoro, viene convalidato un modello numerico che simula il funzionamento di celle SOFC a bottone con alimentazione di H_2, CH_4 e CO, puri o in miscela con N_2, He o CO_2. Il modello è dinamico, monodimensionale, eterogeneo e isotermo, e permette di descrivere l'andamento del potenziale di cella al variare della densità di corrente, della temperatura, della pressione e della composizione di alimentazione, sia nel caso di curve di polarizzazione, sia nel caso (dinamico) di spettri di impedenza EIS. La diffusione dei gas all'interno degli elettrodi porosi è stata descritta attraverso il modello Dusty Gas, comprensivo del contributo dei flussi viscosi e dei gradienti di pressione negli elettrodi (significativi in celle elettrodo-supportate). I processi anodici considerati comprendono le reazioni elettrochimiche di ossidazione di H_2 e CO e le reazioni catalitiche di Steam Reforming e Water Gas Shift, quantificati attraverso equazioni cinetiche globali. Il modello è stato verificato sulla base di dati di riferimento in letteratura [1, 2] ed esteso all'analisi di dati ottenuti in laboratorio su celle IT-SOFC di tipo Pd-Cu-CeO_2/CZ80/LSM. Sono state analizzate curve di polarizzazione e impedenza misurate in presenza di miscele H_2/H_2O, H_2/CO, H_2/CO_2, CH_4/H_2O. Nel caso di miscele H_2/CO e H_2/CO_2, i risultati numerici suggeriscono l'attivazione della reazione di elettro-ossidazione di CO anche in presenza di H_2. Questa positiva sinergia fornisce una via aggiuntiva di produzione di corrente, la cui attivazione permette di estendere il campo operativo della cella verso densità di potenza più elevata.

Si ringrazia il MIUR (Roma) per il finanziamento (PRIN 2010/2011, 2010KHLKFC)

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IND-P20

Electrochemical characterization of co-precipitated *RE*$BaCo_2O_{5+\delta}$ (*RE* = La, Y)

A. Donazzi[a]*, R. Pelosato*[b]*, C. Cristiani*[b]*, G. Dotelli*[b]*, M. Mariani*[a]*, I. Natali Sora*[c]

[a]*Dipartimento di Energia, Politecnico di Milano, 20156 Milano*
[b]*Dipartimento di Chimica, Materiali e Ingegneria Chimica, Politecnico di Milano*
[c]*Dipartimento di Ingegneria Industriale, Università di Bergamo, 24044 Dalmine (BG)*

alessandro.donazzi@polimi.it

RE$BaCo_2O_{5+\delta}$ layered perovskite oxide compounds (*RE* = Rare Earth ion) are promising cathodes for Intermediate Temperature SOFCs, thanks to their high electronic conductivity, high oxygen vacancy concentration, good ion transport capability and high oxygen surface exchange coefficients [1]. In this work, a simple and cost-effective co-precipitation synthesis in aqueous medium was applied to prepare $LaBaCo_2O_{5+\delta}$ (LBC) and $YBaCo_2O_{5+\delta}$ (YBC) cathodes. The chemical and electrochemical properties of both materials were characterized with different techniques (XRD, SEM, TPO, DTA/TG, 4-point DC conductivity measurement, EIS tests on symmetric cells). The coprecipitation synthesis revealed a promising method to prepare perovskitic cathodes: for both LBC and YBC, the measured Area Specific Resistance values were lower than those reported in the literature for the same materials prepared via different routes (mainly, solid state reaction [2]). This result was possibly due to the higher defectivity introduced in the crystal structure by the co-precipitation method. In the case of LBC (the most active cathode), a kinetic investigation was performed (600–800°C, 5–100% O_2 v/v) and the results were analyzed based on equivalent circuits. The main reaction steps were identified (O^{2-} ion transfer at high frequency, O_2 adsorption at medium frequency), and their activation energy and O_2 reaction order were quantified. Ageing tests (500 h time on stream, 500–800°C) revealed quick and strong deactivation in the case of YBC, caused by interactions with the electrolyte (LSGM) and instability of the perovskite structure. In the case of LBC, good stability was observed with limited increase of the polarization resistance. Post-mortem XRD analysis confirmed the absence of interactions between LSGM and LBC and no formation of secondary phases.

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IND-P21

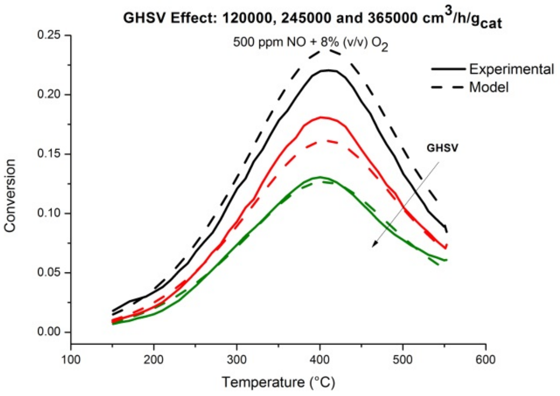
Experimental and Detailed Kinetic Modeling Study of NO Oxidation Over a Cu- Zeolite Catalyst

Amir Reza Fahami, Isabella Nova, Enrico Tronconi

Dipartimento di Energia, Laboratory of Catalysis and Catalytic, Politecnico di Milano,
Piazza L. Da vinci 32 ,20133,Milano, Italy

enrico.tronconi@polimi.it

Ammonia Selective Catalytic Reduction (SCR) is one of the main techniques to abate NO_x emissions from stationary and mobile sources [1]. Detailed understanding of NO oxidation to NO_2 on SCR catalysts (Cu/Fe-Zeolite) is fundamental to describe the mechanism of Standard NH_3-SCR (NH_3+NO+O_2) [2]. In the present work, a kinetic model based on a detailed Redox mechanism has been developed and a systematic set of transient kinetic runs have been carried out over a commercial Cu-zeolite catalyst to address the effects of different operating variables on NO oxidation. These experiments have been then employed to estimate the intrinsic rate parameters for the proposed mechanism, based on a heterogeneous one-dimensional isothermal and isobaric plug flow reactor model. The presented figure demonstrates e.g. the measured and calculated effects of gas hourly space velocity (GHSV) on the conversion of 500 ppm NO to NO_2 in the presence of 8 % (v/v) oxygen and in the absence of water. The proposed model is able to represent accurately the experimental data in a wide temperature window (150 – 550 °C), accounting for the effects of GHSV, O_2, H_2O, NO and NO_2 feed contents.



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IND-P22

An Innovative Technique For The Sustainable Production of Pure Nitric Oxide

Amir Reza Fahami, Isabella Nova, Enrico Tronconi

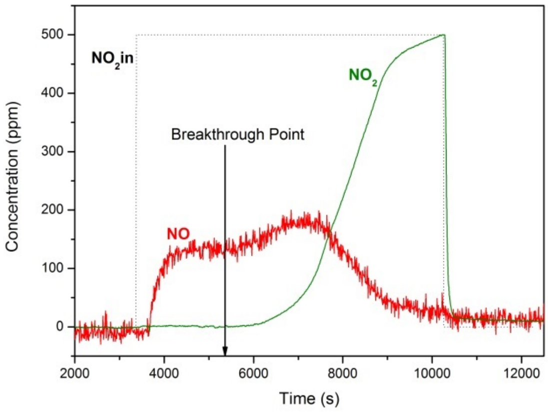
Dipartimento di Energia, Laboratory of Catalysis and Catalytic, Politecnico di Milano,
Piazza L. Da vinci 32 ,20133,Milano, Italy

enrico.tronconi@polimi.it

Gaseous nitric oxide (gNO) is an FDA approved drug for treatment of many maladies and illnesses like Pulmonary Hypertension in the full term infant and non-healing lesions and fungal dermatophyte infections. Likewise, other therapeutic potential of gNO addresses treatment of some disorders in human and animal body as a vasodilatation agent [1]. In view of the need of pure gNO and the challenging barriers facing its production, the present work introduces an original, inexpensive, safe and very simple catalytic technique to produce gNO. In this work, $BaO/\gamma-Al_2O_3$ is employed to first adsorb NO_2 and then release pure NO according to the following global reaction [2], well known in Lean DeNOx catalysis:

$3NO_2 + BaO \rightarrow Ba(NO_3)_2 + NO$

The overall stoichiometry of this reaction shows the release of one molecule NO for the consumption of three molecules of NO_2, while stable nitrates are left on BaO. This stoichiometry is confirmed by our experiments, wherein the produced NO was found equal to one third of the reacted NO_2 within ±5%. The data in the presented figure indicate that 1 gram of the prepared catalyst was able to produce 2e-4 moles of NO before Breakthrough Point (BTP).



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IND-P23

Separazione di CO_2 da correnti gassose umide utilizzando membrane a fibra cava in poliimmide Matrimid 5218

Francesco Falbo, *Franco Tasselli, Adele Brunetti, Enrico Drioli, Giuseppe Barbieri*

Consiglio Nazionale delle Ricerche, Istituto per la Tecnologia delle Membrane
(ITM-CNR), Via P. Bucci, Cubo 17C, 87036 Rende (CS) ITALIA.

f.falbo@itm.cnr.it

In questo lavoro sono state preparate membrane a fibra cava in poliimmide Matrimid 5218 secondo il processo di filatura dry-wet mediante tecnica di inversione di fase indotta da non solvente. Con le fibre prodotte sono stati assemblati moduli a membrana che sono stati utilizzati al fine di separare la CO_2 da correnti gassose di interesse industriale. Le proprietà di trasporto dei moduli a membrana sono state valutate alimentando gas puri, CO_2, N_2, CH_4 e miscele gassose binarie contenenti CO_2 e N_2 a differenti temperature (25, 50, 60 e 75°C) a differenti valori di umidità relativa (0 e 100%) e fino a 6 bar di pressione.

Sono stati ottenuti interessanti valori di selettività CO_2/N_2, compresi tra 31 e 28, e CO_2/CH_4, compresi tra 33 e 30, fino a 60°C [1]. I valori di fattore di separazione CO_2/N_2 ottenuti per le miscele sono inferiori, solo del 20%, rispetto alle selettività ottenute nelle stesse condizioni. Le misure effettuate al 100% di umidità relativa hanno mostrato che la presenza di vapore acqueo, nella corrente gassosa di alimentazione, influenza le prestazioni dei moduli a membrana in particolare è stata osservata una riduzione di selettività, anche se non significativa (circa del 15%), per tutte le temperature analizzate. Un simile andamento è stato osservato anche alimentando le miscele evidenziando una buona resistenza delle membrane al vapore acqueo [1].

Si ringrazia il progetto di ricerca PON 01_02257 FotoRiduCO₂ – “Studio e sperimentazione di sistemi di foto conversione con luce solare di CO_2 in metanolo, da utilizzare come combustibile”. Co-finanziato dal Ministero dell’Istruzione, Università e Ricerca nell’ambito del PON “Ricerca e competitività 2007-2013.

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IND-P24

Palladium nanoparticles supported on mesoporous silica: applications in continuous-flow Mizoroki-Heck reactions

Graziano Fusini[a,b], *Adriano Carpita*[b], *Claudio Evangelisti*[a], *Alessandro Mandoli*[b], *Rinaldo Psaro*[a]

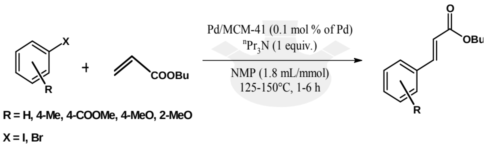
a Istituto di Scienze e Tecnologie Molecolari-CNR, Via G. Fantoli 16/15 , 20138, Milano, Italy
b Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, 56126, Pisa, Italy

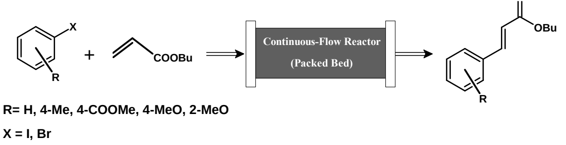
graziano.fusini@for.unipi.it

The possibility to combine the favourable features of continuous-flow systems with those of supported nanostructured catalysts, within the same fluidic device (Continuous-Flow Reactors, CFRs), can represent a significant strategic advantage in the perspective of the progressive intensification of organic production processes and their future economic and environmental sustainability [1].

Herein we wish to report our recent results in the Mizoroki–Heck alkenylations under batch and continuous-flow ligandless conditions, by using Metal Vapour Synthesis (MVS) derived Pd nanoparticles [2] deposited on MCM-41.

In a first approach, the experiments were performed in the batch mode with Pd/MCM-41 (1 wt.% of Pd) suspended in a stirred flask. Then, an effective packed-bed continuous mini-reactor was developed, by filling pieces of Teflon tubing (2 mm internal diameter) with the same material. The resulting device was employed for carrying out the reactions in the flow mode, with pneumatic pumping.





The catalytic behaviour of Pd/MCM-41 catalyst will be compared with those of commercial heterogeneous palladium catalysts in terms of catalytic activity, productivity and palladium leaching in the reaction mixture. In addition, Transmission Electron Microscopy (TEM) analysis of freshly prepared Pd/MCM-41 catalyst and recovered after catalytic studies will be reported.

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IND-P25

Theoretical study of the ligand effect in gold(I) homogeneous catalysis

Carlo A. Gaggioli, Giovanni Bistoni, Francesco Tarantelli, Paola Belanzoni, Gianluca Ciancaleoni, Leonardo Belpassi

Dipartimento di Chimica, Biologia e Biotecnologie, Università degli Studi di Perugia, Via Elce di Sotto, 06123, Perugia, Italy

carlo.gaggioli89@gmail.com

Gold(I) complexes of the L-Au(I)-S type (where L is a ligand and S is a substrate) have been increasingly used in homogeneous gold catalysis for their ability to activate unsaturated substrates towards nucleophilic attack [1]. The most popular model to describe the chemical bond between an unsaturated substrate and the metallic fragment is the Dewar-Chatt-Duncanson (DCD) one, which basically considers this bond constituted of two components, i.e. σ donation from S to the gold fragment and a π back-donation from the latter to S. The DCD components are widely used in catalysis to discuss the ligand effect on the reactivity; however, their complete characterization, either of experimental or theoretical nature, is still lacking. Also for this reason, the development of new catalysts continues to be based on a trial and error procedure, and only few works try to be predictive for the outcome of a reaction [2]. The present work has been therefore directed to the accurate assessment of the nature of coordination bond along the lines of the DCD model, in order to achieve, as a final goal, a predictability of the electronic effect of the ligand in gold catalysis. Our study mostly relies on the Charge-Displacement analysis [3] that is able to quantify the DCD components [4] and even to put them in quantitative relation with geometrical and spectroscopical parameters of the substrate [5]. For a specific gold catalyzed reaction (intramolecular hydroamination of alkynes) we discuss a correlation between the electronic properties of the catalyst with kinetic parameters such as the activation energy.

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IND-P26

Pd membranes downstream to a CPO reactor for H_2 production: relationship between nanostructure, performances and stability

S.Gentiluomo[a], *S.Abate*[a], *G.Centi*[a], *S.Perathoner*[a], *F.Basile*[b], *R.Mafessanti*[b]

a Dipartimento di Ingegneria Elettronica, Chimica e Ingegneria Industriale, Università di Messina, Viale F. Stagno d'Alcontres 31 , 98166, Messina, Italia
b Dipartimento di Chimica Industriale, Università di Bologna, Via del Risorgimento 4 , 40136, Bologna, Italia

abates@unime.it

In the perspective to introduce new industrial energy-processes in hydrogen or syngas production, the use of palladium composite membranes for H_2 separation not integrated directly in the reaction environment is a novel technology [1]. The feasibility of this option is closely linked to the development of palladium composite membranes which should have high H_2 flux, but at the same time high permselectivity and stability during operations. Pd thin films supported on ceramic alumina asymmetric tubes are prepared by a conventional electroless plating deposition method after activation with an impregnation-decomposition technique. We will report on the effects of controlled heating treatments of the membrane on morphology and thickness of the Pd film, and the relationship between membrane characteristics, and performances when the membrane module is coupled downstream to a CPO reactor. We will demonstrate that controlled heating treatments of the membranes improve the spreading of small Pd particles as well as the mechanical strength, due to the formation of Pd-aluminate species. The low roughness of the surface and the small Pd grains size evidenced by AFM analysis, lead to an increase of the H_2 flux which is 3 times higher with respect to samples prepared without a controlled thermal treatment. Finally, results obtained on a pilot plant coupled downstream to a CPO reactor will show that it is possible to get a hydrogen purity slightly higher than 99% with a stable behavior for several hours of time-on-stream.

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IND-P27

Selective oxidation of cyclic alkenes and substituted phenols over grafted non-ordered Nb-SiO_2 catalysts

C. Tiozzo[a], O.A. Kholdeeva[b], I.D. Ivanchikova[b], R. Psaro[a], M. Guidotti[a]

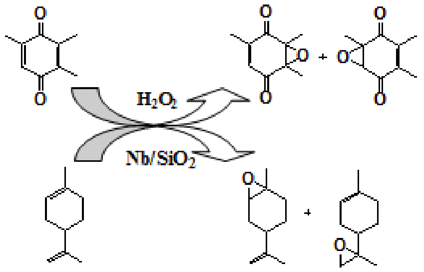
a CNR-Institute of Molecular Sciences and Technologies, Via C. Golgi 19, Milano, Italy
b Boreskov Institute of Catalysis, Lavrentieva 5, Novosibirsk, Russia

m.guidotti@istm.cnr.it

Nb-containing silica catalysts have shown promising catalytic performances in water-containing liquid-phase oxidation reactions and a higher stability towards metal leaching and hydrolysis, with respect to widely used Ti-silica catalysts. Thanks to post-synthesis grafting methods, it is possible to obtain catalysts with a tailored metal loading and an optimized accessibility of the surface sites [1,2].

Two kinds of grafted Nb/SiO_2 catalysts were synthesised starting from niobocene dichloride via solvent-less dry impregnation or conventional liquid-phase grafting technique onto non-ordered silica supports (ca. 1-2 wt% Nb). Such solids were used in the presence of aqueous H_2O_2 for the selective oxidation of cyclic alkenes, unsaturated terpenes and substituted phenols of interest for fine and specialty chemistry: cyclohexene, 1-methylcyclohexene, limonene, carveol, α-terpineol, isopulegol, carvone and 2,3,6-trimethylphenol.

In epoxidation reactions, Nb-silica catalysts showed high yields (up to 73%) and excellent selectivities to the desired epoxides (up to 98%), also in short reaction times (down to 1 h). In trimethylphenol oxidation, Nb/SiO_2 systems showed a moderate-high phenol conversion, but a moderate selectivity to desired trimethylbenzoquinone (65% max). Interestingly, these catalysts were able to epoxidise electron poor C=C bonds too, as in carvone and trimethylbenzoquinone. The catalysts obtained by liquid-phase grafting presented a high fraction of isolated Nb(V) sites and were more active than dry-impregnation ones.



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IND-P28

Pd Nanoparticles Stabilized by Anionic Surfactants: An Efficient Catalyst for Hydrogenation Reactions in Water

Giorgio La Sorella,[a] *Patrizia Canton,*[a] *Giorgio Strukul,* [a] *Alessandro Scarso*[a]

a) Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca'Foscari di Venezia,
Dorsoduro 2137, 30123, Venezia, Italia

giosister@yahoo.it

In recent years, one of the main targets of the scientific research isthe development of catalytic systems that work in water: a solvent safe and sustainable. One of the simplest and at the same time effective methods is the use the nanosized apolar core of supramolecular micellar aggregates as reaction media[1]. Recently, our research group has shown that micellar systems can be effectively employed in many reactions (asymmetric oxidations, hydration of nitriles and alkynes and C-C cross coupling reactions) as well as to stabilize Pd nanoparticles and to confer substrate selectivity to the catalytic system selecting substrates on the basis of their lipophilicity [2]. These results moved our attention to the possibility to use anionic surfactants to modulate the structure and the catalytic activity of Pd nanoparticles.

In this work we present the development of catalytic systems based on Pd nanoparticles obtained using anionic surfactants such as sodium dioctilsulfosuccinate (DOSS), poly(ethyleneglycol)4-nonylphenyl -3- sulfopropil etere potassium salt (Ralufon ®) and sodium dodecylsulfonate and their use in hydrogenation reactions of aryl-carbonyl and aryl-alcohol groups and in the hydro-dechlorination reactions of aromatic substrates in water.

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IND-P29

New solvothermal synthesis of Zeolitic Imidazolate Framework ZIF-90 for preparation of mixed-matrix membranes

Paola F. Liguori, *Giovanni Golemme*

Dipartimento di Ingegneria per l'Ambiente e il Territorio e Ingegneria Chimica, Università della Calabria, Via P. Bucci 45/A, 87036 Rende, Italia.

paolafrancesca.liguori@unical.it, ggolemme@unical.it

Zeolitic imidazolate frameworks (ZIFs), a subfamily of metal-organic frameworks (MOFs), are promising membrane materials due to their microporous pore networks as well as superior hydrothermal and chemical stabilities.[1] Recently, ZIFs have been intensively studied as promising candidates for the preparation of mixed-matrix membranes (MMM) due to their high intrinsic gas and vapor permeability,[2] good chemical and thermal stability and remarkable affinity for polymeric materials.[1] Among various ZIFs, zinc (2-carboxyaldehyde imidazolate)$_2$ (ZIF-90) (Fig.1) has gained particular attention for its capability to separate H_2 from CO_2, CH_4, C_2H_6, and C_3H_8.[3,4] The imidazole linker of ZIF-90 contains a carbonyl group, which hinders the permeation of bulky molecules and can favorably interact with several polymeric matrices. By modifying the synthesis route, with a novel solvothermal synthesis method we have synthesized ZIF-90 nanocrystals (200 nm) with yields up to 95%. The ZIF-90 nanoparticles will be used to prepare ZIF-90 based MMMs for gas separation.

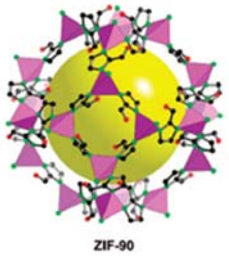

Fig.1

The work leading to these results has received funding from the research project PON01_01840 "Programma di Energie Rinnovabili e Micro-Cogenerazione per l'Agroindustria - Microperla"; and the European Community's Seventh Framework Program (FP7 2007-2013) Project PONa3_00370 MATERIA.

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IND-P30

Coke formation on Pt-Sn(K)/γAl_2O_3 in partial dehydrogenation reaction

Carlo Lucarelli[a], Chiara Molinari[b], Angelo Vaccari[b]

[a] Dipartimento di Scienza e Alta Tecnologia, Università dell'Insubria,
Via Valleggio 11,22100 Como, Italy
[b] Dipartimento di Chimica Industriale "Toso Montanari",
ALMA MATER STUDIORUM - Università di Bologna,
Viale Risorgimento 4, 40136 Bologna, Italy

carlo.lucarelli@uninsubria.it

Catalytic partial dehydrogenation (PDH) is a promising way for H_2 production, in particular for applications on-board of vehicles, aircrafts, etc. The main problem is the carbon formation on the catalyst surface, that gives rise to a rapid deactivation. 1wt.%Pt-1wt.%Sn/ γ-Al_2O_3 and 1wt%Pt-1wt.%Sn-0,5wt.%K/γ-Al_2O_3 catalysts were tested in PDH reaction of single hydrocarbons, complex hydrocarbon blends and commercial jet fuel A1 [1]. The addiction of Sn significantly increases the catalytic activity and stability, due to the formation of different Pt-Sn alloys, that control the Pt activity. Tuning the acidity of the catalysts it is possible to reduce the carbon formation and modify its morphology, in particular the diamond like-graphite/amorphous carbon ratio. In fact, the addiction of K increases the life time of the catalyst of about 10 times. The acidity of the support also catalyzes the cracking reactions, leading to a highest conversion of linear aliphatic hydrocarbons and highest coke formation. Feeding a blend of different hydrocarbons, the coke formed is similar to that obtained feeding the single more reactive hydrocarbons. The increase of pressure favors the formation of graphitic carbon, more stable towards regeneration treatments. At the same time, the H_2 partial pressure plays an important role on the catalyst deactivation; operating under pressure, a small H_2 recycle is enough to avoid a complete dehydrogenation of the hydrocarbons and limit the coke production. The formation mechanism of this latter was defined in terms of reaction pathway and parameters involved.

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IND-P31

Metal-to-Ligand Alkyl Migration on Rare Earth Metal Complexes: Synthesis, Characterization and Catalytic Activity in the Isoprene Polymerization.

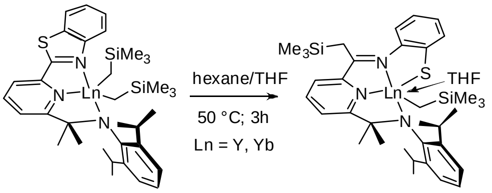
L. Luconi[a], *G. Tuci*[a], *A. Rossin*[a], *D. M. Lyubov*[b], *A. A. Trifonov*[b] *and G. Giambastiani*[*a]

a Institute of Chemistry of OrganoMetallic Compounds, ICCOM-CNR, Via Madonna del Piano10, 50019 Sesto F.no, (Fi), Italy.
b G. A. Razuvaev Institute of Organometallic Chemistry, RAS, Tropinina 49, GSP-445, 603950 Nizhny Novgorod, Russia.

lapo.luconi@iccom.cnr.it

Neutral Ln^{III}-dialkyl (Y^{III}, Lu^{III}, Er^{III}, Yb^{III}) complexes stabilized by tridentate {N^-,N,N} monoanionic thiazole or benzothiazole amidopyridinate ligands have been synthetized and completely characterized. Notably, a progressive rearrangement of the coordination sphere takes place on the benzothiazole containing systems through an unprecedented metal-to-ligand alkyl migration and subsequent thiazole ring-opening; the generation of monoalkyl aryl thiolate organolanthanide species stabilized by a tetradentate {N^-,N,N,S^-} dianionic ligands will be discussed on both an experimental and theoretical ground (Scheme 1).[1] Selected complexes from this series, in their cationic form, have shown remarkable diene polymerization activities; their catalytic performance in the isoprene (IP) polymerization will be discussed.[2]

Scheme 1



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IND-P32

Valuable feedstock from waste materials

M. Malavolti[a], *A. Brandi*[a], *D. Giomi*[a], *O. Piccolo*[b], *A. Salvini*[a]

a Dipartimento di Chimica "Ugo Schiff", Università degli Studi di Firenze, Via della Lastruccia 13, 50019, Sesto Fiorentino (FI), Italy
b SCSOP, Via Bornò 5, 23896 Sirtori, Italy

marino.malavolti@unifi.it

Nowadays recycling and reprocessing waste materials is becoming a primary issue. As described in previous works [1, 2], a method for producing BioDiesel (BD) from triglycerides using chlorotrimethylsilane (TMSCl) as "mediator" has been reported. In this process, transesterification and esterification are performed at the same time. The acidic condition allows to use substrates coming from the recovery of food waste materials such as fried oil or animal fats from slaughter, that have a very high content in free fatty acids (FFA), avoiding the production of soaps and emulsions, that determine serious problems in the currently applied alkaline-catalyzed process. Moreover, in the reported procedure, at the end of the reaction the mixture divides in two phases that can be easily separated. The upper one contains FAME (fatty acid methyl esters), ready for the distillation. The lower phase is a mixture of glycerol and α-monochlorohydrin.

Now, with the aim to optimize the selective conversion into α-monochlorohydrin or α,γ-dichlorohydrin, the reaction of glycerol with TMSCl has been studied. In particular, α,γ-dichlorohydrin, precursor of epichlorohydrin, is obtained in an easier way with respect to the known processes [3, 4], based on the use of gaseous HCl.

Since the two processes use the same reagent (TMSCl), they could be integrate for the complete conversion of triglycerides into valuable commodities.

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IND-P33

Experimental and modeling study of the Enhanced-SCR: a novel approach to boost the low-T activity of a Fe-Zeolite SCR catalyst

Fabio Marchitti, *Isabella Nova*, *Enrico Tronconi*[*],

Laboratory of Catalysis and Catalytic Processes, Dipartimento
di Energia, Politecnico di Milano, Piazza Leonardo da Vinci
32, 20133 Milano, Italy

[*]*enrico.tronconi@polimi.it*

Due to the demand of vehicles with reduced fuel consumption, which results in lower mean exhausts temperatures, novel and more efficient exhausts aftertreatment technologies are under development. In this contest the NH_3-SCR reactions play one of the major role in the DeNOx processes for HD vehicles. It has been already demonstrated [1, 2] that addition of aqueous solutions of NH_4NO_3 (AN) to a NO–NH_3 containing feed results in the “Enhanced SCR” (E-SCR) reaction over V_2O_5–WO_3/TiO_2 and Fe-ZSM-5, which is responsible for a catalyst performance improvement. Both fundamental and practical aspects have been investigated over a core monolith (6 cm^3) cut from a full-size commercial Fe-zeolite catalyst. In order to understand the potential and all the mechanistic implications associated with AN addition, both steady state and transient runs have been carried out in a wide range of temperature (180-500°C) and at four different GHSVs. The results clearly demonstrate that the AN additive greatly enhances the DeNOx performances at all the investigated temperatures: the improvement is consistent with the evidence of NO_2 in-situ generation. All the experimental data have been successfully fitted by a simple kinetic model.

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IND-P34

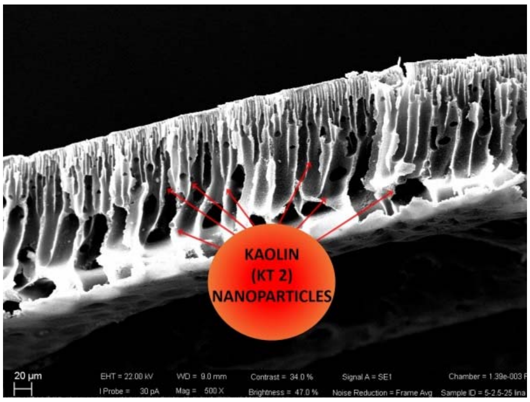
PES/Kaolin membranes preparation for wastewater treatment

<u>Tiziana Marino</u>[a], *Lina Rezzouk*[b], *Alberto Figoli*[a], *Nacer-Eddine Chelali*[b], *Abderrazak Bouzid*[b]

a Institute on Membrane Technology, ITM-CNR, Via Pietro Bucci, 17/C, 87030, Rende (CS), Italy.
b Institute of Science and Technology, Laboratory Materials and Electronic Systems, LMSE, Université Mohamed El Bachir El Ibrahimi de Bordj Bou Arréridj El-Anasser, 34030, Bordj Bou Arréridj, Algéria.

t.marino@itm.cnr.it

In this work, flat sheet polyethersulfone (PES)/kaolin membranes were prepared *via* Non-solvent Induced Phase Separation (NIPS). Kaolin nanoparticles (KT2) [1], mainly composed of silica (49.30 wt%) and alumina (33.50 wt%), were obtained from naturally available kaolin clay of Algerian East (Guelma). The morphology and the performance of the prepared organic/inorganic membranes were strongly affected by the casting solution composition and the exposure time of the nascent membranes to the atmospheric humidity.



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IND-P35

Exploring the catalytic properties of palladium supported catalysts in transfer hydrogenolysis of glycerol

F. Mauriello[a], H. Ariga[b], M.G. Musolino[a], R. Pietropaolo[a], S. Takakusagi[b], and K. Asakura[b]

a Dipartimento di DICEAM, Università Mediterranea di Reggio Calabria, Loc. Feo di Vito, I-89122, Reggio Calabria, Italy
b Catalysis Research Center, Hokkaido University, Kita-ku N21W10, 001-0021, Sapporo (Hokkaido), Japan

francesco.mauriello@unirc.it

Glycerol, the major by-product in the industrial production of biodiesel, can be converted through the hydrogenolysis reaction into valuable products such as 1,2-propanediol, 1,3-propanediol and ethylene glycol [1].

One of the main targets in the field of green chemistry is currently to make the hydrogenolysis process self-sustainable, for as it concerns hydrogen supply, in order to reduce the costs related to its purchase, transport, and storage and to minimize safety problems in industrial hydrogenation process [2].

The present contribution aims to clarify the effect of individual parameters such as surface area, metal particle size, oxidation state of palladium, role of the support and presence of bimetallic clusters that may affect the catalytic properties of palladium catalysts in transfer hydrogenolysis of glycerol [3].

The catalytic results are interpreted in terms of metal–metal or metal–support interaction that modify the electronic properties of palladium thus enhancing its catalytic properties in the conversion of glycerol as well as in the selectivity to 1,2-propanediol and 2-propanol.

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IND-P36

Idrolisi acida diretta di biomasse lignocellulosiche e cellulosiche mediante catalizzatori a base di Zr/P/O

Mattia Melloni[a], *Gherardo Gliozzi*[a],*Gabriele Salvi*[a], *Alessia Mancini*[a], *Fabrizio Cavani*[a,b], *Rossella Bortolo*[c], *Carlo Perego*[c], *Marco Ricci*[c]

a Dipartimento di Chimica Industriale "Toso Montanari", Alma Mater Studiorum Università di Bologna, Viale del Risorgimento 4 , 40136, Bologna, Italia
b Consorzio INSTM, Research Unit of Bologna, Firenze, Italia
c Eni S.p.A., Centro Ricerche Energie non Convenzionali Istituto Eni "G. Donegani", Via Fauser 4, Novara, Italia

mattia.melloni2@unibo.it

La trasformazione di biomasse lignocellulosiche in sostanze chimiche di valore è strategica nel quadro del concetto di bio-raffineria. Il punto di partenza di questa trasformazione è la destrutturazione della lignocellulosa, con conseguente depolimerizzazione delle frazioni cellulosiche ed emicellulosiche a monosaccaridi. Le difficoltà principali in questa fase sono rappresentate dalla resistenza della guaina esterna di lignina e dall'elevato impaccamento delle catene cellulosiche. Per questo motivo, vi è un grande interesse nello sviluppo di sistemi catalitici acidi eterogenei efficaci nell'idrolisi di lignocellulosa.

Nel nostro lavoro sono state confrontate le prestazioni catalitiche di diversi sistemi acidi eterogenei, impiegati nell'idrolisi diretta di farina di conifera grezza[1]: in particolare, lo zirconio fosfato (Zr/P/O) è caratterizzato da una resa relativamente alta in monosaccaridi, paragonabile a quella ottenuta con il catalizzatore commerciale di riferimento (Amberlyst 15). Partendo da questi risultati, è stata condotta un'analisi dettagliata sulla reattività del sistema a base di Zr/P/O nell'idrolisi di cellulosa microcristallina sia grezza che dopo pretrattamento in mulino a sfere, confrontandola poi con quella di un altro sistema catalitico acido a base di Nb/P/O. Partendo da cellulosa microcristallina, dopo pretrattamento in mulino a sfere, il sistema a base di Zr/P/O mostra un notevole aumento della conversione, e un'elevata selettività in glucosio.

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IND-P37

Role of catalyst composition in middle temperature WGS reaction

Francesco. Basile[a], *Pascal Del Gallo*[b], *Raphael Faure*[b],
Giuseppe Fornasari[a], *Daniel Gary*[b], *Chiara Molinari*[a],, *Angelo Vaccari*[a]

[a] Dipartimento di Chimica Industriale «Toso Montanari», ALMA MATER STUDIORUM – Università di Bologna, Viale Risorgimento 4, 40136 BOLOGNA (Italy)
[b] Centre de Recherche Claude-Delorme, Air Liquide, B.P. 126, 78354 Jouy-en-Josas (France),

chiara.molinari10@unibo.it

The last years have seen increasing interest in middle temperature water gas shift (MTS), to decrease the operational costs carrying out the reaction in just one step unlike the current industrial processes. Aim of this study was to develop new catalysts able to operate at 300°C ca., with high activity, selectivity and, mainly, stability with time-on-stream. Cu/Zn/Al hydrotalcite-type (HT) precursors were prepared by co-precipitation [1], followed by calcination at 550 °C for 8 h. Tests were performed in a fixed bed reactor feeding a $CO:CH_4:CO_2:H_2$ = 18,8:4,6:4,6:72,0 (v/v) gas mixture, operating at S/DG = 0.55 or 0.25 v/v, 1.5 MPa, 250-350 °C and GHSV values between 3,600 and 14,400 h^{-1}. At first, the effect of Cu-content in Cu/Zn/Al catalysts has been defined, evidencing an increase of activity moving from 10 to 20 wt.% , while a further increase worsened dramatically the activity. The best performances being obtained with a catalyst with 20 wt.% of Cu and (Cu+Zn)/Al molar ratio equal to 2.0 [2]. The partial substitution of Zn^{2+} ions by Mg^{2+} and Ba^{2+} ions evidences the role of the basicity; small Mg contents improved the CO conversion, promoting the redox mechanism [3]. High amounts of Mg^{2+} ions worsened the CO conversion, because the decrease of the synergetic Cu/ZnO interactions. Ba^{2+} ions improved the activity, increasing the basicity that stabilizes the hydroxyl groups. Finally, the thermal stability of the catalysts were significantly improved by replacing a small amount of Al^{3+} ions by La^{3+}, Ce^{4+} and Zr^{4+} ions.

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IND-P38

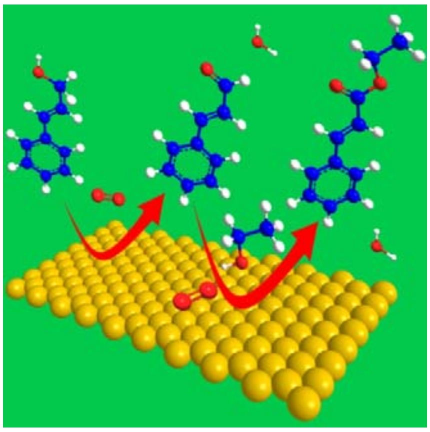
Aerobic Direct Oxidative Esterification of Alcohols by Gold Nanoparticles: The Active Role of the Nanoporous Support

Annarita Noschese[a], *Antonio Buonerba*[a], *Alfonso Grassi*[a]

[a] *Dipartimento di Chimica e Biologia and NANOMATES Research Centre for NANOMAterials and nanoTEchnology at Salerno University*
Università degli Studi di Salerno, Via Giovanni Paolo II - 84084 Fisciano (SA), Italy

annaritanoschese@gmail.com

Gold nanoparticles supported in a nanoporous polymer matrix[1] were found highly active and selective in the aerobic direct oxidative coupling of allyl or benzyl alcohols with alkyl alcohols leading to the corresponding alkyl esters under mild conditions.[2] E.g. cinnamyl alcohol was readily coupled with a series of alkyl alcohols (for example methanol, ethanol, *n*-butanol) via a cascade reaction including the preliminary aerobic oxidation to cinnamaldehyde followed by the in situ oxidation of the intermediate hemiacetal resulting from the base catalyzed reaction of the alcohol with the aldehyde.



The rate constants for the two steps were evaluated and the corresponding activation energies of 57.8±11.5 kJ/mol and 62.7±16.7 kJ/mol were determined in the oxidative esterification of cinnamyl alcohol with *n*-butanol. The active role of the nanoporous host polymer matrix adopted as support was discussed on the basis of the kinetic investigation. The polymer matrix enables a fast access of aromatic reactants to the catalytic sites through the nanochannels of the polymer crystalline phase whereas the reactivity of the aliphatic counterparts is controlled by diffusion through the amorphous part of the polymeric support.

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IND-P39

Syntheses of Polyamides and TiO_2-polyamide nanocomposites from natural and renewable sources

Rosangela Oliva[a], *Antonella Salvini*[a], *Marco Aldo Ortenzi*[b]

[a]*Dipartimento di Chimica "Ugo Schiff", Università di Firenze, Via della Lastruccia 3-13, 50019, Sesto Fiorentino (Fi), Italia*
[b]*Dipartimento di Chimica, Università di Milano, Via Golgi 19, 20133, Milano, Italia*

rosangela.oliva@unifi.it

In recent times, the use of biopolymers has increased considerably in many different fields, because of their easy degradation in products not harmful for the environment and because they are obtained from natural renewable sources.

Polyamides obtained from natural raw material are very interesting, since it is possible to synthesize products with different chemical-physical characteristics according to the choice of monomers and it is also possible to obtain a good control of the degree of polymerization.

Water soluble oligoamides have been obtained from derivatives of natural substances, that are biocompatible, biodegradable, cheap and with high stability such as L-tartaric acid, α,α-trehalose and L-lysine.

Different kinds of polyamides have been synthesized from α,α- trehaluronic or L-tartaric acid dimethylester and different aliphatic or aromatic diamines and polyamines. Copolymers with L-tartaric acid and adipic acid have been also synthesized. Finally, diamines derived from natural products was evaluated.

The natural aminoacid, L-lysine, industrially produced by fermentation technologies, has given good results in the synthesis of oligoamides with dimethyl L-tartrate.
Several nanocomposites with core-shell structure and potential antimicrobial and antifungal activity have been also synthesized using functionalized TiO_2 nanoparticles.

IND-P40

CO_2 to fuels *via* N and Cu co-doped titania photocatalysts

A. Olivo[a], M. Signoretto[a], V. Trevisan[a], E. Ghedini[a], F. Pinna[a], C.L. Bianchi[b], A. Naldoni[c]

a Department of Molecular Sciences and Nanosystems, Ca'Foscari University Venice and Consortium INSTM, RU of Venice, Dorsoduro 2137, 30123 Venezia, Italy
b Department of Chemistry, University of Milan, Via Golgi 19, 20133 Milano, Italy
c CNR-Istituto di Scienze e Tecnologie Molecolari, Via Golgi 19, 20133 Milano, Italy

albertoolivo@hotmail.it

The two most challenging issues of our society are the increasing emissions of carbon dioxide from human activities and the depletion of fossil fuels. Photocatalysis is a key technology to abate the CO_2 emissions and to transform them into fuels [1]. Among them, methane is important product, that can be obtained from carbon dioxide photoreduction using water as a reducing agent. Titania is a good photocatalyst for this reaction, but its performances can be improved by doping. [2] In this work the performances of Cu-N-doped TiO_2 photocatalyst in CO_2 reduction have been studied.
The dopants' presence and their synergy add a distinct enhancement in methane production. Furthermore, the effect of copper amount in co-doped TiO_2 has been studied and CH_4 production is sensitive to this parameter. The best catalytic results have been obtained with a small copper amount (0.2 wt. %): when copper content is higher, a detrimental effect on photoactivity has been observed.

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IND-P41

How to reach high selectivity in the epoxidation of linear alkenes over Ti-SiO$_2$

C. Palumbo, C. Tiozzo, R. Psaro, N. Ravasio, M. Guidotti

CNR-Institute of Molecular Sciences and Technologies, Via C. Golgi 19, Milano, Italy

c.palumbo@istm.cnr.it

In industrial processes, as in the HPPO (Hydrogen Peroxide Propylene Oxide), propene is selectively epoxidised over titanium-silicalite 1 (TS-1).[1] In the academia, Ti- and Nb-based catalysts grafted on mesoporous SiO$_2$ have so far shown promising efficiency in the epoxidation of functionalized bulky alkenes.[2,3] Herein we report about a selective catalytic epoxidation of terminal and internal linear alkenes such as 1- and 2-octene. A series of Ti-SiO$_2$ catalysts was prepared *via* dry impregnation (DI, 2% wt. metal)[2] and liquid-phase grafting (liq, 2% wt. metal).[2] Their catalytic activity was evaluated in various solvents at 80°C. Remarkably, in α,α,α-trifluorotoluene (PhCF$_3$), the formation of side-products was significantly reduced and high conversions were achieved in the presence of Ti-SiO$_2$ as catalyst and *tert*-butyl hydroperoxide (TBHP) as oxidant (Table 1). Moreover DI and liq catalysts were compared, observing a drastic increase in selectivity and conversion in the case of liquid phase grafted one.

Alkene	**Catalyst**	**Solvent**	**1 h**		**24h**	
			Conv^a [%]	**Sel^b[%]**	**Conv^a [%]**	**Sel^b[%]**
	liq	CH_3CN	66	20	98	28
	DI	$PhCF_3$	24	68	58	81
	liq	$PhCF_3$	33	98	73	>98
	liq	$PhCF_3$	10	> 98	> 98	> 98

Table 1. Reaction conditions: 5 mL solvent; 100 mg Ti-SiO$_2$ catalyst; 1 mmol alkene; 1.1 mmol TBHP; 80°C; batch reactor. a: conversion of alkene; b: selectivity to epoxide.

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IND-P42

A new process for maleic anhydride synthesis: the oxidehydration of 1-butanol

G. Pavarelli[a,b], *F. Cavani*[a,b], *J.-L. Dubois*[c], *I. Mitsova*[d], *L. Simeonova*[d]

a Dipartimento di Chimica Industriale "Toso Montanari", Università di Bologna,
Viale del Risorgimento 4, 40136 Bologna, Italy;
b CIRCC, Research Unit of Bologna University;
c ARKEMA, Colombes, France;
d Orgachim JSC, Russe, Bulgaria

giulia.pavarelli@unibo.it

The switch from oil to biomass as the main source for the chemical industry is an important global initiative in the aim of developing a more sustainable growth. In this context, bio-butanol is an interesting bio-platform molecule for the synthesis of chemicals [1]. Here, we report about a study aimed at investigating the possibility of transforming 1-butanol into maleic anhydride, by means of gas-phase oxidation catalysed by vanadyl pyrophosphate. This bifunctional catalyst combines the proper acidity required to dehydrate 1-butanol into 1-butene, and redox-type properties for the mild oxidation of the intermediately formed olefin into maleic anhydride. Vanadyl pyrophosphate, which is also active and selective in 1-butene and *n*-butane oxidation [2], could successfully catalyse the one-pot reaction starting from chemical 1-butanol. Various reaction parameters were investigated, and under optimised conditions maleic anhydride yield achieved was over 40% at 360°C, with total alcohol conversion. The reaction performance was greatly affected by reactants partial pressure, because the strong interaction between the alcohol and vanadyl pyrosphosphate led to a surface-saturation effect, which inhibited maleic anhydride formation. Reactivity experiments were also conducted starting from bio-sourced 1-butanol.

The research leading to these results has received funding from the European Union Seventh Framework programme (FP7/2007-2013), under grant agreement n. 241718 EuroBioRef.

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IND-P43

Water-soluble Rh-thioligand catalysts

O. Piccolo[a], *S. Paganelli*[b], *P. Pontini*[b], *V.D. Rathod*[b] , *R. Tassini*[b]

[a] *SCSOP, Via Bornò 5, 23896 Sirtori (Italy).*
[b]*Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari Venezia, Calle Larga S. Marta 2137, 30123 Venezia (Italy).*

contact@scsop.it

The use of both water as co-solvent for biphasic reactions and easily recyclable water-soluble catalysts are highly desirable for the realization of green and sustainable processes [1-3]. Since some years we are interested to study the hydrogenation and hydroformylation processes catalyzed by metal complexes modified with water-soluble sulphur containing ligands as thio-oligopeptides [4] or very simple and cheap water-soluble low molecular weight thioligands such as (L)-Cysteine and [(S)-1-[(S)-3-mercapto-2-methylpropanoyl]pyrrolidine-2-carboxylic acid] (Captopril®) [5]. In these last months our study was addressed to the use of rhodium complexes modified with some new water soluble thioligands: a) the dihydrothioctic acid sodium salt (DHTANa), a molecule which presents two –SH groups capable, in principle, to work as a bidentate ligand for the rhodium atom; b) the DHTANa-dimethyl thioether; c) the oligopeptide glutathione, in its reduced form. All the catalysts were easily prepared by mixing in water the catalytic precursor $[Rh(COD)Cl]_2$ and the thioligand of choice. Preliminary results obtained in the hydrogenation reaction of different unsaturated substrates were very promising, showing good catalytic activities. Moreover, the water-soluble catalyst Rh(DHTANa) was used also in the aqueous biphase hydroformylation of styrene producing exclusively the two corresponding aldehydes with 80-86% selectivity towards the branched aldehyde 2-phenylpropanal. Noteworthy, all these new catalytic systems were easily recycled in the investigated catalytic processes and no leaching phenomenon was observed.

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IND-P44

Structure-properties relationship of $La_{0.6}Sr_{0.4}Co_{1-x}Fe_{x-0.03}M_{0.03}O_{3-\delta}$ (x=0.2-0.8; M=Ni, Pt, Rh) as IT-SOFCs cathodes

F. Puleo[a], *S. Guo*[a,b], *A. Longo*[a,c], *V. La Parola*[a], *G. Pantaleo*[a], *D. Banerjee*[d], *A. Martorana*[e] *and L.F. Liotta*[a].

a Institute for Study of Nanostructured Materials (ISMN)-CNR, Palermo, Via Ugo La Malfa ,
90146, Palermo, Italy.
b Northwestern Polytechnical University, Xi'an 710072 PR China.
c Netherlands Organization for Scientific Research (NWO), 6 rue Jules Horowitz, BP220,
38043 Grenoble CEDEX, France.
d Dutch-Belgian Beamline (DUBBLE), European Synchrotron Radiation Facility (ESRF),
B.P. 220, F-38043 Grenoble, France.
e Physics and Chemical Department, University of Palermo, Viale delle Scienze Ed. 17,
90128, Palermo, Italy.

fabrizio.puleo@pa.ismn.cnr.it

Thanks to their mixed ionic/electronic conductivity and high catalytic activity for oxygen exchange reaction, $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF) perovskites have received much attention as cathode materials for intermediate solid oxide fuel cells (IT-SOFCs) operating at relatively low-temperature, 600-800 °C [1]. Lowering the operating temperature, however, decreases the electrode kinetics. So, new materials composition and/or controlling the cathode properties through new syntheses are required in order to improve oxygen reduction and both, electronic and ionic conductivities. LSCF cathodes with metal substitution in B-site prepared by different methods, such as solid-state reaction or by impregnation of the perovskite with the metal dopant precursor, have been extensively investigated as new materials [2,3]. We have recently evidenced by EXAFS analysis the promotion of $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ and of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ by incorporation of palladium in the B-site of the perovskite structure through one pot synthesis by citrate method [4]. A dual effect of Pd in promoting the electrical and ionic conductivity of $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ perovskite was found. On these bases, the present study aims to investigate the structural and reduction properties of LSCF oxides with different Co/Fe content doped by Ni, Pt and Rh. Special attention to the effect of the doping metal insertion on the perovskite oxygen vacancies formation was paid.

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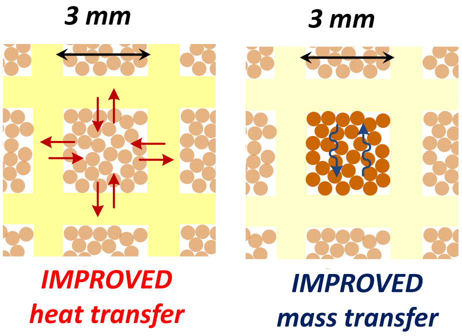
IND-P45

Fundamental assessment of gas-to-particle mass transfer in micro-channel reactors

*Stefano Rebughini, Alberto Cuoci, Matteo Maestri**

Politecnico di Milano, Piazza Leonardo da Vinci 32, I-20133 Milano, Italy

matteo.maestri@polimi.it



Micro-channel reactor technology is considered one of the key-factor for the intensification of advanced chemical process for energy and environment. Particular attention has been given to micro-channel packed bed reactors which consist of a miniaturized packed bed placed inside the channels of a honey-comb matrix. This novel reactor combines the excellent radial heat transfer properties of the honeycomb matrix, with the high catalytic-per-volume area of the packed bed. Nevertheless, due to the unconventional geometry of such devices, all the previous expertise developed for reactor design cannot be straightforwardly applied[1] in this context and a detailed assessment of the mass transfer phenomena is required. In view of this, we perform a detailed analysis of gas-to-particle mass transfer properties in micro-channel reactors by the means of Computational Fluid Dynamics simulations, using the catalyticFoam [2] code.

This analysis shows that literature correlations cannot be applied for the design of micro-channel reactors. In particular a remarkable dependence of the Sherwood number on the particle-to-tube diameter is observed, which is not account in any correlations reported in literature. This behavior is related to the preferential channeling of the flow in correspondence of the external wall of the monolith and not specific to the micro-dimensions of the channel.

On the whole, this contribution clearly points out the importance and potentiality of fundamental approaches for the assessment of transport properties in novel reactor technologies[3].

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IND-P46

Contributo Ritirato

IND-P47

Cost-effective preparation of nanostructured transparent titania coating for phtovoltaic glass surfaces

M. G. Salvaggio[a], *R. Passalacqua*[a*], *S. Abate*[a], *S. Perathoner*[a],*G. Centi*[a], *M. Lanza*[b], *A. Stassi*[c]

[a]*Dipartimento di Ingegneria Elettronica, Chimica e Ingegneria Industriale, Università di Messina* e *INSTM/CASPE, V.le F. Stagno d'Alcontres 31, 98166, Messina, Italia*
[b]*CNR - IPCF, V.le F. Stagno d'Alcontres 37, 98158, Messina, Italia*
[c]*CNR - ITAE, Via S. Lucia sopra Contesse 5, 98126, Messina, Italia*

rpassalacqua@unime.it

Photoactive TiO_2 transparent coatings having self-cleaning and antireflection (AR) properties were prepared by a nanosol/dip-coating method. [1-2]
Various factors in the preparation procedure (nanosol acid concentration, dip-coating speed, calcination temperature, multistep dip-coating) affect both optical and nanostructure properties. [3-4] Films with good optical characteristics and high transmittance (in the 94-96 % range) can be obtained at low speed of dip-coating (6 mm/s) and high HNO_3 concentration (0.5 N).
The control of the preparation parameters allows to get titania coatings having good adherence, stability and mechanical resistance, with high transparency and good AR properties, together with suitable surface nanostructure and photocatalytic properties for their use as self-cleaning material. The procedure allows a high material utilization and can be considered a suitable method for cost-effective preparation of coating films in PV cells. Moreover, the method can be used to cover flexible photovoltaic supports which can hold out up to 400 °C.

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IND-P48

Outer sphere versus inner sphere Ru-mediated imine hydrogenation

A. Salvini[a], *I. Scodeller*[a], *W. Oberhauser*[b], *G. Manca*[b], *A. Ienco*[b], *L. Luconi*[b]

[a] *Department of Chemistry "Ugo Schiff", University of Florence, via della Lastruccia 3-13, 50019 Sesto Fiorentino Italy,*
[b] *ICCOM- CNR, Area di Ricerca CNR, via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy,*

antonella.salvini@unifi.it

The industrial production of amines is an important challenge because of their wide use as solvent, agrochemicals and pharmaceuticals. Amines can be synthesized by the catalytic hydrogenation of imines using molecular dihydrogen, which is a sustainable synthesis method from an environmental and economic point of view.

Secondary amines have been obtained by the selective hydrogenation of imines mediated by ruthenium(II) bis(acetate) complexes of the formula $Ru(CO)_2(OAc)_2(P^nBu_3)[P(C_6H_5X)_3]$ (OAc = acetate, X = H, Me, OMe), which are characterized by two different phosphane ligands located *trans* to each other.

The presence of two different phosphanes in the precatalyst and the use of protic solvent such as trifluoroethanol or methanol gave high substrate conversion along with a high selectivity. *Operando* spectroscopic studies combined with a computational investigation at the B97D-DFT level of theory including also solvent effects by using a Conductor like Continuum Polarizable Model (CPCM) were carried out.

The combination of evidences, collected from batch catalytic reactions, spectroscopic studies and theoretical calculations, led us to conclude that catalytic imine hydrogenation, mediated by the above mentioned Ru-catalysts, proceeds in alcoholic reaction media by an outer sphere mechanism (i.e. without substrate coordination to Ru) with a cationic Ru-monohydride complex as key catalytic species.

IND-P49

Photocatalytic membranes based on TiO_2 catalysts and fluorinated polymers

Miriam Sellaro, Enrica Fontananova, Enrico Drioli, Giuseppe Barbieri

Consiglio Nazionale delle Ricerche, Istituto per la Tecnologia delle Membrane
(ITM-CNR), Via P. Bucci, Cubo 17C, 87036 Rende (CS) ITALIA.

m.sellaro@itm.cnr.it

The immobilization of catalysts in membranes has been identified as a promising strategy to develop highly efficient and eco-friendly catalytic chemical processes. When a catalyst is embedded within or on the surface of a membrane, the characteristics of the membrane material and the membrane structure can positively influence the catalytic performance, by selective sorption and diffusion of the involved chemical species (reagents and/or products) and by electronic and conformational effects on the catalyst activity. Moreover, catalyst embedding in membranes allows to reuse the same catalyst several times favoring a lower environmental impact [1].

In this work two TiO_2-based photocatalysts have been immobilized into different polymeric membranes, constituted by Hyflon (a perfluoro amorphous polymer) and Nafion (a perfluorosulfonic acid polymer). These fluoro polymeric materials have been chosen because of their excellent UV-resistance properties and their good film forming characteristics.

The influence of the membrane preparation conditions on catalysts dispersion has been investigated and the obtained catalytic polymeric membranes have been subjected to different characterization techniques, in order to verify the structural and spectroscopic integrity of the embedded catalysts. Transport properties and catalytic activity of the membranes have also been investigated.

The research project PON 01_02257 FotoRiduCO$_2$ – “Studio e sperimentazione di sistemi di foto conversione con luce solare di CO_2 in metanolo, da utilizzare come combustibile” – co-funded by MIUR within PON “Ricerca e Competitività 2007-2013” is gratefully acknowledged.

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IND-P50

Modeling hydrocarbon poisoning of zeolite SCR catalysts

*Tommaso Selleri, Isabella Nova, Enrico Tronconi**

Dipartimento di Energia, Politecnico di Milano, Piazza Leonardo da Vinci 32,
20133, Milano (Italy)

enrico.tronconi@polimi.it

Despite being the leading technology in the NOx abatement from lean burn engines, NH_3-SCR still presents some fundamental issues that need to be understood, such as the low-T and cold start behavior. In these conditions the upstream DOC is not operative, leading to a significant hydrocarbon (HC) slip that impacts negatively on the activity of the SCR catalyst. Furthermore, medium- and long-term performances are affected due to coking and strong T gradients occurring during catalyst regeneration.

The aim of the present work is to develop a reliable numerical simulation tool of the HC poisoning process, useful for the design of effective SCR systems. As proposed in literature [1], the deactivation process is modeled according to a dual site approach, including: i) a redox site (S1), where NO and O_2 are activated and HC poisoning occurs due to partial oxidation, intermediate adsorption and coke formation; ii) an acid site (S2), responsible for ammonia adsorption. This approach correctly accounts for the transient and long term deactivation effects well reported in literature [2] and is based on a lumped HC molecule. The HC compound undergoes an activation step on the catalyst leading to the poisoning of redox metal sites. Effects on the ammonia storage and desorption dynamics, even if limited, are accounted for according to a spillover effect similar to the one described in. The model has been validated against experimental and literature data, showing good agreement. In particular lab scale stationary tests on powdered Fe-ZSM-5 zeolite catalysts evaluating the combined effect of propylene poisoning and T increase [3] are predicted correctly. Moreover the model is able to correctly represent the NO conversion dynamics when propylene pulses are fed to the SCR reactor in isothermal experiments [4] over Fe zeolite catalysts.

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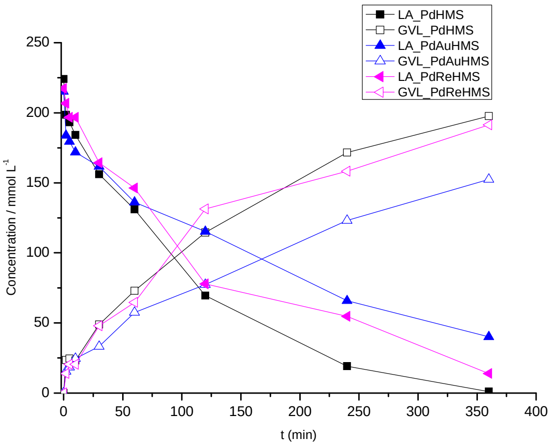
IND-P51

Effect of Au on Pd/HMS or Ti HMS as catalysts for the hydrogenation of levulinic acid to γ-valerolactone

Maria Luisa Testa [a]*, *Louis Corbel-Demailly* [b], *Valeria La Parola* [a],
Catherine Pinel [b], *Anna Maria Venezia* [a]

a CNR-ISMN Palermo, via Ugo La Malfa 153, 90146 – Palermo, Italy
b IRCELYON, 2 Avenue Albert Einstein 69626 – Villeurbanne, France

marialuisa.testa@cnr.it



Nowadays, for a sustainable production of fuels, one of the most important approach is the valorization of biomass residue. From the acid treatment of lignocellulosic materials, platform chemical levulinic acid (LA) can be easily obtained.[1] LA can be further converted into many valuable chemicals i.e. lactones, cyclic ethers or diols, useful as alternatives to the current petrochemical products [2].

The effect of different supports, silica HMS and Ti doped silica HMS, on the catalytic performance of mono (Pd) and bimetallic (Pd-Au, Pd-Re) catalysts, containing 2 wt% of each metal, for the hydrogenation of levulinic acid in water was studied. The catalytic behavior of the materials was evaluated in terms of conversion of the starting levulinic acid and selectivity to γ-valerolactone. The surface and structural properties of the catalysts were investigated by means of X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) performed on fresh and spent materials. A synergic effect of Au and Ti on Pd sample was observed with the consequent formation of a PdTi alloy responsible of the good performance of the catalyst.

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IND-P52

Niobium oxide based catalyst for methyloleate epoxidation

<u>Rosa Turco</u>[a],Rosa Vitiello[a],Riccardo Tesser[a], Antonella Gervasini[b],Paolo Carniti[b], Luciana Minieri[c],Pasquale Pernice[c], Antonio Aronne[c], Martino Di Serio[a]

a Dipartimento di Scienze Chimiche, Università di Napoli, via Cintia, 80126, Napoli, Italia
b Dipartimento di Chimica, Università di Milano, Via Golgi 19,20133 ,Milano, Italia
c Dipartimento di Ingegneria Chimica,dei materiali e delle produzioni industriali Università di Napoli, Piazzale V. Tecchio 80, 80125 Napoli, Italia

rosa.turco@unina.it

In the last decade, niobium based systems have received particular attention due to their catalytic activity in several important chemical reactions, especially when high acidity and water tolerance are needed in the process[1]. Different niobium surface species (isolated, polymerized or bulk) on SiO_2 may be formed, depending on the preparation method, the support material, the kind of niobium precursor and the niobium loading [1]. These species are responsible for properties and catalytic activity. In this work, niobium oxide supported on silica and silica-niobia mixed oxides were prepared by different techniques [3,4], in order to obtain solids characterized by niobium species with different molecular structure. This aspect was investigated testing the catalysts in the epoxidation reaction of methyloleate with aqueous hydrogen peroxide. This reaction is very interesting for industry, because it leads to the useful intermediates for lubricants and plasticizers productions. It was found a difference in the activity and the selectivity in the epoxidation of methyloleate for different niobium based catalysts. The difference in the activity can be justified with the difference in specific surface area of the different catalysts, while the difference in the selectivity is due to the difference in the niobium dispersion.

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IND-P53

A Novel Perfluorinated Membrane for the Separation of Organic Solvents

C. Ursino[a], *S. Simone*[a], *A. Sanguinetti*[b],*E. Dinicolo*[b],*B. Gabriele*[c],*A. Figoli*[a]

[a] *Institute on Membrane Technology, ITM-CNR c/o University of Calabria, Via P. Bucci 17/C, 87036, Rende (CS), Italy*
[b] *Solvay Specialty Polymers Italy, Viale Lombardia 20 , 20021, Bollate (MI), Italy*
[c] *Department of Chemistry and Chemical Technologies, University of Calabria,Via P. Bucci 12/C, 87036 Rende (CS), Italy*

a.figoli@itm.cnr.it

Solvent recycling is one of the main issues of the chemical and pharmaceutical industries. The total estimated amount of waste solvents is 800.000/900.000 ton/years, and the main methods of recovery, as distillation and evaporation, are difficult and expensive. Therefore, the use of separation processes using membrane technology is becoming more and more diffuse. The main advantages of this technology are: low energy use, high ability to separate thermolabile compounds, the possibility to operate without the addition of chemicals, environmental friendliness and ease of use [1]. The main limitation of membranes is connected with their stability to aggressive chemical solvents, as methanol, 2-propanol, toluene, hexane, or DMF.

For this reason, we have developed a novel perfluorinated polymer, Co-ECTFE, which is more easily processable and possesses a lower melting point grade with respect to commercial ECTFE [2] (a copolymer of ethylene and chlorotrifluoroethylene commercially known as Halar® ECTFE). Thanks to the high chemical resistance of Co-ECTFE, this polymer represents a very promising new material for preparing membranes able to carry out separations processes of organic solvents even under harsh conditions.

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Solvay Specialty Polymers Italy is gratefully acknowledged for funding this work.

IND-P54

A 1D+1D model of the SCR reactor: impact of the inhibiting effect of NH_3 on the oxidation of Hg^0

N. Usberti[a], *A. Beretta*[a], *L. Lietti*[a], *P. Forzatti*[a], *M. Di Blasi*[b], *A. Morandi*[b]

[a] *Dipartimento di Energia, Politecnico di Milano, piazza L. da Vinci 32, 20133 Milano*
[b] *ENEL Enel Ingegneria e Ricerca SpA, via Pisano 120-56122 Pisa*

alessandra.beretta@polimi.it

Among the various air pollutants emitted from coal-fired power plants, elemental mercury is a major environmental issue that has attracted considerable attention in recent year. It is now well known in literature that the presence of a SCR-DeNO$_X$ unit affects mercury speciation, since the SCR catalyst favors the highly desired conversion of Hg^0 to the ionic species Hg^{2+} in the presence of HCl.

A heterogeneous model of the SCR reactor with honeycomb monolith catalyst is developed; it solves the mass balances of the reacting species along the axial (1D) and radial (1D) direction, using a lumped approach to describe the gas-solid mass transfer and a differential approach to describe diffusion and reaction within the catalyst wall. The model describes the coexistence of the DeNOx reaction and the highly desired oxidation of Hg^0. It is well known from the literature that the conversion of Hg^0 is negatively affected by NH_3, but the extent of such an inhibition is uncertain because of the inherent complexity of the mercury speciation measurement. We thus apply the model to examine the concentration and reaction rate profiles inside the monolith wall and comprehend the way and extent of the interference of NH_3 on Hg oxidation. Lab scale and pilot scale tests over commercial catalysts allow to focus the analysis on realistic conditions. Both the DeNO$_X$ and the Hg oxidation processes are affected by external and internal mass transfer limitations; NH_3 concentration drops very rapidly across the radial direction, but Hg^0 profiles are similarly concentrated in a thin superficial layer. Thus, the main operating parameter which affects the extent of NH_3 inhibition is the Area Velocity, that is the sizing of the full scale reactor. However, a parametric analysis provides useful elements for envisaging the desired catalyst characteristics which can promote Hg^0 conversion and minimize NH_3 inhibition.

IND-P55

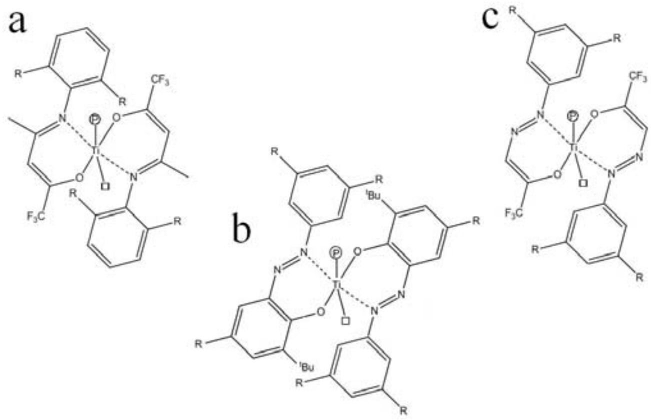
Reaction mechanisms in homogeneous olefin polymerization catalysis

Vincenzo Villani[a], *Gaetano Giammarino*[a]

a Dipartimento di Scienze, Università della Basilicata, Campus Macchia Romana,85100, Potenza, Italy

vincenzo.villani@unibas.it

The understanding of the propagation and termination mechanisms in homogeneous polymerization of olefins is today a hot topic [1,2].



Mecking *et al.*[3] showed that a bis(enolatoimine)Ti catalyst (**a**), with *ortho*-fluorinated aryl groups, is able to achieve living ethene polymerization.

Recently, Hecht *et al.* [4] have developed a new class of octahedral bis(phenoxy-azo) complexes (**b**) able to give syndiospecific propagation in styrene polymerization.

Here we present our findings, based on DFT calculations of the reaction mechanisms for the living and syndiospecific polymerization using these catalysts. We also propose an alternative catalyst (**c**), which is a combination of the former ones: its stability and its catalytic ability have been studied.

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IND-P56

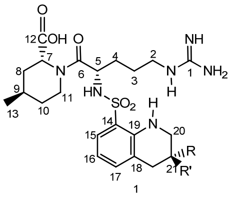
Impiego di biocatalizzatori per trasformazioni selettive nella sintesi di molecole farmacologicamente attive

Samuele Ciceri[a], *Paride Grisenti*[b], *Patrizia Ferraboschi*[a]

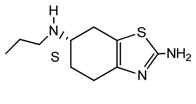
a Dipartimento di Biotecnologie Mediche e Medicina Traslazionale, Università Statale di Milano, Via Saldini 50, 20133, Milano, Italia
b EUTICALS SpA, Via Volturno 41/43 , 20089, Rozzano (MI), Italia

samuele.ciceri@guest.unimi.it

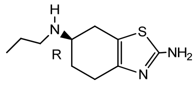
Nel corso della sintesi di composti farmacologicamente attivi che presentano strutture polifunzionali e contengono uno o più centri stereogenici sono richieste trasformazioni chemoselettive, regioselettive, stereoselettive realizzabili attraverso l'impiego di biocatalizzatori (enzimi purificati o microrganismi).
Scopo del nostro lavoro è stato l'ottenimento di alcuni principi farmacologicamente attivi con metodi biocatalitici che avrebbero potuto apportare miglioramenti, rispetto alle preparazioni già note, in termini di rese e di semplificazione della via di sintesi.
Con l'utilizzo della lipasi da *Pseudomonas fluorescens* sono stati ottenuti i sintoni enantiomericamente puri per l'ottenimento dell'(R) e (S)-argatroban, un antitrombotico sintetico.
L'utilizzo del microorganismo *Saccharomyces cerevisiae* ha consentito la preparazione del sintone otticamente puro per ottenere sia l'(S)-pramipexolo (Mirapex), un ammino tetraidrobenzotiazolo di origine sintetica utilizzato nel trattamento del morbo di Parkinson, sia l'(R)-pramipexolo (Dexpramipexolo), attualmente in fase di studio per il trattamento della SLA (Sclerosi Laterale Amiotrofica).
Attraverso una trasformazione regioselettiva, catalizzata dalla proteasi Alcalase CLEA, è stato possibile preparare la capecitabina (Xeloda), un antitumorale a struttura nucleosidica.



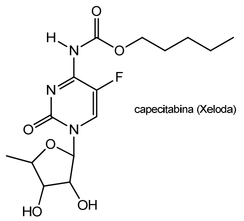
R = CH$_3$; R' = H (21R)-argatroban
R = H; R' = CH$_3$ (21S)-argatroban



(S)-pramipexolo



(R)-pramipexolo



capecitabina (Xeloda)

IND-P57

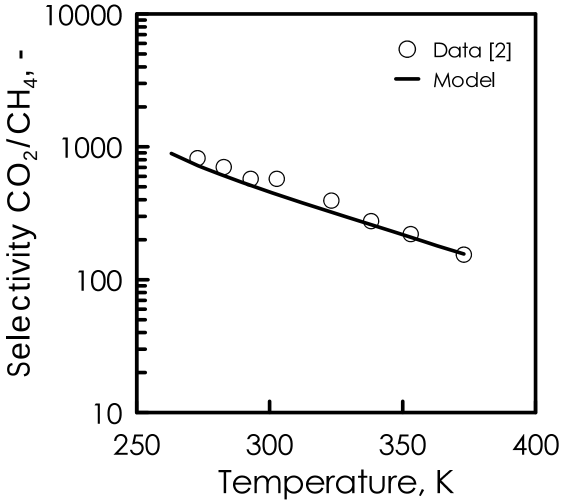
Permeation performances of light gases through DD3R zeolite membranes

Zito P.F.[a], *Caravella A.*[b], *Brunetti A.*[c], *Drioli E.*[a, b], *Barbieri G.*[b]

a Dept. of Environmental and Chemical Engineering, University of Calabria, Via P. Bucci, Cubo 44A , 87036, Rende (CS), Italy
b National Research Council – Institute on Membrane Technology (ITM-CNR), Via P. Bucci, Cubo 17C , 87036, Rende (CS), Italy

p.zito@itm.cnr.it

DD3R zeolite is investigated for its promising performances in liquid and gas separation. In this work, the permeation performances of a DD3R membrane are investigated for quaternary gas mixture (CH_4, CO_2, CO and N_2) over temperature and feed pressure range of [253-333] K and [200-1000] kPa, respectively [1]. A multicomponent approach based on Maxwell-Stefan equations is adopted to describe permeation through the zeolite layer. The figure below shows the CO_2/CH_4 selectivity evaluated in this work compared with some literature data [2], this providing the required model validation. As shown in the figure, DD3R exhibits excellent performances in terms of CO_2/CH_4 selectivity (within 100-1000). The presented approach can be effectively used to forecast the performance of zeolite membranes under conditions of industrial interest starting from laboratory-scale experimental tests. Moreover, it can be extended to zeolite types other than the DD3R ones, further enlarging the generality of this methodology.



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Chimica Inorganica

Plenary

INO-PL1

The Positives about the Negative: Compounds with Multinary Polyanions

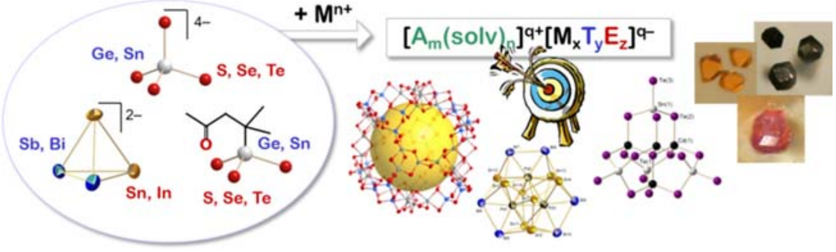
Prof. Dr. Stefanie Dehnen[a]

a Dipartimento di Chimica e Wissenschaftliches Zentrum für Materialwissenschaften,
Philipps-Universität Marburg, Hans-Meerwein-Straße, D-35032 Marburg, Germany

dehnen@chemie.uni-marburg.de

Multinary, non-oxidic metallates and metallides are currently actively investigated by many research groups, leading from structural studies through functional analyses to innovative materials design.[1] Binary main group element aggregates proved to be useful synthetic tools for diverse structural and functional motifs within ternary transition metal/main group element clusters and networks.[2] Whereas chalcogenidotetrelate ions $[E^{14}_xE^{16}_y]^{q-}$ (E^{14} = Ge, Sn; E^{16} = S, Se, Te) basically represent heavier homologues of silicates or borates, the inversely polarized pnictogentrielide/tetrelide ions $[E^{13/14}_xE^{15}y]^{q-}$ ($E^{13/14}$ = Ga, In; Ge, Sn, Pb; E^{15} = As, Sb, Bi) belong to the Zintl anion family.

Products of reactions with transition metal compounds represent unprecedented, ternary clusters or networks, according to the general type $[M_xE^{13/14}_yE^{16}_z]^{q-}$, or ternary intermetalloid clusters $[M_xE^{13/14}_yE^{15}_z]^{q-}$, respectively. The physical properties of the compounds, ranging from (photo-)semi-conductors or ion conductors to bond-activating nano-capsules, are dependent on the nature of the involved elements and the observed structure type.[3–6] Very recently, also ionothermal techniques were successfully applied for the synthesis of novel salts of such complex anions.[7]



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INO-PL2

Biogenesis of iron-sulfur proteins: From biochemical mechanisms to disease

Roland Lill

Institut für Zytobiologie, Medical Faculty, Philipps-Universität Marburg,
Robert-Koch-Str. 6, 35032 Marburg – Germany

Lill@staff.uni-marburg.de

Iron-sulfur (Fe/S) clusters are evolutionary ancient, inorganic cofactors of proteins with functions in catalysis, electron transfer and regulation. Fifteen years ago we and others discovered that Fe/S cluster synthesis and assembly into apoproteins in a living cell does not occur spontaneously but is a complicated catalyzed process. Since then, my group has been interested in identifying the machinery and defining the molecular mechanisms that assist this biosynthetic process in eukaryotes (see recent reviews [1-3] for in depth summaries). To date, some 30 biogenesis proteins are known that are conserved from yeast to man. The process is essential for cell viability because of numerous Fe/S proteins participating in central cellular processes of life such as DNA synthesis and repair, protein synthesis, and respiration.

Generation of cellular Fe/S proteins starts in mitochondria and is accomplished by the iron-sulfur cluster (ISC) assembly machinery which was inherited from bacteria during evolution. Cytosolic and nuclear Fe/S protein assembly also depends on this machinery, yet additionally requires the mitochondrial ISC export apparatus and the cytosolic iron-sulfur protein assembly (CIA) machinery. While we have a good picture of the general outline of Fe/S protein biogenesis, the molecular mechanisms underlying the individual reactions are only now being unraveled using biochemical, biophysical, bioinorganic and ultrastructural methods. Knowledge of these pathways helps in Synthetic Biology to construct artificial pathways for the synthesis of biofuels and fine chemicals. Moreover, better understanding of this essential cellular process will facilitate the elucidation of various “Fe/S diseases” in which biogenesis components are functionally impaired resulting in complex hematological, metabolic or neurodegenerative phenotypes.

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INO-PL3

The Reactivity of Halides of High-Valent Group 5 and 6 Elements with Organic Compounds: from Coordination Chemistry to Activation Reactions

Fabio Marchetti

Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, I-56126 Pisa, Italy

fabmar@dcci.unipi.it

Niobium and tantalum pentahalides, molybdenum pentachloride and tungsten hexachloride are easily-available solid compounds, whose coordination chemistry was scarcely elucidated in the past. We have been involved in a systematic exploration of the reactivity of such halides with stoichiometric amounts of oxygen- and/or nitrogen-containing organic species. This approach provides the way to a variety of inorganic structural motifs [1]. Furthermore, the coordination to the metal centre may represent the preliminary step of transformation of the organic substrate, which usually takes place selectively and under mild conditions [2]. In a number of cases, the process results in the formation of stable metal-anion salts containing otherwise reactive organic cations [3]. The metal-halide bond energy value and the availability to the metal centre of a one-electron reduced oxidation state are the two key factors which drive the activation reactions, and provide uniqueness with respect to the parallel chemistry exhibited by high-valent main group element halides. Examples will be given with reference to arenes, natural α-aminoacids, alkyl-ureas, amines, etc.

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Chimica Inorganica

Keynote

INO-K1

Structure-properties correlation studies on functional oxide nanostructures

Lidia Armelao

Istituto per l'Energetica e le Interfasi del Consiglio Nazionale delle Ricerche and Dipartimento di Scienze Chimiche - Università di Padova, Via Marzolo, 1 – 35131 Padova, Italy

lidia.armelao@unipd.it

The ever-increasing advanced performances required in all technological fields rely on the possibility to design and fabricate innovative materials with improved functional characteristics. In this framework, a great challenge is represented by the development of soft and versatile chemical processes that allow the realization of materials with a fine control on composition, microstructure and dispersion of doping species.

Due to the coexistence of unique electrical, magnetic, catalytic and optical properties, simple and multicomponent oxide-based materials have attracted renewed interest in the last years. Among them, pure and doped ZnO[1,2] and GeO_2[3] exhibit intriguing optical properties. ZnO is promising for future optoelectronic devices and suitable as a host material for optically active dopants. The blue luminescent GeO_2 material is highly sought after for optical waveguides and optoelectronic communication devices. The emission behavior of oxide nanostructures closely depends on structural aspects. Doping with transition metal ions also offers an effective method to adjust their luminescent behavior. The ability to produce ZnO and GeO_2 materials with tailored and well-defined properties under controlled and sustainable processing conditions is therefore highly desirable.

The present contribution focuses on the synthesis of pure and doped ZnO and GeO_2 nanosystems with different shape and size, and on the study of their light-emitting properties. The luminescence behavior investigated both in the energy and time domain through the innovative synchrotron techniques[4] X-ray excited optical luminescence (XEOL) and time-resolved X-ray excited optical luminescence (TR-XEOL) shows a remarkable correlation to materials composition as well as to structural and morphological aspects.

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INO-K2

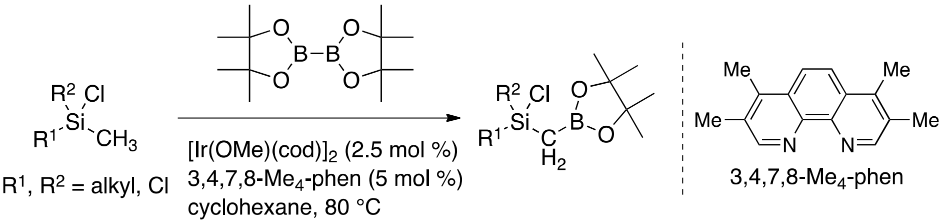
Interplay of Silicon and Boron in Transition Metal Catalysis

Michinori Suginome

Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

suginome@sbchem.kyoto-u.ac.jp

Silicon and boron play indispensable roles in synthetic organic chemistry, as demonstrated by general utilization of organosilicon and -boron compounds as reagents and synthetic intermediates. Their synergy makes transition metal catalysis even more fruitful. We established in 1996 that the silicon-boron bonds of silylboronic acid derivatives are activated by transition metal catalysts, leading to the addition to carbon–carbon multiple bonds. Since then, a variety of transition-metal-catalyzed silaboration reactions have been developed.[1,2] Such productive interplay of silicon and boron in catalysis is not limited to the chemistry of silylboronic acids. More recently, we found that Ru-catalyzed C-H silylation at the *ortho*-positions of arylboronic acids and □-positions of methylboronic acid are promoted by removable directing groups attached onto the boron atoms.[3,4] This method allowed highly site-selective, efficient silylation of organoboron compounds. There is another mode of the silicon-boron interplay. We've established a reaction system in which the methyl groups on the silicon atom are selectively C-H borylated in the presence of an iridium catalyst.[5] This is the first catalytic reaction that allows conversion of chloromethylsilanes, which are the common starting materials obtained by the Rochow's direct process, at their methyl groups, leaving the chlorine atoms on silicon intact. A similar reaction system even allows the borylation of tetraalkylsilanes, which in most cases are inert toward chemical reactions.



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INO-K3

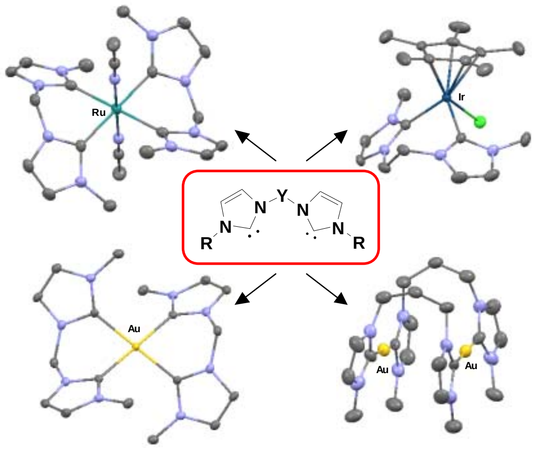
Late transition metal complexes with di-(N-heterocyclic carbene) ligands

Marino Basato[a], *Andrea Biffis*[a], *Cristina Tubaro*[a]

a Dipartimento di Scienze Chimiche, Università di Padova, Via Marzolo 1, 35131, Padova, Italy

marino.basato@unipd.it

Metal-coordinated carbene moieties have been mainly considered as reactive fragments in several catalytic organic transformations, like for example, the reactions involving the decomposition of diazo compounds (cyclopropanations, C-H insertions, C-C coupling). However, in the last two decades, much interest has been growing in the chemistry of the particular class of N-heterocyclic carbenes (NHCs) as not reactive ligands: these resulted to show excellent coordinating properties towards transition metal centres both in low and medium-high oxidation state, allowing the synthesis of robust catalysts. In this contribution we will present our recent results on the synthesis of novel diNHC metal complexes and on their applications in catalysis, biochemistry and material science.[1] The obtained results confirm the extraordinary coordinating flexibility of the carbene ligand and fully justify the strong research efforts on this relatively new chemistry.



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INO-K4

Structure, Reactivity and Dynamics of Non-classical Transition Metals Hydrides: from Molecular Complexes to Nanoporous Materials

A. Albinati

Dipartimento di Chimica, Università di Milano, Via C. Golgi 10, 20133 Milano.

alberto.albinati@unimi.it

The study of the interaction of a H_2 molecule (dihydrogen) with a transition metal centre has been a very active area of research since Kubas' seminal discovery, in 1984, that dihydrogen can form σ-complexes with transition metals (the so-called non-classical hydrides). Dihydrogen complexes, in fact, are key intermediates in many important reactions such as hydrogenations, hydrosylations and enzymatic reactions. More recently, the importance of the formation of "$M\text{-}\eta^2H_2$" bonds in hydrogen-storage materials has been emphasized as a means of increasing the binding energies of dihydrogen in nanoporous materials beyond that offered by physisorption alone.

Single crystal neutron diffraction has been of paramount importance in providing information on the nature of the "$M\text{-}\eta^2H_2$" bond, on the degree of activation of the H_2 ligand upon coordination and on the influence of the ancillary ligands on the reactivity. The results of a series of accurate, low temperature (T≈ 20K), single-crystal neutron diffraction studies will be discussed, focussing on the complex $[Ru(H_2)_2(H)_2(PCyp_3)_2]$ (Cyp = cyclopentyl) (**1**).

We note, however, that any discussion of the chemical behaviour of hydrido-complexes will be incomplete without a proper description of their dynamics; unique information can be obtained by spectroscopic methods, in particular Inelastic Neutron Scattering (INS) experiments. Using high-resolution INS data, we were able to obtain the rotational tunnelling frequencies of the H_2 ligand (in the range 0.3 – 1.5 meV) and the associate rotational barriers in non-classical hydrides. These experimental values are in excellent agreement with those obtained from DFT calculations. Rotational tunnelling spectroscopy has also been successfully used to unambiguously prove the presence of "$M\text{-}\eta^2H_2$" species in transition metal doped zeolites (e.g.: in Fe, Cu doped ZSM-5). Moreover, by combining the T dependence of the INS spectra (Quasi Elastic Neutron Scattering) with DFT calculations it has been possible to determine the H/H_2 exchange mechanism in complex (**1**).

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INO-K5

Cristallografia e polimeri: dai risultati epocali degli anni 1950-60 ai nuovi materiali organici

Stefano Valdo Meille

Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Politecnico di Milano, via Mancinelli,7, 20131, Milano, Italia

valdo.meille@polimi.it

I polimeri cristallini sono stati oggetto di studi cristallografici fin dagli albori della cristallografia. I risultati pionieristici sui polimeri naturali nella prima metà del '900, gli studi di Bunn sui primi polimeri sintetici negli anni '40, la proposta dell'α-elica per i polipetidi (Pauling, 1951) e della doppia elica del DNA di Watson e Crick nel 1953, restano tra i più vividi esempi del potenziale esplicativo della determinazione di strutture molecolari tridimensionali e della correlazione tra struttura e proprietà molecolari. La determinazione da parte di Natta e di Corradini delle strutture cristalline dei polimeri stereoregolari da loro ottenuti è risultata essenziale per la comprensione dei processi di polimerizzazione stereospecifica e per le sue applicazioni.

Lo sviluppo successivo della cristallografia dei polimeri ha potuto usufruire meno di quella delle piccole molecole o delle proteine, dei progressi della strumentazione e della potenza di calcolo di questi decenni. Ciò per la disomogeneità e il disordine intrinseco dei materiali polimerici, che ne limitano la qualità e le dimensioni dei cristalli. D'altra parte i polimeri organici, non solo cristallini, sono componenti essenziali per molte delle attuali applicazioni sia strutturali, che funzionali, specialmente nello sviluppo di nuovi dispositivi. La determinazione della struttura dei polimeri, anche con metodologie relativamente nuove come quella delle polveri, risulta la premessa necessaria, non solo per comprenderne la funzionalità ma anche per il controllo della organizzazione gerarchica molecolare e supramolecolare fino alla morfologia dei domini delle differenti fasi che costituiscono i moderni materiali.

Se i dati disponibili consentono spesso solo la determinazione di quelli che, con Corradini, chiamiamo "modelli limite ordinati", completati al più da modelli di disordine, per affrontare la complessità dei nuovi sistemi, la modellazione ha un peso sempre crescente. Tuttavia, se non opportunamente orientata, non è ancora in grado di prevedere le strutture cristalline sperimentali e quindi uno dei compiti più importanti della cristallografia, non solo dei polimeri, è tuttora quello di orientare e validare proprio le procedure di modellazione.

INO-K6

Halogen Bonding: From Crystal Engineering to Function Engineering

Pierangelo Metrangolo[a,b], Gabriella Cavallo[a], Giuseppe Resnati[a], Giancarlo Terraneo[a]

a Laboratory of Nanostructured Fluorinated Materials (NFMLab), Department of Chemistry, Materials, and Chemical Engineering "Giulio Natta", Politecnico di Milano, Via L. Mancinelli 7, 20131, Milano, Italy

b VTT – Technical Research Centre of Finland, PL 1000, 02044 VTT, Finland

pierangelo.metrangolo@polimi.it

The main differences between hydrogen and halogen bonding are that (i) halogen bonding is more directional than hydrogen bonding; (ii) the strength of halogen bonding can be easily tuned by simple single halogen-atom mutation; (iii) halogen bonding is more hydrophobic whereas hydrogen bonding is hydrophilic. Each of these features has recently allowed taking some important advances over past applications of supramolecular chemistry in materials design.[1] For example, the directionality of halogen bonding has provided with unique design tools for preparing photoresponsive, liquid-crystalline complexes from non-liquid-crystalline constituents, with truly unique optical performances.[2] Moreover, we have employed the tunable interaction strength of halogen bonding to gain fundamental understanding of light-induced mass migration in photoswitchable polymer-azobenzene complexes; namely no other noncovalent interaction allows controlling the polymer-chromophore interaction strength without altering the electronic properties of the chromophore.[3] The hydrophobicity of halogen bonds has in turn allowed us to devise the smallest ion transporter ever,[1] which, together with our recent work on halogen-bond-triggered supramolecular gelation,[1] opens up new avenues in the design of supramolecular systems.

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INO-K7

The thin inorganic line of angiogenesis: hovering between physiology and pathology

Diego La Mendola[a]

[a] *Dipartimento di Farmacia, Università di Pisa, Via Bonanno Pisano 6,56126, Pisa, Italia*

lamendola@farm.unipi.it

The process by which new blood capillaries grow from pre-existing vessels is known as angiogenesis. Physiological angiogenesis occurs in reproduction, growth and development, as well in wound healing. It is regulated by a very sensitive interplay of endogenous growth factors and inhibitors, and their imbalance can cause disease. The angiogenesis has been implicated, in more than 70 disorders, among them cancer, autoimmune diseases, diabetic retinopathy and atherosclerosis. Conversely, insufficient angiogenesis underlies conditions such as stroke, coronary heart disease and delayed wound healing, where inadequate blood vessels growth leads to poor circulation and tissue death. Recent findings have put into the light that angiogenesis is a prominent feature of neurological diseases, either as pathophysiological factor or as a response to injury. Copper(II) is well known to play an essential role in neurodegenerative diseases and it has been also demonstrated to be an essential angiogenesis cofactor *in vivo*. It is known that, during angiogenesis processes, the extracellular translocation of cellular copper occurs. Serum copper(II) levels are raised in a wide variety of human cancers and are related to the disease severity. However, the specific molecular mechanism of metal involvement and its activity targets remain unclear. The topics presented include the interaction of copper ions with some of angiogenic factors such as angiogenin, vascular endothelial growth factor (VEGF) and histidine-proline rich glycoprotein (HPRG),[1] highlighting how the metal ion is able to drive and activate some of the metabolic pathways involved in angiogenesis.

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INO-K8

Insulin-degrading enzyme: a metalloprotease whose activity can be modulated for therapeutic purposes

Giuseppe Grasso,[a] *Danilo Milardi,*[b] *Valeria Lanza,*[b] *Francesco Bellia,*[b] *Jerzy Silberring,*[c,d] *Przemyslaw Mielczarek,* [c,d] *Enrico Rizzarelli*[b]

a Department of Chemical Sciences, University of Catania, 95125 Catania (Italy)
b Istituto di Biostrutture e Bioimmagini, C.N.R., 95125 Catania (Italy)
c Department of Biochemistry and Neurobiology, AGH University of Science and Technology, Mickiewicza 30, 30-059 Krakow, Poland
d Centre for Polymer and Carbon Materials, Polish Academy of Sciences, Sklodowskiej-Curie 34, 41-819 Zabrze, Poland

grassog@unict.it

In recent years, Insulin-Degrading Enzyme (IDE) has drawn attention because of its capability to degrade β-amyloid peptides and it is currently studied as a pharmacological target for Alzheimer's disease. Our group has already reported that IDE activity can be modulated both by metal ions such as copper(I) and copper(II) and/or by other biomolecule such as ubiquitin, but the role of such interactions is unclear. In this work, we have studied and characterized the interaction between IDE and ubiquitin. Moreover, new perspectives regarding the role of this metalloprotease will be unveiled.

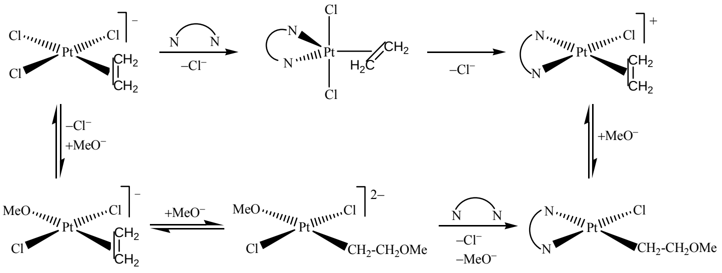
INO-K9

Sterical and electronic effects in [PtCl(η^1-CH_2–CH_2OR)(*N^N*)] and [PtCl(η^2-CH_2=CH_2)(*N^N*)]$^+$, *N^N* = dinitrogen ligand, complexes.

Michele Benedetti, Chiara R. Girelli, Daniela Antonucci, Francesco P. Fanizzi.

University of Salento - Department of Biological and Environmental Sciences and Technologies - Via Monteroni, 73100 - Lecce, Italy.

michele.benedetti@unisalento.it



The chemistry of platinum complexes with unsaturated ligands is interesting from the synthetic, coordination, organometallic, and bioorganometallic point of view [1-3]. For this reason we previously studied the reaction of the Zeise's anion, [$PtCl_3(\eta^2$-CH_2=$CH_2)]^-$, with alcohols (ROH), in the presence of strong bases and *N^N* dinitrogen ligands, see Scheme [3,4]. In this communication, we will report on the synthesis and reactivity of new [PtCl(η^2-CH_2=CH_2)(*N^N*)]$^+$ and [PtCl(η^1-CH_2–CH_2OCH_3)(*N^N*)] complexes, with different *N^N* diimine and diamine ligands, characterized by variable sterical hyndrance. Moreover, the factors determining the stability and reactivity of these complexes will be highlighted and discussed, in relation to NMR signals exhibited by the different complexes bearing hindered or unhindered diamine or diimine ligands.

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INO-K10

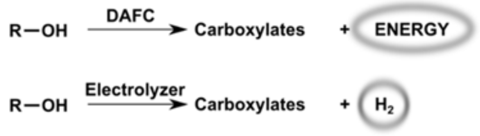
Energy & Chemicals from Renewable Resources by Electrocatalysis

Francesco Vizza[a], *Marco Bellini*[a], *Manuela Bevilacqua*[a], *Massimo Innocenti*[ab], *Alessandro Lavacchi*[a], *Andrea Marchionni*[a], *Hamish Miller*[a], *Jonathan Filippi*[a], *Lianqin Wang*[a,c]

a Istituto di Chimica dei Composti OrganoMetallici,Consiglio Nazionale delle Ricerche (ICCOM-CNR), Via Madonna del piano 1 50019, Sesto Fiorentino (FI), Italy,
b Dipartimento di Chimica, Università di Firenze, Via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy,
c Department of Chemical and Pharmaceutical Sciences, University of Trieste, Via L. Giorgieri 1, 34127 Trieste, Italy

francesco.vizza@iccom.cnr.it

The selective production of chemicals from renewable resources with contemporaneous release of energy is perhaps the most desired target of sustainable chemistry. Here, we report that this can be achieved using renewable alcohols, by means of two electrochemical devices: *direct fuel cells* and *electrolyzers*.[1] In either case, an aqueous solution of the fuel in the anode compartment is oxidized on an electrocatalyst that is appropriately designed to promote selectively the partial oxidation of the anolyte with high stability and fast kinetics. We have found that anode electrocatalysts based on nanosized Pd particles or organometallic complexes, are able to accomplish this goal in alkaline environment in conjunction with cathode electrocatalysts and solid electrolytes. When the oxidation process is carried out in a direct alcohol fuel cell (DAFC), electrical energy is released, while the alcohol is selectively converted to the corresponding alkali metal carboxylate. In an electrolyzer, containing an anode electrocatalyst similar to that employable in a DAFC, the alcohol is also converted to the corresponding alkali metal carboxylate, while hydrogen gas is produced at the cathode upon water reduction.



R = $-CH_2CH_3$, $-CH_2CH_2OH$, $-CH_2CHOHCH_2OH$, $-CHOHCH_3$

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INO-K11

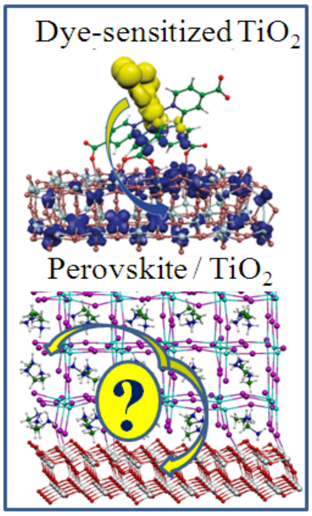
Modeling Materials and Processes in Hybrid/Organic Photovoltaics: From Dye-sensitized to Perovskite Solar Cells

Filippo De Angelis[a]

a Computational Laboratory for Hybrid/Organic Photovoltaics (CLHYO), CNR-ISTM, Via Elce di Sotto 8, I-06123, Perugia, Italy

filippo@thch.unipg.it

Dye-sensitized solar cells (DSCs) have maintained a clear lead over competing technologies in hybrid/organic photovoltaics, with top certified efficiency exceeding 11%. In 2012, the first reports of high efficiency solid-state DSCs based on organohalide lead perovskites completely revolutionized the field, with current certified efficiencies close to 18%. Many of the advances in the DSCs field have relied on the computational design and screening of new materials. We illustrate the performance of the simulation toolbox along with the fundamental modeling strategies using selected examples of relevant isolated device constituents, including dyes/perovskite absorbers, metal-oxide surfaces/nanoparticles, and hole transporters. We analyze the interfaces that control the device operational mechanism, i.e. dye-sensitized TiO_2/hole transporter and organohalide lead perovskite/TiO_2, and the results reveal fundamental aspects of the device's operational mechanism. DSCs modeling is relatively mature, while the recent "perovskite storm" has presented new problems and new modeling challenges which are presented along with selected results.



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INO-K12

Is rust a real must? From design to application of multi-functional Fe_2O_3-based nanomaterials

G. Carraro,[a] *C. Maccato,*[a] *A. Gasparotto,*[a] *D. Barreca*[b]

a Dip.to di Scienze Chimiche, Università di Padova e INSTM, Padova, Italia
b IENI-CNR e Dip.to di Scienze Chimiche, Università di Padova e INSTM, Padova, Italia

giorgio.carraro@unipd.it

Iron oxides are appealing low-cost and versatile materials thanks to their promising properties for several technological applications. In this work, a flexible synthetic approach, which provides a simultaneous structural and morphological control on the obtained iron oxide-based materials, is presented. The optimization of chemical vapor deposition (both thermal and plasma-assisted) routes starting from a fluorinated iron(II) diketonate-diamine compound [1] enabled the selective production not only of the α-Fe_2O_3 phase, but also of the scarcely investigated β- and ε-Fe_2O_3 polymorphs.[2,3] In addition, selected iron oxide systems have been used as *host* matrices for the dispersion of *guest* metal or metal oxide nanoparticles by sputtering or atomic layer deposition.[4] The prepared iron(III) oxide-based nanostructures have been tested in various applicative fields, such as photo-assisted processes (*i.e.* H_2 generation, photoinduced hydrophilicity and photocatalytic organic pollutant degradation) and sensing of toxic and flammable gases, displaying a broad range of attractive properties directly tuneable as a function of the preparative conditions.[2,3,4]

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Chimica Inorganica

Oral

INO-O1

Defects and photochemical properties of bare and Cerium-doped Zirconium dioxide

Maria Cristina Paganini, Chiara Gionco, Elio Giamello…

a Dipartimento di Chimica, Università di Torino., Via Giuria 7, 10125, Torino, Italia

mariacristina.paganini@unito.it

Zirconium dioxide has been studied in the last decades because of its large range of applications as ceramic material , in optical devices, gas sensors and catalysts (both as catalyst and catalyst support) [1]. On the other hand also Cerium oxide has attracted researchers attention because of its redox properties related to the oxygen storage capacity (OSC) and release. [2,3]

In the last few years the mixed system CeO_2-ZrO_2 based materials have been widely employed as catalysts for the conversion of automotive and industrial plants emissions into non-toxic compounds.

Recently zirconia based mixed oxides have been used for photocatalysis processes. The high zirconia band gap (more than 5 eV) implies the use of UV light in the photoactivation but also the presence of particularly attractive reduction and oxidation potentials.

In our study we synthesized ZrO_2-CeO_2 mixed oxides with different CeO_2 loading (0.5-1-5 wt%) via sol-gel process. From structural (XRPD) and spectroscopic (DR-UV-Vis and EPR) systematic characterization we derived important information about the nature of defects in the lattice of the material and we checked also the photo-activity of the mixed oxides with visible light. Preliminary photo-catalytic experiments have been performed to test reductive and oxidative properties of these mixed oxides. Encouraging results have been obtained especially with the sample having lower ceria loading (0.5%). Both reduction and oxidation activity of the sample have been verified through paramagnetic resonance technique. The photoformation of both electrons (reacting with oxygen and producing superoxide anions) and holes necessary to entail photocatalytic processes has been demonstrated irradiating with visible light (lamp cut off at 420nm). This phenomenon, which is not observed for bare ZrO_2, is due to the presence of empty Ce^{4+} states in the zirconia band gap.

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INO-O2

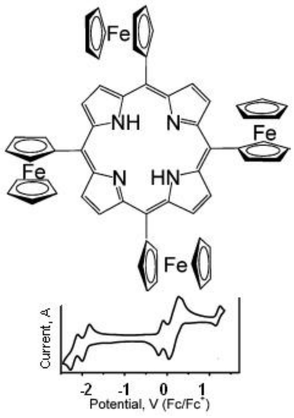
The effects of electronic delocalization and metal-metal coupling on the core levels of tetraferrocenylporphyrins

A. G. Marrani[a], *P. Galloni*[b], *A. Vecchi*[b], *R. Zanoni*[a]

a Dipartimento di Chimica, "Sapienza" Università di Roma., P.le A.Moro 5 , 00185, Rome,Italy
b Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma "Tor Vergata", Via della ricerca scientifica, 00133, Rome, Italy

andrea.marrani@uniroma1.it

Meso-ferrocenyl substituted porphyrins have so far received little attention, although they seem very promising both from the fundamental (*i.e.* multiredox processes, magnetic coupling and unpaired electron density migration) and practical (*i.e.* optoelectronic materials for application in high-speed photonic or redox devices) points of view. Here we report an investigation by XPS and electrochemical methods on the long-range metal-metal coupling exhibited by the free base and metallated (Co, Ni, Cu, Zn) compounds and the unpaired electron delocalization in mixed valence species.[1] Furthermore, the separation of four single-electron oxidations of the ferrocenyl moieties has been performed by accurately selecting proper solvent/electrolyte couples. The multiplicity of accessible reversible redox states in these molecules is of paramount importance for the development of multi-bit molecular memory devices.[2]



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INO-O3

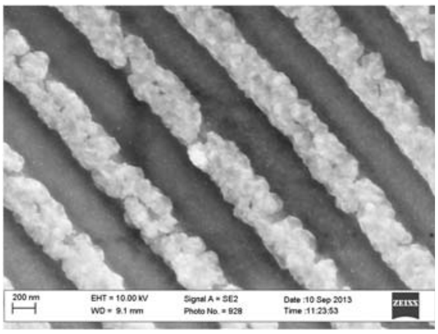
Cu_2O/TiO_2 Nanostripes Grown on a DVD Template

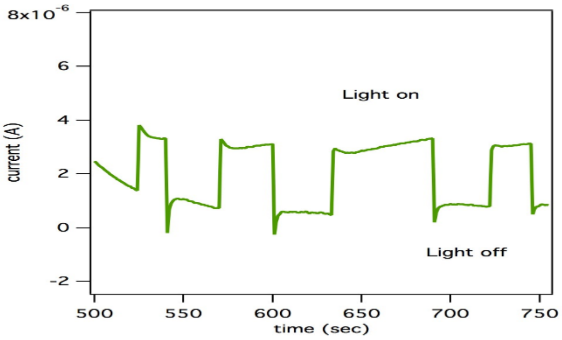
Gian Andrea Rizzi, Christian Durante , Michele Zanatta, Giuseppe Giallongo, Luciano Colazzo, Laura Calvillo, Armando Gennaro, Gaetano Granozzi

Dipartimento di Scienze Chimiche, Università degli Studi di Padova., Via Marzolo, 1 , 35131, Padova, Italia

gianandrea.rizzi@unipd.it

Cu_2O nanostripes have been grown by pulse-electrochemical deposition on a digital versatile disc (DVDs) template. The silver-coated spiral distribution of rectangular-shaped grooves was coated with a TiO_2 thin film, prior to Cu_2O deposition, obtained by a modified sol-gel method [1] where oxalic acid is used in place of the usual mineral acids to peptize the precipitated hydrous titania formed from the hydrolysis of titanium iso-propoxide. This leaves no inorganic residues, after UV-curing, resulting in a higher quality film, mainly composed of TiO_2-anatase. As demonstrated by AFM measurements, the DVD grooves are covered by a 120-130 nm thick TiO_2 film, while the thickness of the TiO_2 deposit on the ridges is about 50 nm. This inhomogeneous thickness leads to the growth of Cu_2O nanostripes only on the DVD ridges. A highly regular and reproducible Cu_2O/TiO_2 nanostructure is obtained. This system has been characterized by SEM, XPS, Raman and photocurrent measurements. A possible use of this electrode in visible light responsive Chemical Oxygen Demand determination is suggested.





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INO-O4

Chemical functionalization of semiconductor nanocrystals: modulation of solubility and implementation of chiroptical properties

Marcello La Rosa [a], *Christophe Linchenau* [a], *Tommaso Avellini* [a],
Serena Silvi [a], *Alberto Credi* [a]

a Photochemical Nanosciences Laboratory, Dipartimento di Chimica "G.Ciamician",
Università di Bologna, Via Selmi 2 , 40126, Bologna, Italy

marcello.larosa3@unibo.it

Inorganic semiconductor nanocrystals, also called quantum dots (QDs), are single crystals a few nanometers in diameter, whose size and shape can be controlled by adjusting the experimental parameters used during the synthesis [1]. Therefore, owing to their peculiar photophysical properties, QDs are attractive nanomaterials for application in several fields, such as medicine, diagnostics, materials science and optoelectronic devices.

QDs are commonly synthesized in apolar organic solvents; however, as several uses need water soluble and/or biocompatible nanoparticles, it could be necessary to replace the native hydrophobic ligands with hydrophilic ones after the synthesis. Molecules with multiple thiol groups, such as dihydrolipoic acid (DHLA), are very useful for the ligand exchange. DHLA, generally, can be obtained from lipoic acid (LA) upon reduction with $NaBH_4$ [2] or by irradiation with UV light [3].

In these work we describe a method based on a borohydride-loaded ion-exchange resin [4,5] which, among other advantages, enables a facile modulation of the QD solubility in various solvents.

Finally we are interested to investigate if functionalization with enantiopure DHLA can endow the QDs with chiroprtical properties, and how these properties change with the size of nanocrystals.

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INO-O5

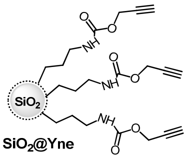
Novel synthesis of gold nanoparticles supported on functionalized silica

Silvia Fazzini[a], *Maria Cristina Cassani*[a], *Barbara Ballarin*[a], *Elisa Boanini*[b], *Jean Sébastien Girardon*[c], *Daniele Nanni*[a]

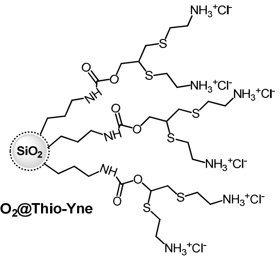
a Dipartimento di Chimica Industriale "Toso Montanari", Università di Bologna, Via Risorgimento 4, 40136, Bologna, ItaliaCap, Città, Nazione
b Dipartimento di Chimica "Giacomo Ciamician", Università di Bologna, Via Selmi 2 ,40126, Bologna, Italia
c Unité de Catalyse et de Chimie du Solide - UMR CNRS 8181 Université Lille 1 Nord de France, 59655 Villeneuve d'Ascq Cedex, France.

silvia.fazzini2@unibo.it

Recently, we presented stable silica-supported gold nanoparticles (Au_{NPs}) suitable for catalysis, obtained by using as the only reactants a gold precursor, chloroauric acid ($HAuCl_4$), and commercial polyethyleneimine-functionalized silica beads (SiO_2-PEI), with the need for neither external reducing agents nor conventional stabilizing moieties. [1]
In this work we describe another convenient method to prepare silica-supported gold nanoparticles. The silica nanoparticles were synthetized, first, by co-condensation of tetraethoxysilane and an organo-silane alkyne-terminated (**SiO_2-Yne**), [2] and then post-functionalized by thiol/yne coupling with cysteamine (**SiO_2@Thio-Yne**). By simply adding the obtained systems to an aqueous solution of $HAuCl_4$ the spontaneous formation of Au_{NPs} was observed in both cases and in very short times with diameters in the range of 10 to 20 nm. These new systems were fully-characterized by FT-IR, XPS spectroscopy, DLS , UV-Vis and TEM microscopy.



SiO_2@Yne



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INO-O6

Characterization of hybrid polymers for the conservation of cultural heritage

L. Bergamonti [a], C. Graiff [a], C. Isca [a], G. Predieri [a], D. Bersani [b], P.P. Lottici [b], L. Bellot-Gurlet [c], P. Colomban [c], C. Paris [c]

a Chemistry Department, University, Area delle Scienze 17/a, 43124 Parma, Italy
b Physics and Earth Sciences Department, Area delle Scienze 7/a, 43124 Parma, Italy,
c MONARIS, UMR 8233 UPMC/CNRS, Place Jussieu 4, 75252 Paris, France

giovanni.predieri@unipr.it

The cultural heritage artifacts are subject to degradation processes, both natural and anthropogenic, whose rate and type strongly depend on the nature of the constituent materials and on the characteristics of the surrounding environment, including pollutants, moisture, light, salts, temperature excursions and mechanical stress. Another important form of decay, mainly for ligno-cellulosic materials (wood and paper), is the biological deterioration caused by various microorganisms such as bacteria, fungi and algae.

In the framework af a research programme on the use of new hybrid siloxane materials [1] for the conservation of cultural heritage, here we present the characterization, by spectroscopic techniques, of new polymers for the consolidation of stones and ligno-cellulosic materials and for their protection against physico-chemical and biological deterioration. These polymers are hybrid organic-inorganic polyamidoamines (PAA's) functionalized with hydrophilic and siloxanic groups.

PAA's are polymers characterized by the presence of amide and tertiary amino groups, obtained by polyaddition of bis-acrylamides with primary amines or secondary diamines in protic polar solvents. Functionalized PAA's, both as-prepared and applied to different types of manufacts, have been characterized by means of vibrational spectroscopies.

In addition, time evolution of the polymerization reactions has been monitiored with Raman spectroscopy by following the decrease of the C=C stretching band of bisacrylamide at 1629 cm^{-1}, with respect to the intensity of the carbonyl group stretching at ca. 1650 cm^{-1}.

Financial support from Renner Italia S.p.A. (Minerbio, BO) is gratefully acknowledged.

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INO-O7

An Iridium Organometallic Complex as Functional Mimic of Hydrogenase

Alberto Bucci[a], *Gianfranco Bellachioma*[a], *Cristiano Zuccaccia*[a], *Alceo Macchioni*[a]

[a]*Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia, Via Elce di Sotto 8,06123, Perugia, Italia*

albechm@gmail.com

The production of solar fuels through an artificial photosynthesis process represents an attractive alternative to fossil fuels [1]. H_2 has attracted a lot of interest, as solar fuel, but its use is limited by its explosiveness and low volumetric energy density [2]. For these reasons, it would be extremely important to realize an efficient system capable to perform catalytic reversible hydrogenation and dehydrogenation reactions, in order to transform hydrogen in a safer and easier to handle product. Although many organometallic complexes are capable to carry on reversible hydrogenation of a large variety of inorganic or organic substrates [3], only few of them efficiently interconvert the NAD^+/NADH redox couple [4]. The latter is a fundamental process catalyzed in Nature by hydrogenase [5]. Herein we show that the iridium organometallic compound [Cp*Ir(pycxa)Cl] (Cp*= 1,2,3,4,5-P*entamethylcyclopentadienyl*; pycxa= 2-Pyridinecarboxamide) is a competent catalyst for the interconversion NADH/NAD^+. From UV-Vis measurements it was found that catalyst (**1**) shows a remarkable TOF of 4 min^{-1} for the dehydrogenation reaction of NADH and a TOF of 2 min^{-1} for the hydrogenation reaction of NAD^+.

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INO-O8

Bimetallic carbide carbonyl clusters

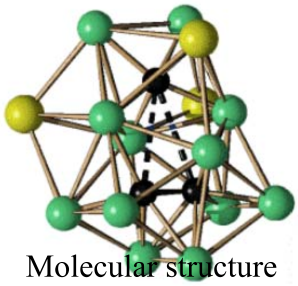
Iacopo Ciabatti, Cristina Femoni, Maria Carmela Iapalucci, Giuliano Longoni, Stefano Zacchini

Dipartimento di Chimica Industriale "Toso Montanari", Università di Bologna, Viale Risorgimento 4-40136 Bologna, Italy.

iacopo.ciabatti2@unibo.it

Bimetallic and polycarbide clusters are interesting both at the molecular level, in view of their enhanced stability and physical properties, and as precursors for the preparation of metal nanoparticles with controlled composition.[1]

In this communication, we describe some bimetallic molecular carbonyl clusters stabilised by interstitial carbide atoms. The comparison of the structures of different Ni-Co,[2] Co-Pd,[3] Co-Au and Ni-Au carbido clusters shows the tendency to give species with complete, partial or none segregation of the two metals. The different architecture of the structures depend on optimisation of the different M-M and M-CO interactions as a consequence of the metal's nature. Most attention will be reserved to the atypical structures of Ni-Au carbido cluster.



Molecular structure $Ni_{12}C(C_2)Au_3$ cage (green, Ni; yellow, Au; black, C)

In particular, the new molecular $[Ni_{12}C(C_2)CO_{17}(AuPPh_3)_3]^-$ (**1**) represents the first example of carbonyl cluster containing one carbide atom and one acetylide unit. Sub-van der Waals contacts are present between the carbide and acetylide suggesting the incipient formation of more extended C-C bonding. The study of molecular carbide clusters such as **1** may contribute also to a better understanding of the formation of C-C bonds within a metal cage.

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INO-O9

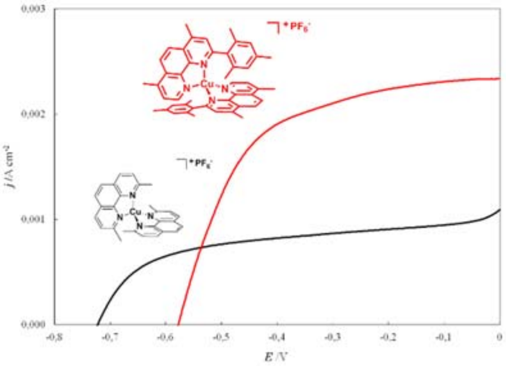
Copper Complexes as Electron Mediators in DSSCs

Mirko Magni[a], *Carlo Alberto Bignozzi*[b], *Stefano Caramori*[b], *Alessia Colombo*[a], *Claudia Dragonetti*[a], *Patrizia Mussini*[a], *Dominique Roberto*[a]

a Dipartimento di Chimica, Università degli Studi di Milano,
Via Golgi 19, 20133, Milano, Italia
b Dipartimento di Scienze Chimiche e Farmaceutiche, Università degli Studi di Ferrara, Via Fossato di Mortara 17, 44121, Ferrara, Italia

mirko.magni@unimi.it

The fossil fuels depletion puts the challenge to humanity to replace such energy sources with renewable and more ethic ones. The Sun could be considered a practically inexhaustible energy source on Earth whose light could be converted into electric energy exploiting the photovoltaic effect. In this context dye-sensitized solar cells (DSSCs) could be an actual opportunity. This work is focused on copper complexes with 1,10-phenanthroline ligands as possible alternative mediators to the common I_3^-/I^- redox couple which however suffers of some drawbacks. A rational study on the modulation of the electrochemical behavior of these copper complexes was performed in order to obtain useful information for their clever design; different substituents (varying their electronic and steric properties) placed in different positions on the phenanthroline scaffold were considered. Electrolytes containing the copper complexes were tested in dye-sensitized solar cells combining photoelectrochemical studies with fast pulsed laser experiments. The effect of iron polypyridine co-mediators was also considered. As an example we cite the significant performances obtained with the bulky asymmetric substituted bis-(2-mesitil-1,10-phenanthroline) copper hexafluorophosphate complex (see Figure) respect to the "benchmark" bis-neocuproine one [1].



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INO-O10

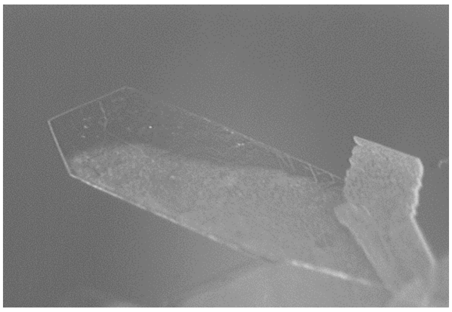
Crystal growth in gelled solution: application to coordination compounds

Silvia Rizzato[a], *Alberto Albinati*[a], *Massimo Moret*[b]

a Dipartimento di Chimica, Università di Milano, Via Golgi 19 , 20133, Milano, Italy
b Dipartimento di Scienza dei Materiali, Università di Milano Bicocca, Via Roberto Cozzi 55, 20125, Milano, Italy

silvia.rizzato@unimi.it

The use of gels or viscous materials as growth media for a wide range of compounds, including proteins and inorganic and organic compounds has been reported in the literature. In the presence of gel, sedimentation and convection currents are greatly suppressed and the mass transport of the molecules mainly occurs by diffusion, resulting, usually, in lower nucleation density and better crystal quality.[1a]



We have tested the possibility of using a variety of gel and resin-like systems as dispersion matrixes to increase the size and quality of the crystals as well as a medium useful to “stabilize” the crystal, modify the crystal habit and obtain new crystal forms of the same species (i.e. polymorphs, hydrates, solvates, etc.).[1b]

Here we report some new interesting phenomena of gel inclusions and morphological alterations observed *in crystallization experiments of coordination compounds, such as, coordination polymers, by using gels as diffusion media;* interferometric measurements have been used for *in situ* monitoring the mass transport in the gelled/fluid phase during the crystallization process.[2]

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INO-O11

Donor-acceptor properties of atropisomeric diphoshines in Nickel di-carbonyl and Rhodium-chloro-carbonyl complexes

Marco Fusè[a], *Giorgio Facchetti*[a], *Daniele Zerla*[a], *Michela Pellizzoni*[a], *Edoardo Cesarotti*[a], *Raffaella Gandolfi*[a], *Isabella Rimoldi*[a], *Carlo Castellano*[b], *Francesco Demartin*[b]

[a]*Dipartimento di Scienze Farmaceutiche, Sez. Chimica Generale e Organica "A. Marchesini", Università degli Studi di Milano, Via Venezian 21, 20133 Milano (Italy);* [b] *Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milano (Italy)*

marco.fuse@unimi.it

Since Tolman's review[1], a landmark in organometallic chemistry, the donor-acceptor properties of phosphines have been subject of intense experimental and theoretical studies. Most part of researches were devoted to mono-phosphines but only few studies to chelating di-phosphine[2]. The assumption that the effects of substituent on phosphorus in bidentate phosphines is the same as in the monodentate ones is not obvious. We have investigated the electronic and steric properties of a series of atropisomeric aryl and heteroaryl phosphines by the synthesis and characterization of the corresponding Nichel dicarbonyl and Rhodium chloro carbonyl complexes and determined the structure of [(Bitiamp)Ni(CO)$_2$] by single crystal X-ray determination.

We will discuss the linear correlations found among the IR stretching frequencies of the complexes and the pK$_a$ or E$^\circ$ of the free ligands and with the catalytic activities in hydrogenation of olefins.

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INO-O12

Vanadium-based molecular assemblies as efficient catalytic systems for relevant oxidation processes

N. Marino[a,b], G. Cruciani[c], J. Velasquez Ochoa [d], F. Cavani[d], R. P. Doyle[b], G. De Munno.[a]

[a] Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, via P. Bucci 14/c, 87036 Rende (CS), Italy.
[b] Department of Chemistry, Syracuse University, Syracuse, NY 13244-4100, United States.
[c] Dipartimento di Fisica e Scienze della Terra, Università di Ferrara, Via G. Saragat 1, 44122 Ferrara, Italy.
[d] Dipartimento di Chimica Industriale 'Toso Montanari', Università di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy.

nadia.marino@unicat.it; nmarino@syr.edu

Molecular vanadium-pyrophosphate (VPPi) assemblies seem like interesting species to investigate, since they can be regarded to as mimetic of the solid-state systems known as 'VPO' (Vanadium-Phosphorous-Oxide), whose industrial relevance as well as extreme complexity is well acknowledged. The catalytic potential inherent in the solid state structure of vanadyl(IV)pyrophosphate, $(V^{IV}O)_2P_2O_7$, generally accepted as the *in-situ* generated catalytic bulk phase for the selective oxidation of butane into maleic anhydride, is especially inspiring toward the idea of using discrete, VPPi coordination complexes for catalytic purposes. However, such molecular VPO systems have proven elusive so far. Recently, a unique example of VPPi complex was uncovered, namely $\{[(VO)bipy(H_2O)]_2(\mu\text{-}P_2O_7)\}$ (**1**),[1] suggesting that mild vanadium-phosphate chemistry is indeed possible, and offering up a strategic platform for future investigations. Preliminary catalytic tests have already highlighted great potential for this species, and mechanistic studies are being currently undertaken. Herein we present the results of these studies. A new potential application for this class of understudied materials is also put forward.

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INO-O13

Innovative composite biomimetic scaffold rapid prototyping for bone reconstruction

I. G. Lesci[a], L. Ciocca[b], L. Del Bianco[c], G. Fracasso[a], O. Mezini[a], N. Roveri[a]

a Department of Chemistry "G. Ciamician", University of Bologna, via Selmi 2, I-40126 Bologna, Italy
b Department of Oral Science, University of Bologna, Via S. Vitale 59 40125 Bologna Italy
c Department of Physic and Astronomy, University of Bologna, via Irnerio I-40127 Bologna Italy

isidorogiorgio.lesci@unibo.it

The ability to control the architecture and strength of a bone tissue engineering scaffold is critical to achieve a harmony between the scaffold and the host tissue. The scaffold attempts to mimic the function of the natural extracellular matrix, providing a temporary template for the growth of target tissues. The study of nanocrystalline calcium phosphate physical-chemical characteristics and, thereafter, the possibility to imitate bone mineral for the development of new advanced biomaterials is constantly growing. Recently, it has been reported that magnetic nanoparticles embedded in scaffolds have a positive influence on cell adhesion, proliferation and differentiation, especially under an external magnetic field [1]. The aim of this pilot study was to develop an experimental model appropriate for testing of a new composite scaffold material, used in combination with CAD-CAM technology to prepare customized scaffolds to restore full-thickness defects of the mandible. The biomaterial was synthesized using mineralized collagen, lactoferrin, and poly(ε-caprolactone) (PCL). In order to verify these effects and to throw light on the complex mechanism of the magnetic nanoparticles-cells interaction, which is still to be unveiled, we have prepared a novel scaffold material containing magnetite nanoparticles. The nanoparticles have a mean size of 10 nm and show superparamagnetic behavior at room temperature. The scaffold exhibited a relatively low degree of crystallinity, very close morphological and dimensional similarity to natural bone crystals, and a very high degree of HA admixture with the collagen of the composite material.

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INO-O14

Organo-modified Gadolinium Fluoride nanoparticles as dual optical and MR-imaging

Fabio Carniato, Lorenzo Tei, Mauro Botta

Dipartimento di Scienze e Innovazione Tecnologica, Università del Piemonte Orientale
"Amedeo Avogadro", Viale T. Michel 11 – 15121, Alessandria, Italia

carniato@unipmn.it

Gd-based MRI nanoprobes have the ability to carry a high payload of imaging reporters enabling a significant signal amplification.[1] Among the large number of inorganic NPs, we have recently investigated citrate coated gadolinium fluoride NPs which showed high chemical stability and high relaxivity.[2] Other organic coatings can be also used to stabilize $NaGdF_4$ NPs surface, leading to an improvement of the water suspendibility and to a modification of their relaxometric behavior. To reach this goal, $NaGdF_4$ NPs with EDTA and EDTA functionalized with a free carboxylic group (EDTA-COOH) or PEG_{2000} molecules (EDTA-PEG) were synthesized. In addition, further functionalization with fluorescein or rhodamine dyes was explored, aiming to develop novel dual imaging nanoprobes for optical and MR- imaging applications.

$NaGdF_4$ functionalized with EDTA-COOH and EDTA-PEG show enhanced hydrophilicity, whereas EDTA-based NPs tends to aggregate in aqueous suspension as a consequence of the reduced charge density. NMRD profiles, measured in water at 310K, of $NaGdF_4$ NPs functionalized with EDTA-COOH and EDTA-PEG present a shape typical of slowly tumbling systems, with a peak centered at 20 MHz, as consequence of a significant contribution from the second sphere water molecules H-bonded to the organic coating. Instead, EDTA-based $NaGdF_4$ shows a completely different profile, characterized by a decrease of r_{1p} value with increasing frequency. $NaGdF_4$-EDTA-COOH and $NaGdF_4$-EDTA-PEG were finally functionalized with modified fluorescien and rhodamine dyes. The final NPs were then incubated in ovarian carcinoma cells (SKOV-3) and tested as dual MRI/optical probes. MRI and confocal fluorescence microscopy analyses indicated that NPs were well incubated in the cytosol and that no alteration of the cells membrane occurred at low NPs loading.

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INO-O15

35 Years of Phosphorus Chemistry in Florence: a Legacy of Luigi Sacconi

Maurizio Peruzzini

Consiglio Nazionale delle Ricerche, Istituto di Chimica dei Composti Organometallici (ICCOM – CNR); Via Madonna del Piano, 10 – 50018 Sesto Fiorentino (FI)

maurizio.peruzzini@iccom.cnr.it

Luigi Sacconi (1911 – 1992) has been one of the giants of Italian Chemistry in the second half of last century attaining undisputable worldwide reputation for his achievements in coordination and organometallic chemistry and for being the founder of an excellent school of inorganic chemistry. This latter has raised international status through a dedicated group of excellent inorganic chemists actively working either at the Department of Chemistry of the University of Florence and the ICCOM CNR Institute (formerly ISSECC).

In the last period of his academic life Sacconi pioneered a very attractive albeit neglected research area, *i.e.* the coordination chemistry of white phosphorus, producing extremely spectacular results which demonstrated how the chemistry of this extremely reactive element may be nicely controlled within the coordination sphere of a transition metal ligand system.

In this communication, a perspective report of the chemistry developed by Sacconi and his coworkers actively working in this area since the late seventies will be summarized and some of the most intriguing results will be highlighted and compared with recent breakthrough achievements obtained either in Florence and elsewhere.

Apart presenting these interesting results, this communication is aimed at paying homage to a handful of talented scientists who have contribute to this great adventure.

Dedicated to the indelible memory of my Friends and Colleagues Piero Stoppioni (1944 – 2014), Massimo Di Vaira (1940 - 2011) and Stefano Midollini (1942 – 2012) who educated me to love experimental synthetic phosphorus chemistry.

Thanks are expressed to Fabrizio Mani (University of Florence) for sharing with me some precious memories of the inorganic school of Florence and to the "Fondazione Sacconi" (Sesto Fiorentino, FI) for keeping alive the vivid memory of that time in Florence.

INO-O16

New Ge-rich polar intermetallics with 2D and 3D covalent structural motifs

S. De Negri[a], *P. Solokha*[a], *A. Saccone*[a], *D.M. Proserpio*[b]

[a]*Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Genova, Via Dodecaneso 31,16146, Genova, Italia*
[b]*Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milano, Italy*

serena.denegri@unige.it

Zintl and polar intermetallic phases, whose components are electropositive metals and electronegative elements around the "Zintl line", are intermediate among metallic, ionic and covalent solids. These compounds represent a scientific challenge from the point of view of structure and chemical bonding description [1]. Moreover they often show interesting electric and magnetic properties, making them suitable for applications as superconductors, thermoelectric materials and enhanced magnetocaloric materials [2].

In this context we have been studying for some years the formation, crystal structure and chemical bonding of ternary germanides containing a rare earth element (R) and a metal (M) of the *s* or *d* block [3]. Recent results on such compounds are presented here, focusing on Ge-rich representatives of formulae R_2MGe_6 (*oS*72–$Ce_2(Ga_{0.1}Ge_{0.9})_7$ or *mS*36–La_2AlGe_6 structure type) and R_4MGe_{10-x} (*mS*60-$La_4MgGe_{9.63}$ structure type) with M = Mg, Zn, Pd. The structure of these compounds is formed by topologically similar extended two- and three-dimensional Ge covalent fragments interconnected by M atoms to form a framework whose channels are filled by R atoms. Electronic structure calculations suggest that the M atoms participate in covalent bonding with Ge.

The existence of such phases is influenced by the nature of R and M, which is also responsible for subtle structural changes, generally not affecting the Ge-Ge distances and the shape of their covalent fragments, but leading in some cases to different crystal structures. The interplay between composition and crystal chemistry in these series of compounds will be particularly discussed.

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INO-O17

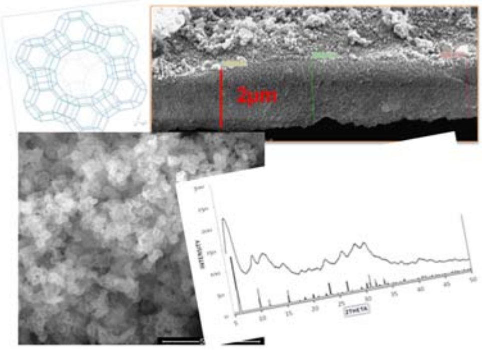
Soft synthesis of FAU nanozeolites and microporous membranes.

Teresa F. Mastropietro[a], *Enrico Drioli*[a,b], *Teresa Poerio*[b]

a Department of Environmental and Territorial Engineering and Chemical Engineering,
University of Calabria, Via P. Bucci, 87036, Rende, Italy
b National Research Council, Institute for Membrane Technology (ITM–CNR) c/o University
of Calabria, Via P. Bucci,87036, Rende, Italy

teresafina.mastropietro@gmail.com

Nanozeolites exhibit valuable properties and superior performances with respect to conventional zeolite materials. [1] In addition, their assembling into hierarchically structured materials and thin films opens the route to novel applications, such as reactive membranes and smart devices. Recently, we have developed an alternative strategy to the conventional seeded-assisted synthesis of Faujasite (FAU) nanozeolites and for their assembling into thin films on ceramic substrates. [2] Nanocrystals with uniform particle size have been produced in high yield in “soft condition”, at near ambient temperature and in absence of organic SDAs, by using supported seeds as structure directing agent. The XRD patterns collected on the samples show the structural features of a FAU(Y) phase. The mean particle size was determined by SEM and DLS, with similar results in the range of 35-60 nm. Besides, continuous microporous thin films, suitable for selective membrane preparation, have been obtained by the *in-situ* assembling of the nanozeolites on α-Al_2O_3 supports. The method can be easily extended to other zeolite topologies and offers good opportunities for industrial applications.



Research partially funded by FP7/2007-2013 under DEMCAMER project (NMP3-LA-2011-262840).

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INO-O18

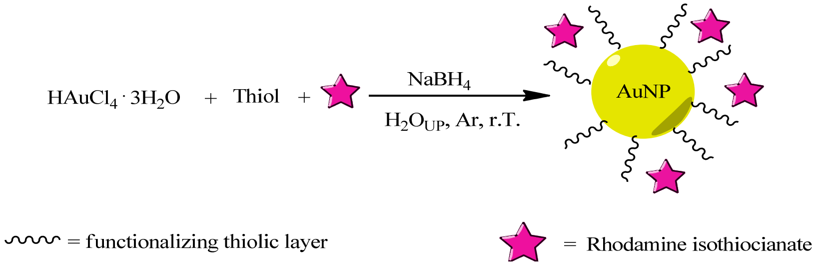
Functional Gold Nanoparticles for biomedical applications

Iole Venditti,[a] *Ilaria Fratoddi,*[a,b] *Francesco Porcaro,*[c] *Chiara Battocchio,*[c]
Giovanni Polzonetti,[c] *Maria Vittoria Russo*[a,d]

[a] *Dpt. of Chemistry, Univ. of Rome Sapienza, P.le A. Moro 5, 00185 Rome, Italy*
[b] *Center for Nanotechnology for Engineering (CNIS), Univ. of Rome Sapienza, P.le A. Moro 5, 00185 Rome, Italy*
[c] *Dpt. of Physics, Unita INSTM and CISDiC Univ. Roma Tre, Via della Vasca Navale 85, 00146 Rome, Italy*
[d] *Center for Protection of Environment and Cultural Heritages (CIABC) Univ. of Rome Sapienza, P.le A. Moro 5, 00185 Rome, Italy*

iole.venditti@uniroma1.it

Nanostructured materials are particularly interesting due to their high surface area-to-volume ratio and synergetic effects, which are promising for energy, medicine, optics, and sensing applications.[1-4] In particular gold nanoparticles (AuNPs) are promising materials as drug delivery systems. In this work we present the results recently obtained for the development of water-soluble gold nanoparticles stabilized with hydrophilic ligands: a dye is bonded on particles, in order to obtain dye doped systems, in analogy to polymeric systems.[5]



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INO-O19

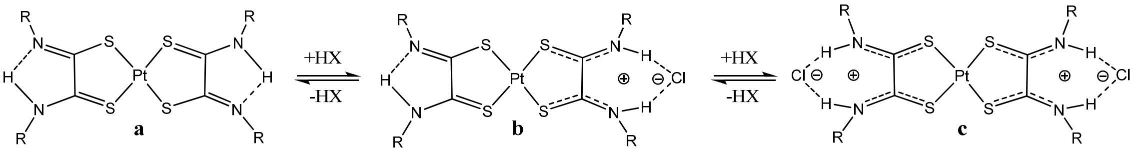
Acid-base behavior of platinum(II) complexes capable to work as carriers of strong acids through bulk liquid membrane.

A.Giannetto, I.Ielo, F.Puntoriero, S.Lanza, S.Campagna

Dipartimento di Scienze Chimiche, Università di Messina Via F Stagno D'Alcontres, 31 98166, Messina, Italy

giannettoa@unime.it

Platinum(II)-bis-dithioxamidate neutral complexes [Pt(HR_2DTO)$_2$] (**a**) link HX strong acids through =N-H---N= system so forming tight ion pairs {([(H_2R_2DTO)Pt(HR_2DTO)]$^+$),(Cl^-)} (**b**) {([Pt(H_2R_2DTO)$_2$]$^{2+}$),(Cl^-)$_2$} (**c**).



When a chloroform solution of (**a**) is put into contact with a concentrate aqueous solution (≥ 1 M) of HX (X = Cl^-, Br^-, I^-, SCN^-, picrate, perchlorate, nitrate, trichloroacetate, trifluoroacetate), it sequentially takes two molecules of HX per mole of (**a**), so transferring HX molecules from the aqueous to the organic phase.

In turn, when a chloroform solution of (**b**) or (**c**) is put into contact with distilled water, HX is transferred from organic phase to water, so that (**a**) species are restored. Then, as one can expect, when a chloroform solution of (**a**) is placed as a bulk liquid membrane between an aqueous solution of HX (source) and distilled water (receiver) in a U tube, HX is carried by the platinum complex through the liquid membrane.[1]

For a deep understanding of the transport mechanism, we undertook a systematic study of the acid-base properties of (**a**), (**b**) and (**c**) species.[2] Here we study temperature effects on the reactions of (**b**) and (**c**) with some nitrogen bases and of (**a**) and (**b**) with hydrochloric acid. We found that the equilibrium constants of the studied processes depends mainly on the entropic variations on going from neutral species (**a**) to (**b**) and (**c**) ion pairs and *vice versa*. This is in agreement with the fact that HX is in a fast exchange among the basic sites of the complex and solvent. As a consequence, when HX is hosted on the complex, solvent molecules around the ion pairs possess a higher degree of organization, so reaching a lower entropy level. This finding is in agreement with the observed increase of local density of the solution during the transportation process. A mechanism based on HX hopping, mediated by solvent, is proposed to explain the transport ability of (**a**).

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INO-O20

Tetraarilporfirine per DSC: effetto dei gruppi ingombranti e dello spaziatore

G. Magnano[a], *G. Di Carlo*[a], *A. Orbelli Biroli*[b], *F. Tessore*[a] *e M. Pizzotti*[a]

a Dipartimento di Chimica, Università di Milano, Via Golgi 19, 20133, Milano, Italia
b Istituto di Scienze e Tecnologie Molecolari del CNR, Via Golgi 19, 20133, Milano, Italia

giulia.magnano@unimi.it

Ad oggi le migliori efficienze per i dispositivi DSC sono state ottenute utilizzando Zn^{II} diarilporfirine di tipo *push-pull* sostituite in posizione *meso*;[1] tuttavia le loro sintesi prevedono molti passaggi che ne riducono drasticamente le rese di produzione.[2] Al contrario, le tetraaril porfirine sostituite in posizione *β* pirrolica sono facilmente ottenibili mediante procedure sintetiche semplici ed efficienti e sono caratterizzate da buone prestazioni di cella.

Recentemente, abbiamo ottimizzato una procedura sintetica per la sintesi di Zn^{II} tetraarilporfirine sia mono che disostituite in posizione *β* pirrolica con sostituenti etinilarilici, ottenendo, per la prima volta, porfirine *push-pull* disostituite in posizione *β*. Tali sensibilizzatori, nelle stesse condizioni di assemblaggio dei dispositivi DSC, hanno raggiungono efficienze di conversione luce-energia paragonabili o migliori rispetto ad alcune Zn^{II} porfirine *push-pull* disostituite in posizione *meso*.[3]

Qui presenteremo l'effetto pancromatico[4] ottenuto introducendo, mediante diversi spaziatori π delocalizzati, un'unità ditieniletilenica in posizione *β* pirrolica a Zn^{II} tetraarilporfirine. Inoltre discuteremo come l'inserzione di lunghe catene alcossiliche in posizione diversa sugli anelli fenilici possa limitare i fenomeni di aggregazione e di ricombinazione di carica, migliorando le efficienze.[5]

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INO-O21

Thermoelectric properties of n-doped Mg_2Si

A. Famengo[a], *S. Boldrini*[a], *S. Battiston*[a] *S. Fiameni*[a] ,*T. Sakamoto*[b,] , *A. Ferrario*[a], *M. Fabrizio*[a]

a Istituto per l'Energetica e le Interfasi IENI-CNR Corso Sati Uniti 4, 35129 Padova, Italy
b Japan Society for the Promotion of Science JSPS, Japan

a.famengo@ieni.cnr.it

Heat from different sources can be converted into electricity by thermoelectric materials. In order to widen thermoelectric energy conversion for large scale current generation or waste heat recovery application, Mg_2Si and related alloys are appealing candidates as thermoelectric materials in the middle-high temperature range[1]. They are characterized by low toxicity, high abundance of the constituent elements and low densities compared to PbTe or $CoSb_3$ used in the same temperature range (500-850K) [2]. The efficiency of a TE material is related to its figure of merit **$ZT=\alpha^2T/(\rho\kappa)$** where α is the Seebeck coefficient, ρ the electrical resistivity and κ the thermal conductivity. The thermoelectric performance can be improved by doping of the Mg_2Si matrix with heavier elements such as Bi or Sb. This results in higher electrical conductivity and lower thermal conductivity. In this work, Bi- and Sb –doped Mg_2Si are obtained by solid state synthesis starting from commercial raw Mg_2Si or element melting. The powders are consolidated into dense pellets (95% of bulk density) by spark plasma sintering. The thermal and electrical conductivity and the Seebeck coefficient are evaluated in the temperature range RT-600°C. The influence of the synthesis conditions is discussed in term of thermoelectric properties of materials.

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INO-O22

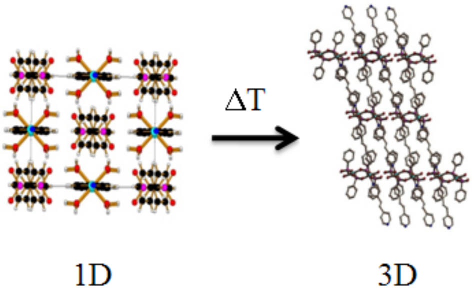
On the Transformation of 1D Coordination Polymer in 3D Network

Andrea Ienco[a], Thierry Bataille[b], Maria Caporali[a], Ferdinando Costantino[a,c], Annalisa Guerri[d], Marco Taddei[c]

a Consiglio Nazionale delle Ricerche, Istituto di Chimica dei Composti Organometallici, Via Madonna del Piano 10, 50019 Sesto Fiorentino (FI), Italy; b Sciences Chimiques de Rennes (UMR 6226) CNRS, Université de Rennes 1, Avenue du General Leclerc 35042 Rennes Cedex, France; c Department of Chemistry, University of Perugia, Via Elce di Sotto 8, 06123 Perugia, Italy; d Department of Chemistry "Ugo Schiff", University of Florence, via della Lastruccia 13, 50019 Sesto Fiorentino Italy

andrea.ienco@iccom.cnr.it

In the last years, we reported several 1D, 2D and 3D coordination polymers based on diphosphinic acid.[1] Here we will discuss the different behavior induced by the temperature of the 1D iso-structural $[Ni(H_2O)_4(bipy)\cdot pc_2p]_n$, **1**, and $[Ni(H_2O)_4(bpye)\cdot pc_2p]_n$, **2** ($pc_2p$= P, P'-diphenylethylenediphosphate; bipy = 4,4' bipyridine, bpye = 1,2-bis(4-pyridyl)ethane).
While in the case of **1**, no crystalline anhydrous phase was obtained, for **2**, the monohydrated $[Ni(H_2O)(bpye)pc_2p]_n$ 3D phase, **3**, and the crystalline anhydrous $[Ni(bpye)pc_2p]_n$ phase, **4**, could be isolated varying the temperature.



This result will be interpreted looking at supra-molecular interactions between the aromatic rings in competition with the other factors (hydrogen bond, solvent, metal geometry) that can influence the formation of the crystals in the solid state.

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INO-O23

First chromonic Silver (I)-based liquid crystals

Bárbara Sanz Mendiguchía[a], *Daniela Pucci*[a], *Elisabeta I. Szerb*[a], *Alessandra Crispini*[a], *Caterina M. Tone*[b], *Federica Ciuchi*[c]

a LASCAMM CR-INSTM Unità della Calabria, Dipartimento di Chimica e Tecnologie Chimiche - CTC, Università della Calabria, Via P. Bucci Cubo 14C , 87036, Arcavacata(CS), Italy
b Dipartimento di Fisica, Università della Calabria, Via P. Bucci Cubo 33B , 87036, Arcavacata(CS), Italy
c IPCF-CNR UOS Cosenza c/o Dipartimento di Fisica, Università della Calabria, Via P. Bucci Cubo 33B , 87036, Arcavacata(CS), Italy

barbara.sanz@unical.it

Chromonics are a very interesting class of lyotropic liquid crystals (LLC), wich have become in the last years an important research topic in several domains[1].

The mayority of chromonic liquid crystals (CLC) reported to date are based on organic systems[2]. However, few metal complexes have also been shown to form CLC phases[3,4]. Because the possibility of higher oxidation states and different coordination geometries, metal complexes offer new opportunities for the design of original CLC mesophases. This renders metal complexes advantegous over their organic counterparts, offering also interesting and advantageous functionalities, like intringuing spectroscopic, catalytic and redox properties.

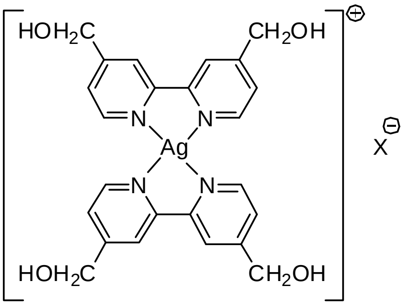

Figure 1. Proposed structures for the Ag(I) complexes 1 and 2 where X represents: CH_3COO- and CH_3CH_2COO- respectively.

Herein, we report the synthesis and characterization of the first Ag(I) complexes spontaneously self-assembled into liquid crystalline chromonic phases in water. The proposed structure of the Ag(I) complexes is presented in Figure 1. These complexes organize into nematic and hexagonal phases in water as a function concentration and/or temperature. Their phase diagram will be presented.

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INO-O24

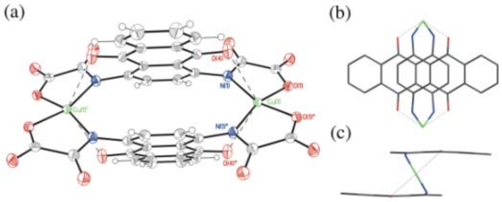
Dicopper(II) Metallacyclophanes as Prototypes of Multifunctional Magnetic Devices

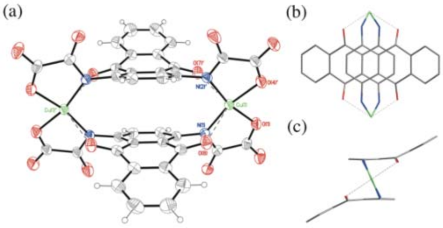
D. Armentano,[a] *G. De Munno,*[a] *M. Castellano,*[b] *M. Julve,*[b] *F. Lloret,*[b] *R. Ruiz-García,*[b] *J. Cano,*[b] *Y. Journaux.*[c]

[a] *Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, 87030 Cosenza, Italy.*
[b] *Instituto de Ciencia Molecular (ICMol), Universitat de València, 46980 Paterna, València, Spain.*
[c] *Institut Parisien de Chimie Moléculaire, UPMC Univ Paris 06, 75252 Paris, France.*

donatella.armentano@unical.it

Metallasupramolecular complexes represent an important advance in molecular spintronics and a useful platform in the development of active components of spintronic circuits and quantum computers for future applications in information processing and storage. The work here presented is an extension of our group's research on the chemistry and physics of dicopper(II) metallacyclic complexes with oxamato-containing dinucleating ligands having potential redox- and photoactive aromatic spacers.[1] Based on these exploratory studies, revealing a strong structure-properties relationship, we can suggest that exchange-coupled dicopper(II) anthraquinophanes can act as effective multielectron reservoirs for oxidation and reduction, offering thus a new design concept for the development of a novel class of charge storage molecular spintronic devices, referred to as molecular magnetic capacitors (MMCs).





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INO-O25

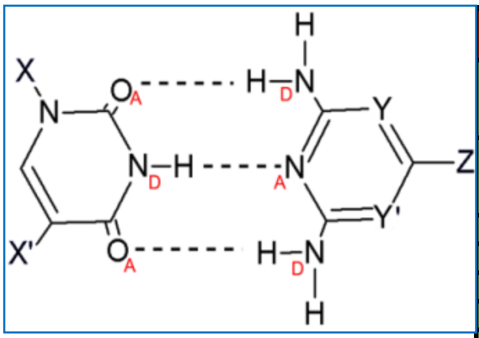
Halogen Bonding in 5-Halonucleobases and in their *Janus*-like cocrystals

G. Portalone[a]*, S. Irrera*[a] *and K. Rissanen*[b]

[a]*Department of Chemistry , 'Sapienza' University, P.le A. Moro 5, I-00185 Rome, Italy*
[b]*Department of Chemistry, University of Jyväskylä, 40014 Jyväskylä, Finland*

gustavo.portalone@uniroma1.it

5*X'*-derivatives (DM*X'*U; *X'* = F, Br, I) of *N*,*N*-dimethyluracil (DMU) and their mixed cocrystals are ideal candidates to ascertain the critical role of halogen bonding (XB) for crystal engineering of *DNA/RNA* bases [1] lacking strong hydrogen bond donors. Five new crystal structures were obtained: DMFU, DMBrU, DMIU, DMFU/DMU and DMBrU/DMIU, of which three manifest XB. The focus of the current work was then expanded to investigate the potential of the XB in planning cocrystals of *DNA/RNA* bases with amino-derivatives of aromatic *N*-heterocycles (Apys), as in the carbon-rich Murchison and Orgueil meteorites low ratio of uracil, thymine and *s*-triazine (ammeline and melamine) were identified. To explore *s*-triazines, which share high structural homology with *DNA/RNA* purine bases, as mimics of prebiological nucleobases, we synthesized cocrystals of 1,5-substituted uracils with appropriate Apys able to realize specific supramolecular interactions in *WC* fashion [2]. 20 cocrystals were examined to test the robustness of the (ADA/DAD) heterosynthon (Fig. 1): invariably, the hydrogen-bonding pattern of Apys complements the *WC* face of nucleobases, mostly in the so-called "*Janus*" fashion. In five cocrystals XBs influence the overall structure organization.



Y, Y', Z ***X, X'***	***N, N, NH₂***	***N, CH, NH₂***	***CH, CH, H***
H, H	1(ADA/DAD)[3] 1(ADA/DAD)[a] 3(ADA/DAD)[a]	1(ADA/DAD)	Not obtained
H, CH_3	3(ADA/DAD)[b]	1(ADA/DAD) 1(ADA/DAD)[a] 1(ADA/DAD)[b]	Not obtained
H, C_2H_5	1(ADA/DAD)[b]	Not obtained	Not obtained
CH_3, H	3(ADA/DAD)	2(ADA/DAD)	1(ADA/DAD)
H, F	1(ADA/DAD)	Not obtained	1(ADA/DAD)[b]
H, Br	1(ADA/DAD)[a]	2(ADA/DAD)[c]	Not obtained
H, I	2(ADA/DAD)[a]	2(ADA/DAD)[a]	1(ADA/DAD)[b]
CH_3, Br	Not obtained	2(ADA/DAD)	Not obtained

Fig. 1: Two-component cocrystals of 1,5-substituted uracils and Apys. Hydrogen/halogen - bonded cocrystals. a) Hydrated. b) DMF solvated. c) DMF/water solvated; amphoteric XB.

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INO-O26

Synthesis, Structure and Antiproliferative Activity of Novel Ru(II)-Arene Complexes with N,O- and O,O-Chelating Ligands

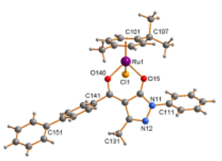
C. Pettinari[a], *R. Pettinari*[a], *F. Marchetti*[b], *F. Condello*[a], *J. Palmucci*[a], *A. Petrini*[a], *S. Orbisaglia*[a], *Paul J. Dyson*[c]

a School of Pharmacy, University of Camerino, Camerino, 62032, Italy.
b School of Science and Technology, University of Camerino Camerino, 62032, Italy.
cInstitut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland.

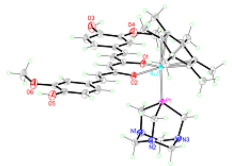
claudio.pettinari@unicam.it

Organometallic compounds are attracting a considerable interest in medicinal chemistry, especially as putative anticancer compounds.1 Of particular interest are ruthenium arene compounds which have been extensively studied and modified to give compounds with various therapeutic effects. As a continuation of previous works on N,O- and O,O-chelating ligands,3 we have investigated how variations in the arene and the chelating ligand influence the electronic, structural, and cytotoxic properties of such complexes and studied their aqueous solution chemistry. Our attention has focused also on ruthenium(II)-arene complexes combined with the 1,3,5-triaza-7-phosphaadamantane (PTA) ligand. We present here the spectroscopic and crystallographic aspects of the new compounds in combination with biological in vitro cytotoxicity assays and hydrolysis studies.

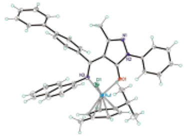
Acylpyrazolones



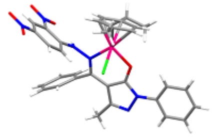
Curcuminoids



β-Ketoamines



Hydrazones



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INO-O27

Interconversion of CO_2 to Formic Acid Using Rhodium-Substituted Carbonic Anhydrase as First Cofactor-Independent Reductase

Paolo Piazzetta[a], *Tiziana Marino*[a], *Nino Russo*[a], *Dennis R. Salahub*[b]

a Dipartimento di Chimica, Università della Calabria, Via Pietro Bucci, 87036, Arcavacata di Rende, Italia

b Institute for Biocomplexity and Informatics, Department of Chemistry, University of Calgary,
2500 University Drive NW, Alberta, Canada

paolo.piazzetta@unical.it

The improvement of the enzymatic specificity, making enzymes able to catalyze new, sometimes unnatural, reactions is a promising frontier in biocatalysis. In this context, the natural activity of some enzymes can be enriched by using several strategies to expand reaction specificity. Carbonic Anhydrase (CA) plays a key role in enzymatic catalytic processes owing to its natural promiscuity toward several substrates. Despite its strong catalytic ability, CA is not able to reduce organic molecules and it can't work as hydrogenase. To bridge this gap one of the new approaches is to replace the native metal ion (Zinc) with rhodium making CA the first cofactor-independent reductase that reduces organic molecules using hydrogen. [1][2] This possibility suggested the exploitation of the natural affinity of CA for CO_2 in order to define a new hydrogenation process of CO_2 to formic acid opening an innovative perspective for an efficient chemical reduction of carbon dioxide. In order to obtain the potential energy surface of the hydrogenation mechanism by rhodium substituted CA (Rh-CA), a computational study at density functional theory level has been undertaken. Our investigation showed how Rh-CA acts as efficient reductase confirming that biological systems are often rising alternatives for chemically difficult conversions.[3]

$$CO_2 + H_2 \xrightarrow[E_{a\,(\mathbf{Rh-CA\ Catalyzed})} = \mathbf{6.4\ kcal\ mol^{-1}}]{E_{a\,(Uncatalyzed)} = 70.1\ kcal\ mol^{-1}} H_2CO_2$$

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INO-O28

A photo- and electroactive shape-persistent tetrahedral molecule constituted by four pyridylpyridinium units

<u>Marianna Marchini</u>, Giacomo Bergamini, Andrea Fermi, Mirko Locritani, Alberto Credi, Margherita Venturi, Fabrizia Negri, Paola Ceroni, Massimo Baroncini

Department of Chemistry "G.Ciamician", University of Bologna, Via Selmi 2, 40126, Bologna, Italy

marianna.marchini2@unibo.it

Pyridinium and bipyridinium chromophores are some of the most extensively studied functional entities by virtue of their photochemical and electrochemical properties. In this contest, we synthesized the tetrahedrally shaped molecule **1**$^{4+}$, containing four pyridylpyridinium units connected via a central carbon atom, that displays good solubility in water[1]. The photophysical and electrochemical properties are not the mere superposition of four pyridilpiridinium monomers **2**$^{+}$: the tetramer displays a strong fluorescence, compared to the weak emission of monomer **2**$^{+}$. The electronic properties of the tetramer can be modulated by acid and redox stimuli. Upon protonation, the emission is strongly quenched and the electrochemical properties approach those of methylviologen. Moreover, the protonated form is able to bind four CB[7] molecules. The resulting species exhibits a revival of the tetramer fluorescence since encapsulation inside CB[7] hinders intra-molecular rotations. Two pyridylpyridinium units of the molecule **1**$^{4+}$ can also be included in CB[8], involving the formation of a supramolecular polymer that precipitate in solution. The same results can be obtained, without macrocycle, by the π-π interaction (pimerization) between two mono-reducted subunits of the protonated molecule.

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INO-O29

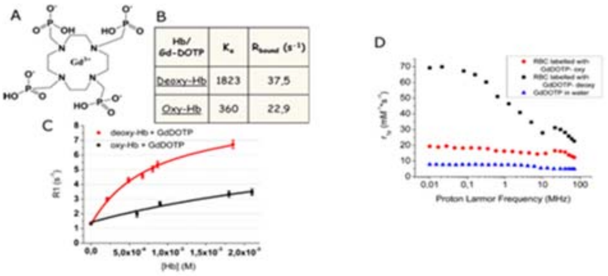
A novel MRI reporter of pO_2 based on a Gd-complex mimicking allosteric effectors of deoxy-Hemoglobin

Enza Di Gregorio, Giuseppe Ferrauto, Eliana Gianolio, Stefania Lanzardo, Silvio Aime

Dipartimento di Biotecnoligie Molecolari e Scienze per la Salute, Università di Torino Via Nizza 52, 10126 ,Torino (IT)

enza.digregorio@unito.it

Assessment of hypoxia is crucial for several major diseases and much attention is currently devoted to the development of imaging probes able to monitor the oxygenation state of tissues. Different methods to evaluate pO_2 have been developed based on the use of different imaging modalities. Herein, the *in vitro* development and *in vivo* application of a novel protocol for hypoxia evaluation by MRI is described. This method relies on the use of Gd-DOTP-labeled Red Blood Cells as probes responsive to the oxygenation state in murine xenograft tumor model and Gd-HPDO3A-labeled RBC as probe reporting on the vascular volume. The application of a ratiometric method to analyze the MR images allows obtaining semi-quantitative measurements of tumor oxygenation state with a high spatial resolution. Relaxometric properties of these agents have been in-depth investigated, by evaluating the binding affinity of the two Gd-compounds towards oxy- and deoxy-Hemoglobin and the enhancement of relaxivity upon binding. Gd-DOTP complex (Fig.1A), thanks to its similarity with the natural allosteric effector 2,3-BPG, displays higher affinity toward deoxy-Hb than oxy-Hb (Fig.1B, C). Moreover, when it is bound to deoxy-Hb, the relaxivity is significantly higher than that observed when Gd-DOTP is free (Fig.1D). Conversely to Gd-DOTP, Gd-HPDO3A does not interact with Hemoglobin. The positive *in vitro* results prompted us to investigate the feasibility of translating *in vivo* this method by administrating consecutively Gd-HPDO3A- and Gd-DOTP-labelled RBCs and applying the ratiometric method to analyze the MRI contrast enhancement. The proposed method can provide direct and quantitative information on the blood vessels volume and semi quantitative maps of oxygenation /deoxygenation level. The evaluation of these two cancer hallmarks can be used for tumor staging and for the evaluation of cancer therapies.



Hb/ Gd-DOTP	K_a	R_{bound} (s^{-1})
Deoxy-Hb	1823	37,5
Oxy-Hb	360	22,9

Fig.1. (A) Structure of Gd-DOTP; B) Ka and R_1-bound values for Gd-DOTP with oxy-or deoxy-Hb;C) Relaxometric Titration of Gd-DOTP with oxy- or deoxy-Hb; D) NMRD profiles of Gd-DOTP-labeled RBCs (oxy and deoxy) and aqueous solution of Gd-DOTP.

INO-O30

The effects of Zinc ion coordination on the $A\beta_{1-42}$ conformational landscape

Adriana Pietropaolo[a], *Enrico Rizzarelli*[b]

a Dipartimento di Scienze della Salute, Università di Catanzaro, Viale Europa, 88100 Catanzaro, Italy
b CNR-IBB UOS di Catania, Via Paolo Gaifami 18, 95126 Catania, Italy

apietropaolo@unicz.it

Amyloid-β protein (Aβ) is one of the main components of senile plaques that are a pathological hallmark of Alzheimer's disease [1]. Several lines of evidences suggest that Aβ can coordinate divalent metal ions such as Zinc and Copper(II) [2]. Low sub-stoichiometric concentrations of divalent metals are suggested to reduce oligomeric stability and protect from aggregation, while higher metal concentrations produce amorphous aggregation [3]. Such formation of amorphous aggregates may protect from oligomer and amyloid formation. Moreover, divalent metals can prevent the formation of active fibrillar structure at a specific stoichiometric ratio of 1:2 Aβ:metal ion [3]. In these regards, Zinc ion has been suggested to affect Aβ aggregation [4] at acidic conditions, which normally indicates inflammatory states, while at physiological pH it suppresses Aβ fibrillogenesis [3]. Intriguingly, at acidic pH the mononuclear coordination site of Zinc ion is the most abundant species [5], while at physiological pH the dinuclear species of Zinc ion result with higher stability [5]. Based on these lines of evidence, we here present a combined DFT and enhanced sampling simulation approach in order to elucidate the conformational landscape of $A\beta_{1-42}$ coordinated with one and two Zinc ions. We found a subtle switch of intramolecular interactions depending on the Zinc coordination environment and on the Aβ:Zinc stoichiometric ratio.

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INO-O31

Cisplatin handover between copper transporters: the effect of reducing agents

A. Galliani[a], M. Losacco[a], A. Lasorsa[a], G. Natile[a], F. Arnesano[a]

[a] Dipartimento di Chimica, Università di Bari ,Via Orabona 4, 70125, Bari, Italia

angelagalliani@libero.it

A growing number of studies reveals that copper (Cu) transporters are involved in the biological response to antitumor platinum (Pt) drugs, which are among the most used chemotherapeutics [1]. The soluble chaperone ATOX1, which brings Cu(I) from CTR1 to the metal binding domains (MBDs) of Cu(I)-ATPases ATP7A and ATP7B, can bind cisplatin (*cis*-$PtCl_2(NH_3)_2$) and participate to the intracellular distribution of Pt-drugs [2]. Also ATP7A and ATP7B can bind and efflux actively Pt-drugs through the vesicles of the trans-Golgi network, hence contributing to the development of tumor cell resistance [3].

Here we report a tandem ESI-MS and NMR spectroscopic characterization of cisplatin binding to ATOX1 and MNK1, the first MBD of ATP7A. In the absence of any reducing agent, we found that Pt binds to the metal binding motif (CXXC) of both proteins, but with significant differences. We also studied the reactivity of these proteins towards cisplatin in conditions mimicking the cellular environment, that is millimolar concentration of the physiological reducing agent glutathione (GSH). It was found that MNK1, but not ATOX1, competes successfully with GSH for binding to cisplatin. Finally, no transfer of cisplatin from ATOX1 to MNK1 occurs in our experimental setting. The latter result appears to be in contrast with literature data reporting the occurrence of such a transfer, although always an exogenous reducing agent, such as tris(2-carboxyethyl)phosphine (TCEP), exerting a strong *trans*-labilizing effect, was present. Our study highlights the complexity of Pt-loading reactions with a special focus on how different platinophiles can influence each other.

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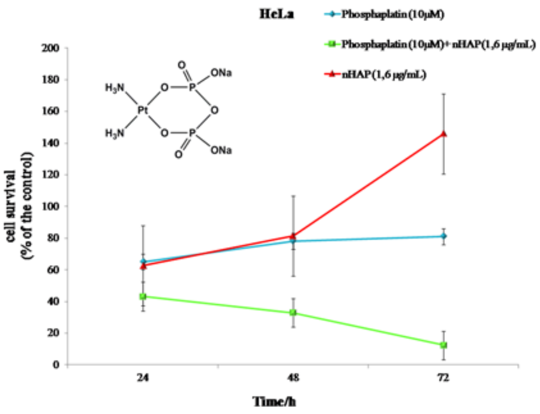
INO-O32

Amplification of cytotoxicity in *phosphaplatins* adsorbed on hydroxyapatite nanocrystals

Michele Benedetti[a], *Federica De Castro*[a], *Chiara R. Girelli*[a], *Danilo Migoni*[a], *Alessandro Romano*[a], *Tiziano Verri*[a], *Marco Lelli*[b], *Norberto Roveri*[b], *Francesco P. Fanizzi.*[a]

[a] *University of Salento - Department of Biological and Environmental Sciences and Technologies - Via Monteroni, 73100 - Lecce, Italy.*
[b] *University of Bologna - Department of Chemistry "G. Ciamician" - Via Selmi 2, 40126 - Bologna Italy.*

michele.benedetti@unisalento.it



Cisplatin, *cis*-[$PtCl_2(NH_3)_2$], and other platinum based drugs are amongst the most active antitumor agents [1]. Recently, *phosphaplatins*, monomeric Pt complexes with phosphates, were studied for their strong antitumor activity even on *cisplatin* resistant cell lines [2]. On the other hand work has shown that hydroxyapatite, [$Ca_5(PO_4)_3(OH)$], nanocrystals (*nHAP*) are internalized in tumour cells by endocytosis, and that many molecules can be adsorbed on *nHAP* [3]. In this context we studied the *in vitro* cytotoxicity (MTT assay), on *Hela* cells, of a *phosphaplatin*, i.e. Na_2{*cis*-[$Pt(NH_3)_2(P_2O_7)$]}, **1**, see Figure, adsorbed on *nHAP*. Interestingly the complex **1**-*nHAP* showed cytotoxicity of about one order of magnitude higher than complex **1** or *nHAP* alone, suggesting the existence of alternative mechanism(s) of uptake and/or cytotoxicity induction, due to the combined action of **1** and *nHAP*, see Figure.

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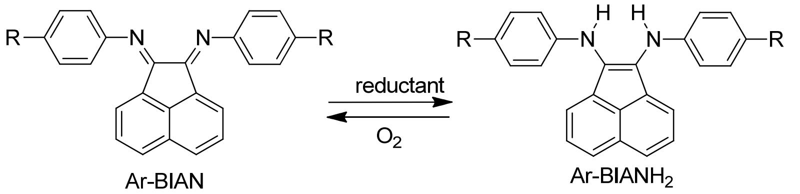
INO-O33

An Unprecedented Trimeric Palladium(0) Complex with Bridging Nitrogen Ligands

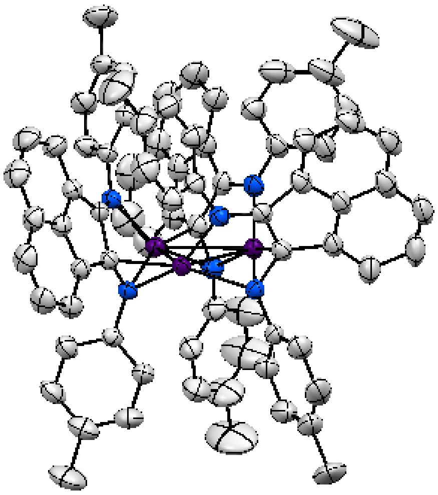
Fabio Ragaini[a], *Francesco Ferretti*[a], *Roberta Gini*[a], *Piero Macchi*[b]

[a] *Dipartimento di Chimica, Università di Milano, Via Golgi 19 , 20133, Milano, Italy*
[b] *Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, CH3012, Bern (CH)*

fabio.ragaini@unimi.it



While studying the deactivation of the palladium catalyst in the CO/styrene copolymerization reaction, we got kinetic evidence for the formation of Pd(Ar-BIAN)(styrene) complexes.[1] We thus attempted preparing such complexes by reacting a Pd(II) precursor in the presence of the olefin and a reduced Ar-BIAN compound of a type recently developed by us.[2] Although the desired complex is apparently intermediately formed, it decomposed to a complex whose identity was independent of the olefin employed. Characterization of this complex by X-ray diffraction showed it to be an unprecedented Pd(0) trimer in which each palladium atom is normally coordinated to an Ar-BIAN molecule (η^1 to both N atoms) and unusually η^2 coordinated to the C=N double bond of another Ar-BIAN molecule, which is in turn normally coordinated to a second Pd atom and so on until the cycle is closed as a trimer.



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INO-O34

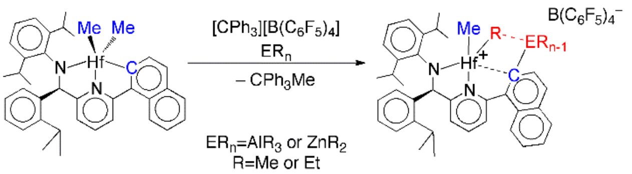
Unusual Hafnium(IV)Pyridylamido – Zn/Al alkyls heterobimetallic adducts

Luca Rocchigiani,[a,c] *Vincenzo Busico,*[b,c] *Antonello Pastore,*[b,c]
Giovanni Talarico,[b] *Alceo Macchioni*[a,c]

a Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia, Via Elce di Sotto 8, 06123, Perugia, Italy
b Dipartimento di Scienze Chimiche, Università di Napoli Federico II, Via Cintia, 80126, Napoli, Italy
c Dutch Polymer Institute (DPI), PO Box 902, 5600 AX Eindhoven, The Netherlands

luca.rocchigiani@progetti.unipg.it

Pyridylamido-Hf(IV)-based organometallic complexes have emerged in the past decade as remarkable catalysts for olefin polymerization having unique properties. Initially reported as the first industrially relevant systems to yield highly isotactic polypropylene with solution-process technology, they attracted even greater attention for their propensity of undergoing reversible chain transfer with main element alkyls (such as AlR_3 and ZnR_2); this can be advantageously used in the preparation of olefin block copolymers via "chain shuttling"[1].



In this contribution, we report the results of an integrated NMR and DFT study aimed at understanding the reactivity of hafnium pyridylamido complexes with dialkylzinc and trialkylaluminium species[2]. Pyridylamido hafnium cations undergo ligand exchange with ZnR_2 or AlR_3 affording unusual heterobimetallic adducts, in which the cyclometallated naphthyl acts a bridge between hafnium and main element. The results of ^1H EXSY NMR experiment, carried out to investigate the dynamicity of such adducts, will be also reported. Finally, we show how the reactivity of the catalyst towards α-olefins is affected by the presence of ZnR_2 or $AlEt_3$.

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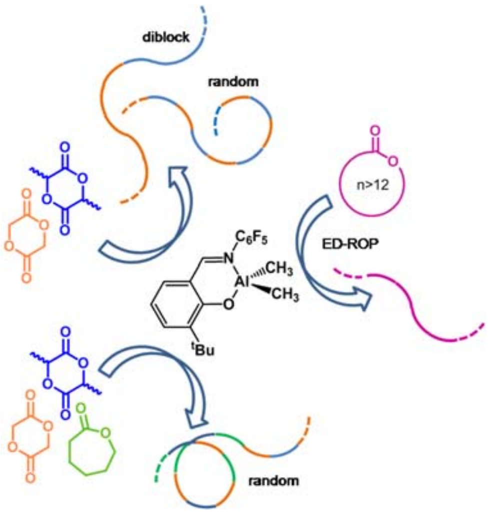
INO-O35

Al-salicylaldiminato Complexes as Versatile Catalysts in the Ring-opening Polymerization of Cyclic Esters

<u>Angelo Meduri</u>[a], Tiziana Fuoco[a], Marina Lamberti[a], Claudio Pellecchia[a], and Daniela Pappalardo[b]

[a] Dipartimento di Chimica e Biologia, Università di Salerno, via Giovanni Paolo II, 13 – 84084 Fisciano (SA), Italy. [b] Dipartimento di Scienze e Tecnologie, Università del Sannio, via dei Mulini, 59/A – 82100 Benevento, Italy.

ameduri@unisa.it



Coordinative ROP is a powerful method to obtain in a controlled manner a wide variety of polymers starting from cyclic lactides and lactones.[1] With an always increasing number of accessible substrates from natural resources[2] there is a call for versatile catalysts apt to (co)polymerize them and unlock the whole potential of ring-opening polymerization.

The designed Al-salicylaldiminato catalysts already proved to be active in the ROP of lactide/ε-caprolactone.[3] Their versatility will be shown to hold also in the glycolide/lactide copolymerization, allowing to obtain random, blocky and diblock copolymers.[4] The effects of the reaction condition, such as temperature, feed and monomer-to-catalyst ratio were assessed. Polymers were characterized by DSC, GPC, and a detailed microstructure analysis was achieved by NMR (^{1}H, ^{13}C, DOSY). Recent experimental results related to the scantly explored glycolide/lactide/ε-caprolactone terpolymerization and to the challenging, entropy-driven, (co)polymerization of macrolactones will be also presented.

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INO-O36

DECORE: A New European Project Aiming at Innovative DEFCs Operating at Intermediate Temperatures

Gaetano Granozzi

Department of Chemical Sciences, University of Padova, Italy

gaetano.granozzi@unipd.it

DECORE (Direct ElectroChemical Oxidation Reaction of Ethanol: optimization of the catalyst/support assembly for high temperature operation) started its activity from January 2013 (four years project). It is a *Small-scale (7 partners) project financed by the EC within the call:* NMP.2012.1.1-1.

The main goal of *DECORE* is to achieve the fundamental knowledge needed for the development of a fuel cell (FC) electrode in acidic ambient, which can operate efficiently as the anode of a direct ethanol (EOH) FC (DEFC) in the temperature range between 150-200 °C (*intermediate*-T). The *intermediate*-T is required for an efficient and selective total conversion of EOH to CO_2. *DECORE* will explore the use of fully innovative supports (oxycarbides) and nano-catalysts (metal carbides, MC_x), never tested in literature as anodes for DEFCs. The new supports are expected to be more durable than standard carbon supports at the targeted temperature. The innovative nano-catalysts would be noble-metal free, so reducing Europe's reliance on imported precious metals. To tailor the needed materials, the active role of the support and nano-catalyst will be studied at atomic level. The Consortium is composed by 5 academic groups (Padova, Coordinator, TUM, Milano-Bicocca, Copenhagen, Laguna, Tenerife), one group from CNR (ICCOM) and one industrial partner (Elcomax GmbH).

The main outcomes from the first 18 months of project will be outlined.

INO-O37

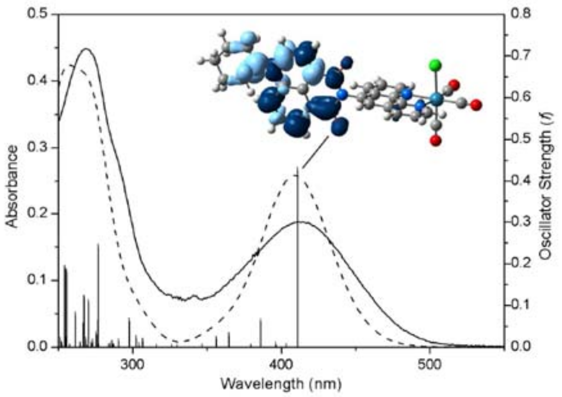
Exploring Organometallic Catalysts for Photo- and Electro-Reduction of CO_2

Carlo Nervi[a], *Federico Franco, Claudio Cometto, Luca Nencini, Cunfa Sun, Roberto Gobetto*

Dipartimento di Chimica e NIS, Università di Torino, Via P. Giuria 7, 10125, Torino, Italy

carlo.nervi@unito.it

Among the worldwide priorities of scientific research the reduction of CO_2 emissions and the quest for a source of sustainable energy occupy a prominent role [1]. There is a great interest in any photo-catalyst able to use the CO_2 as a chemical feedstock to produce the so-called "solar fuels" (possibly in a selective manner). In this contribution we synthesized and characterized several new Re, Mo and W organometallic complexes and evaluated their photo and electro activity towards the reduction of CO_2. Their cyclic voltammetric behaviors under Ar and under CO_2 were evaluated, as well as their catalytic activities during exhaustive electrolysis in CO_2 atmosphere. Several complexes undergoes selective reduction of CO_2 to CO, and their faradic efficiency estimated by quantitative gas chromatography measurements.



Their electro- and photo-catalytic activities were evaluated also in presence of an external source of protons.

Finally, DFT calculation was employed to rationalize the electronic and photophysical properties of the complexes under study.

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INO-O38

$BaCe_{1-x}Zr_xY_{0.15}O_{3-\delta}$ – Y/Gd -Doped CeO_2 cer-cer composites for H_2 separation

Elena Rebollo, Cecilia Mortalò, Stefano Boldrini, Simona Barison, Monica Fabrizio

CNR-IENI Corso Stati Uniti 4, 35127, Padova, Italia

elena.rebollo@ieni.cnr.it

Hydrogen separation from syngas at high temperatures (≥600°C) is one of the most important H_2-producing technologies and it has attracted wide interest in the last decades. Mixed ionic-electronic conductivity (MIEC) ceramic materials have received considerable attention due to their potential application as separation membranes in this kind of processes [1]. In MIEC membranes, the separation and transport of hydrogen occurs in the form of protons and electrons. In a non-galvanic mode, the membrane must have both electronic and proton conductivities [2]. Y-doped $BaCe_{1-x}Zr_xO_{3-\delta}$ (BCZY) perovskite oxides are promising candidates for the development of such membranes because they combine the high proton conductivity of barium cerates with the chemical stability of barium zirconates in CO_2- containing atmospheres, such as syngas conditions [3]. However, the electronic conductivity exhibited by these materials may be not sufficient to work as H_2 separation membranes. The performances of BCZY in this field can be improved by adding a second electronic conductor phase [2]. To this end, in this work, $BaCe_{1-x}Zr_xY_{0.15}O_{3-\delta}$ –$Ce_{1-y}M_yO_{2-\delta}$ (x=0.2, 0.3; y=0.15, 0.20; M=Y, Gd) cer-cer composites have been prepared and studied. Indeed, the addition of doped ceria should increase electronic conductivity in reducing atmospheres. The final purpose is to prepare symmetric dense membranes based on these cer-cer systems. The optimal composition, preparation and sintering conditions of the composites have been studied based on density, XRD, SEM and OM results. The chemical stability versus CO_2 and the electrical conductivity of the composites are presently under investigation. H_2 permeation tests on the dense membranes are programmed in the near future.

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INO-O39

Hematite photoanodes modified with a Fe(III) water oxidation catalyst

Nicola Dalle Carbonare [a], *Stefano Caramori* [a], *Carlo Alberto Bignozzi* [a]

[a] *Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Ferrara, Via Fossato di Mortara 17-27, 44121, Ferrara, Italia.*

dllncl@unife.it

Splitting water into H_2 and O_2 using solar irradiation could be in future a real 'eco-friendly' way to produce fuels for different applications. The possibility to convert solar energy not directly into electricity (Photovoltaic cells) but in chemical bonds represents an attractive way to exploit the immense power of the sun, giving us a necessary tool to reduce the dependence of our society from fossil fuels.

Photoelectrochemical cells (PEC) are made by at least one photoactive electrode immersed in an electrolyte solution that, upon light absorption, is able to generate electron/hole pairs (respectively in the Conduction and Valence Band) and use them to drive water reduction (photocathode) and oxidation reaction (photoanode). Among various candidates to achieve photoinduced water splitting (e.g. WO_3,[1] TaON[2]), hematite (α-Fe_2O_3) has attracted a lot of interest as a cheap photoanodic material, due to its band gap of ca. 2.2 eV, to the correct position of its Valence Band with respect to the H_2O/O_2 potential and to its high stability to photocorrosion in basic medium.

Driven by previous results obtained from our group in efficient hydrogen production with 3J cells modified with Fe(III) compounds,[3] we have performed an exhaustive investigation of hematite photoanodes produced with a simple hydrothermal method and functionalized with an amorphous Fe(III) water oxidation catalyst by SILAR method (Successive Ionic Layer Adsorption and Reaction).[4] The DC photoelectrochemical characterization revealed an evident improvement in the photoanodic activity of electrodes in the presence of the catalyst (Fe-OEC) and Electronic Impedance Spectroscopy (EIS) gave us key information about the dynamics of charge transfer at the interface between the solution and the modified hematite surface.

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INO-O40

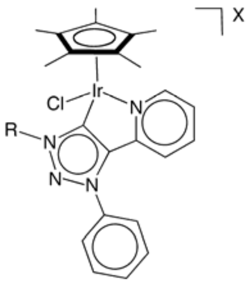
Dramatic Effect of *Me* to *Oct* Substitution in the Activity of Pyridine-Carbene Iridium Water Oxidation Catalysts

Ilaria Corbucci,[a] *Ana Petronilho,*[b] *Helge Müller-Bunz,*[b] *Luca Rocchigiani,*[a]
Martin Albrecht,[b] *Alceo Macchioni*[a]

[a]*Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia, Via Elce di Sotto 8,06123, Perugia, Italia*
[b]*School of Chemistry and Chemical Biology, University College Dublin, Belfield, Dublin 4, Ireland*

alceo.macchioni@unipg.it

The realization of an efficient apparatus for artificial photosynthesis, aimed at producing solar fuels, is strongly hampered by the difficulty of oxidizing water. Several iridium complexes demonstrated to be competent catalysts for water oxidation [1], including those based on pyridine triazolyl-carbene N,C-ligand [2]. It starts to be evident that the catalytic activity may strongly depend on a small modification of the "ancillary" ligands. In this respect, herein we show that changing R group from methyl (**1**) to octyl (**2**) (Figure), causes a dramatic alteration of the catalyst performance when water oxidation is driven by CAN (cerium ammonium nitrate). Particularly, the maximum TOF measured for **2** is remarkable (168 min^{-1}) and about one order of magnitude higher than that of **1** (16 min^{-1}). *In situ* NMR studies [3], performed to shed some light on catalyst transformation during catalysis, are also discussed in this contribution.



[1] A. Savini, et al. *Eur. J. Inorg. Chem.*, 2014, 690 and reference therein.
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INO-O41

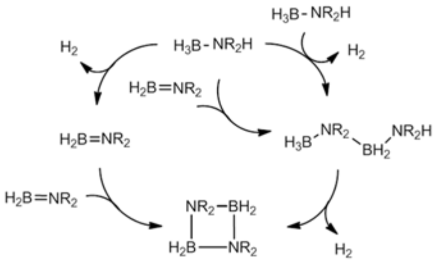
Theoretical insights into amine-boranes dehydrocoupling mechanisms

Valeria Butera[a], *Nino Russo*[b], *Ida Ritacco*[b], *Emilia Sicilia*[b]

a Dipartimento di Scienze dell'Ambiente e del Territorio e di Scienze della Terra, Piazza della Scienza 1, 20126,Milano, Italy.
b Dipartimento di Chimica e Tecnologie Chimiche, Universita` della Calabria, Via P. Bucci 87036 Arcavacata di Rende (CS), Italy.

valeria.butera@unimib.it

The coordination chemistry of amine–boranes is an area of significant current interest, due to the their potential use as chemical hydrogen storage vectors alongside the production of new inorganic polymers. Although a variety of transition metal systems has been found able to release hydrogen and give polymeric materials of useful molecular weight and polydispersities, mechanistic aspects of the involved dehydrogenation and dehydrocoupling reaction mechanisms are still unclear. In this nuanced context, complementarity between experimental and theoretical investigations is indispensable. While experimental studies give considerable information about the reaction products, computational explorations are very helpful to disentangle the involved mechanistic details, providing reliable insight into the overall mechanism of dehydrocoupling. In this context, several transition metal complexes based on Rh, Ir, Pd and the more cost-effective Fe have been investigated using Density Functional Theory. Our detailed investigations have contributed to shed light on the manifold dehydrogenation/dehydrocoupling scenario.



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INO-O42

Effect of space confinement in the assembly of diblock copolymers

S. Piotto [a], S. Concilio [b], P. Iannelli [a]

[a] Dipartimento di Farmacia, Università di Salerno, Via Giovanni Paolo II, 132, 84084 Fisciano (SA), Italia
[b] Dipartimento di Ingegneria Industriale, Università di Salerno, Via Giovanni Paolo II, 132, 84084 Fisciano (SA), Italia

piotto@unisa.it

The most accurate method of calculating the dynamics of a many molecules system is to integrate the Newton equations of motion for all the atoms assuming a certain potential energy function, i.e. a force field. This is inadequate for many chemical processes that occur on microsecond, or longer, timescales.

The dynamic mean-field density functional method, driven from the generalized time-dependent Ginzburg–Landau (TDGL) equation, is here applied for the investigation of the dynamics of block copolymer melts in three-dimensional lattice model. The analysis of the aggregates and their temporal evolution is studied in free space (PBC) and in confined space.

The aim of the present contribution is to investigate the aggregation process of block copolymers in a confined space (1-2). We demonstrate the role of physical rules in determining blend morphology and we consider the implications in protein folding.

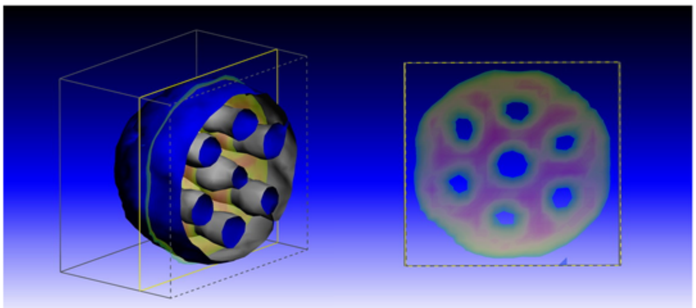

Figure 1 - Segregation in a spherical confinement

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INO-O43

Photoluminescent pigments: effect of doping agents

Gigliola Lusvardi[a], *Gianluca Malavasi*[a], *Ledi Menabue*[a], *Marco Smargiassi*[a], *Bright Materials Company*[b]

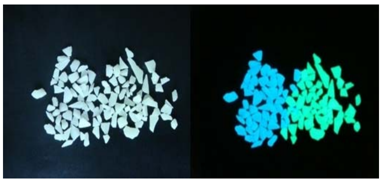
a Dipartimento di Science Chimiche e Geologiche, Università di Modena e Reggio Emilia,
Via G.Campi 183, 41125, Modena
b Via Brennero, Domegliara, Verona [b]

gigliola.lusvardi@unimore.it

Photoluminescent pigments are a type of long decay phosphors that utilizes activating agents to improve its properties. Since its invention, these long lasting phosphors have been greatly improved; particularly, the research focused on rare earth doped aluminates and silicates whose properties and stability were superior to those of sulfide series products, the main long lasting materials studied before.

This contribution is related to the characterization of rare earth activated strontium aluminates with a careful evaluation of the best conditions of synthesis and of the starting materials (e.g., Al/Sr molar ratio, rare earths to Sr molar ratios and amount of fluxing agents).

The morphology, structure (identification of crystalline phases and its stability) and luminescent properties of these samples were investigated by means of scanning electron microscopy, X-ray diffraction and fluorescent spectrophotometry.



Our results indicate that it is possible obtain blue-emitting photoluminescent pigments with new improved properties in term of intensity of emission and persistence during the time.

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INO-O44

Tuning of luminescence in Ir(III) ionic complexes and their soft salts

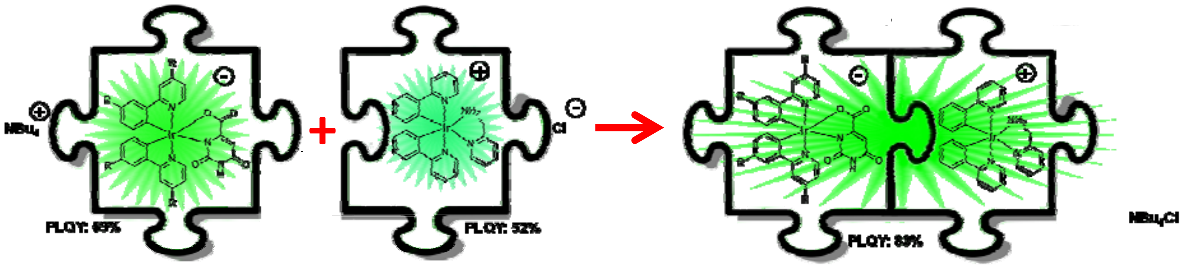
Andreea Ionescu,[a] Elisabeta Ildyko Szerb,[a]

Anna Maria Talarico,[a] Mauro Ghedini[a] and Nicolas Godbert[a]

[a] Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria,
Via P. Bucci , Cap 87036, Rende (CS), Italia

andreea.ionescu@unical.it

Since the pioneer work of Pei *et al* on light emitting electrochemical cells.[1] ionic luminescent Ir(III) complexes have received a particular attention as well as, more recently, their corresponding ion-paired cationic and anionic complexes (or soft salts). While research on cationic Ir(III) complexes accounts already for a rather wide number of examples, only few cyclometallated anionic Ir(III) complexes have been reported so far. In addition, these anionic species feature scarce stability in devices.
In this work, in an attempt to extend the class of anionic Ir(III) complexes available and obtaining more stable emitters, new series of anionic Ir(III) bearing bidentate ligands have been synthesized [2],[3] and will be presented.
Taking advantage of the high stability of these newly luminescent anionic Ir(III) complexes, homometallic soft salts featuring high emission quantum yields have been obtained. An energy transfer mechanism between the two differently charged species allows fine tuning and enhancement of the luminescent properties of the resulting materials.



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INO-O45

The carbothermal transformation of TiO_2 into TiO_xC_y: tracking intrinsic and electrochemical stabilities

Laura Calvillo[a], Stefano Agnoli[a], Marco Favaro[a], Celine Rüdiger[b], Carlos Valero-Vidal[b], Julia Kunze-Liebhäuser[b] and Gaetano Granozzi [a,]*

[a]Department of Chemical Sciences, Via Marzolo 1, 35131 Padova, Italy
[b]Physics Department E19, Technical University of Munich, James-Franck-Str. 1, D-85747 Garching, Germany

gaetano.granozzi@unipd.it

Early transition metal carbides have recently attracted much interest for their possible use in catalysis[1] and electrocatalysis[2], in the latter case both as catalysts and supports. Since some of them can mimic the electronic structure of noble metals for some chemical and electrochemical reactions, they are actually potential substitutes for Pt as electrode material for low temperature fuel cells, promising improved resistance to poisoning and electrochemical stability to corrosion. Very recently, some of us suggested the use of titanium oxycarbides (hereafter TiO_xC_y) as alternative supports for intermediate temperature fuel cells[3]. In this presentation we discuss the results of a study where the transformation of anodic polycrystalline TiO_2 films is traced *in-situ* by photoemission spectroscopy, either in a standard lab equipment or in a synchrotron radiation facility using the Scanning PhotoElectron Microscopy tool. In addition, it has been traced the electrochemical stability of the TiO_xC_y films.

Funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n° [309741]

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[2] D. J. Ham, J. S. Lee, *Energies* 2009, **2**, 873
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INO-O46

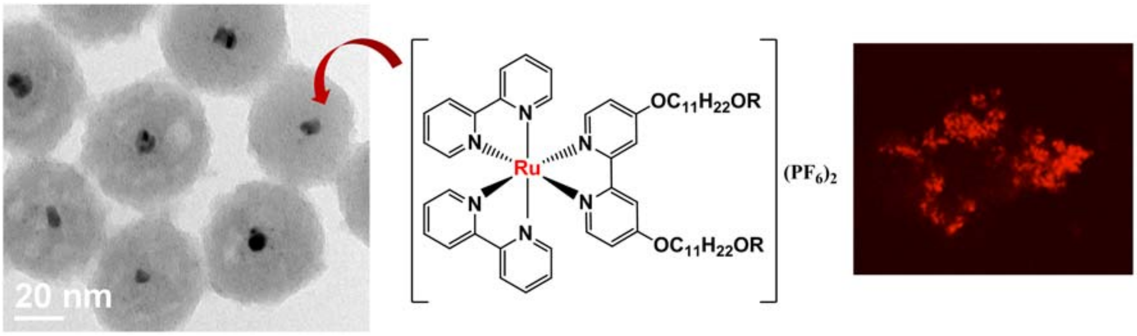
Multifunctional gold-silica nanoparticles: synthesis and photophysical characterization

Loredana Ricciardi [a], Elisabeta I. Szerb [a], Mauro Ghedini [a], Massimo La Deda [a]

[a] Department of Chemistry and Chemical Technology, University of Calabria, I-87036 Rende (CS), Italy.

loredana.ricciardi@unical.it

In this contribution will be presented newly designed luminescent ionic Ruthenium(II) and Iridium(III) complexes doped gold core-polysiloxane shell particles obtained by microemulsion method.[1] The nanoparticles were fully characterized by TEM Microscopy, Dynamic Light Scattering, UV-Vis, steady-state emission and time-correlated single-photon counting spectroscopies.



Their ability to generate $^1O_2$ as well as phosphorescence emission were exploited for practical applications in the biomedical fields. Indeed, their cytotoxicity and photodynamic activities were evaluated *in vitro*. Furthermore, their intrinsic phosphorescence probed by fluorescence confocal microscope, allows their localization into the cytosol of tumor cells. These valuable features designate these materials as multifunctional nanoplatforms for theranostic purposes.

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Chimica Inorganica

Poster

INO-P1

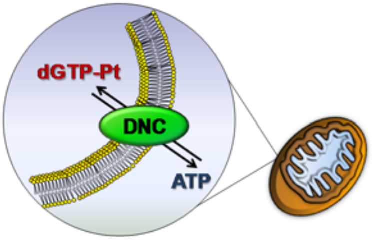
Metalated purines: study of mitochondrial uptake

Antonucci D., Girelli C.R., Migoni D., Carrisi C., Lunetti P., Romano A., Verri T., Capobianco L., Benedetti M. and Fanizzi F.P.[a]

a Department of Biological and Environmental Science and Technology (DISTEBA), Salento University, Lecce, Italy.

antonucci.daniela@gmail.com

Mitochondria play an important role in a significant portion of the pharmacological properties associated with *cisplatin*.[1] Aim of this research was to evaluate the possibility that the model complex platinated deoxyguanosine triphosphate, [Pt(dien)(*N7*-dGTP)], could be transported into mitochondria and then incorporated in mitochondrial DNA. This hypothesis is supported by previous studies that show the incorporation into nuclear DNA of the model complex [Pt(dien)(*N7*-dGTP)].[2] The kinetic characterization has revealed that the deoxynucleotide carrier,[3] solubilised from rat liver mitochondria and reconstituted into phospholipid vesicles, can transport the [Pt(dien)(*N7*-dGTP)] complex with high affinity.[4] Furthermore, the radioactive uptake assay, associated with quantitative analysis of platinum, has provided a strong evidence for a specific import of [Pt(dien)(*N7*-dGTP)] into intact rat liver mitochondria. Finally, we demonstrated also that the complex [Pt(dien)(*N7*-dGTP)] can be incorporated in the mitochondrial DNA. These results may have critical implications in the development of a new generation of anticancer drugs, with a specific cellular target, based on analogues of deoxynucleosides.



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[3] D. Iacopetta, C. Carrisi, G. De Filippis, V. M. Calcagnile, A. R. Cappello, A. Chimento, R. Curcio, A. Santoro, A. Vozza, V. Dolce, F. Palmieri, L. Capobianco *FEBS J.* (2010) 277, 1172.
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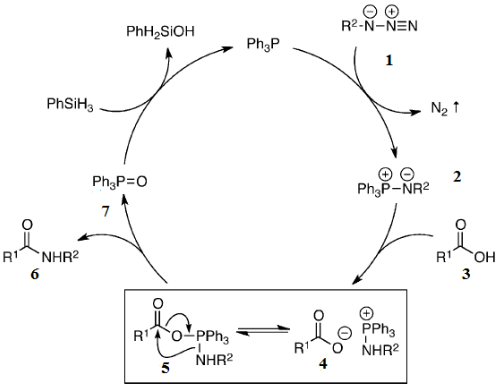
INO-P2

Theoretical Study of the Phoshine-based redox Catalysis in the ligation of carboxylic Acids and Azides

Emanuela Di Santo, Marirosa Toscano, Nino Russo

Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Via P.Bucci ,
Cap 87036 , Arcavacata di Rende (CS) Italy

emanuela.disanto@unical.it



Aryl amides, imides, lactams, and dipeptides are obtained through a direct Staudinger ligation mediated by phosphine-based redox catalysis.[1] The proposed catalytic cycle provides several steps. The initial reduction of azide **1** by PPh_3 to give aza-ylide **2** is followed by the deprotonation of carboxylic acid **3** to provide both the phosphonium carboxylate **4**, and species **5** in which the partially covalent P-O bond activates the carboxylate for nucleophilic acyl substitution. Therefore, the amide C-N bond in formed in species **6**. The final reduction of the phosphine oxide $Ph_3P{=}O$ regenerates PPh_3 and completes the catalytic cycle (see picture). In order to better describe the proposed catalytic cycle, we have undertaken a theoretical investigation of the reaction mechanism.[2] All DFT calculations have been carried out with the Gaussian-09 package, using the hybrid B3LYP functional and 6-31G(d) basis set for all atoms except nitrogen, oxygen and phosphonium, which are described with 6-311+G(d,p). A detailed description of the reaction mechanism is presented, including all involved minima and transition states. The obtained results are compared with existing experimental data.[1]

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INO-P3

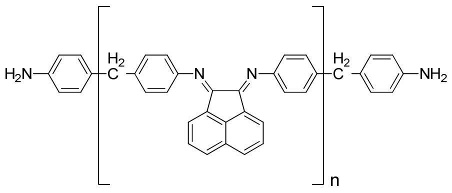
Ruthenium complexes with polymeric α-diimine containing poly[arylimino-acenaphthene] fragments

Francesco Ferretti, Luca Rota, Fabio Ragaini

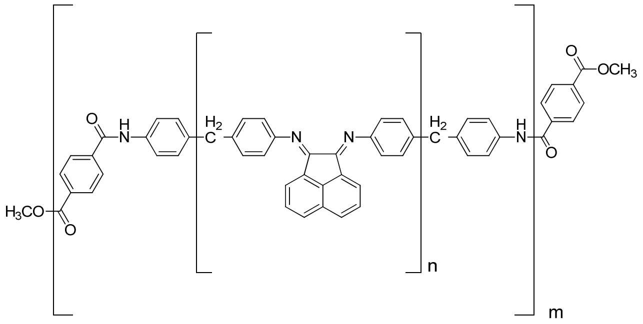
Dipartimento di Chimica, Università degli Studi di Milano, Via C.Golgi 19, 20133, Milano, Italy

francesco.ferretti@unimi.it

α-diimine/Ru, Pd and Ni complexes are very active homogeneous catalysts for several reactions. In particular bis(arylimino)acenaphthene (Ar-BIAN) compounds have been widely studied in polymerizations and reactions involving the use of carbon monoxide. We developed a method for the synthesis of oligomeric Ar-BIAN (oligo-BIAN) from acenaphthenequinone and 4,4'-methylenedianiline and for their use as building blocks in polyamide synthesis (poly-BIAN).



Oligo-BIAN



Poly-BIAN

Such polymeric Schiff bases could be useful both for developing a heterogenized catalyst and for developing multi-nuclear organometallic species that are known to be good catalysts in olefins polymerization reactions.

The investigation of the reaction between [$Ru(CO)_3Cl_2(THF)$] and the synthesized macromolecular Schiff bases showed different coordination modes of the poly-BIAN with respect to the oligo-BIAN and the non-polymeric tolyl BIAN, with the oxygen atom of the terephthaloyl connecting unit becoming the actual binding site in the former case.

INO-P4

Theoretical study of the catalytic mechanism of GABA aminotransferase enzyme

Jenny Pirillo, Tiziana Marino, Nino Russo

Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Via Pietro Bucci, 87036, Arcavacata di Rende (CS), Italy

jenny386@libero.it

γ-Aminobutyric acid aminotransferase (GABA-AT) is a pyridoxal 5'-phosphate-dependent enzyme responsible for the degradation of primary inhibitory neurotransmitter γ-aminobutyric acid (GABA).

Maintaining a certain level of GABA concentration in the brain is important, since low brain's GABA concentrations or decreased GABA function are associated with several psychiatric and neurological disorders including anxiety, depression, insomnia, epilepsy, Parkinson's disease and Alzheimer's disease. GABA-AT represents a validated target for anti-epilepsy drugs because its selective inhibition increases GABA levels in brain.

The most used anti-epilepsy drug is γ-vinyl GABA (vigabatrin) for which several inactivation mechanisms have been hypothesized.

A density functional theory (DFT) has been undertaken with the aim to explore all the possible inactivation mechanisms of GABA-AT by means of vigabatrin.

The gained knowledge at atomistic level of the working mechanism of this inhibitor can be helpful in the rational design of new inhibitor drugs with reduced side effects that at the moment constitute a big problem in the epilepsy therapy.

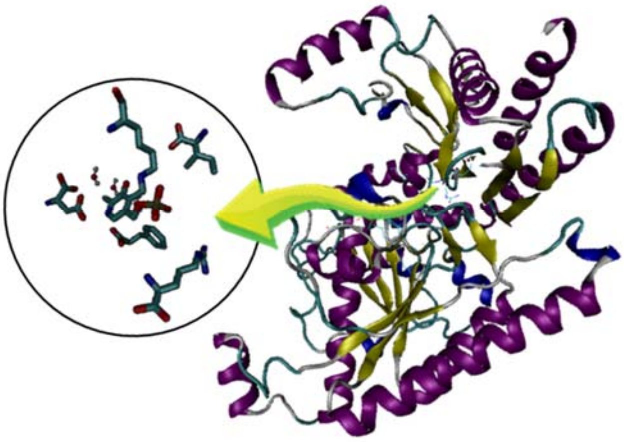


Figure 1. X-ray structure of chain A of the GABA-AT enzyme. In the circle is represented the active site.

INO-P5

Alumina as Acid Catalyst in the MonoMethyl Esterification of Adipic Acid: a Study of Surface Interactions.

*Loretta Storaro**[a], *Elisa Moretti*[a], *Martina Marchiori*[a], *Veronica Santacroce*[b], *Raimondo Maggi*[b]

[a] *INSTM-Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari, Via Torino 155/B 30172-Venezia, Italy*
[b] *"Clean Synthetic Methodology Group", Dipartimento di Chimica dell'Università, Parco Area delle Scienze 17A, I-43124 Parma, Italy*

storaro@unive.it

The selective protection of one of two identical functional groups in symmetrical positions in a molecule, is an important goal in organic synthesis. In this area the preparation of monoesters of symmetrical diacids represents an important challenge, mainly when the cyclic anhydrides are not readily available.

Dicarboxylic acids can be monoprotected by reaction with diazomethane or dimethyl sulfate in the presence of alumina or silica gel [1]; the transesterification approach, utilizing butyl formate in octane, is also used [2].

Here, preliminary studies concerning the monoesterification of adipic acid with methanol are reported.

The reaction was tested with some commercial Al_2O_3 powders and an ordered mesoporous alumina prepared by a surfactant assisted synthesis. The Al_2O_3 catalysts were characterized by different techniques including nitrogen physisorption at 77 K, temperature-programmed desorption of ammonia (NH_3-TPD) and DRIFT-IR spectroscopy. The reaction, carried out at RT for 22 hrs, affords the adipic acid monomethyl ester in 57% yield and 95% selectivity. The effect of the catalyst amount and the role of the water will be discussed.

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INO-P6

Probing the association of frustrated $PR_3/B(C_6F_5)_3$ pairs in solution by NMR spectroscopy

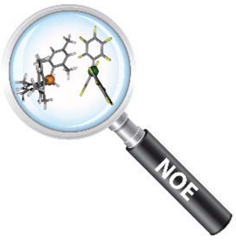
Luca Rocchigiani,[a] *Gianluca Ciancaleoni,*[b] *Cristiano Zuccaccia,*[a]

Alceo Macchioni[a]

a Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia, Via Elce di Sotto 8, 06123, Perugia, Italy
b CNR-ISTM c/o Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia, Via Elce di Sotto 8, 06123, Perugia, Italy

luca.rocchigiani@progetti.unipg.it

Frustrated Lewis pairs (FLP), i.e. the combination of a Lewis acid (LA) and a Lewis base (LB) that cannot fulfill their natural propensity to form dative adducts, are assuming a growing importance mainly due to their capability of activating small molecules such as H_2, CO_2 and unsaturated substrates.[1] It is believed that LA and LB must closely approach each other forming an encounter complex, having the empty orbital of LA pointing towards the lone pair of electrons of LB, in order to contemporary exploit their potential as electron donor and acceptor. Despite this, very little experimental evidence is available about the tendency of LA and LB to associate and their relative orientation in solution. In this contribution, we report the results of an in-depth NMR study which provides unprecedented evidence for the tendency of intermolecular frustrated $PR_3/B(C_6F_5)_3$ pairs (R=CMe_3, 2,4,6-Me-C_6H_2) to associate in toluene and benzene, quantified by diffusion NMR experiments. The results of ^{19}F,^{1}H HOESY experiments, carried in combination with DFT calculations, are also illustrated; they indicate that there is not any preferred approaching orientation between LA and LB.[2]



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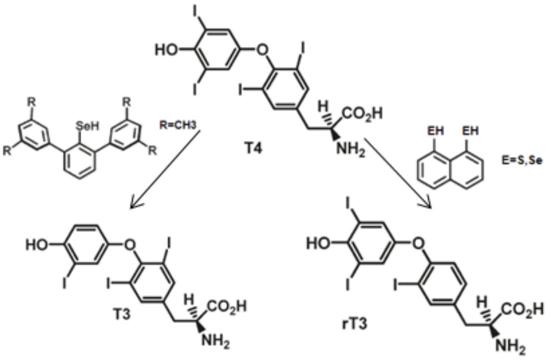
INO-P7

Computational Study of Thyroid Hormones Deiodination by Bio-Inspired Iodothyronine Deiodinase complexes

Mariagrazia Fortino, Tiziana Marino, Nino Russo, Emilia Sicilia

Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Via P. Bucci, 87036, Rende (CS), Italy

mariagrazia.fortino@gmail.com



The type-3 iodothyronine deiodinase (ID-3) enzyme is a member of the iodothyronine deiodinase family, mammalian selenium containing enzymes including three isozymes (type- 1, 2 and 3) involved in the activation and inactivation of thyroid hormones, that explicate rather different biochemical and regulatory actions associated to a different tissue distribution. ID-3 catalyzes the conversion of T4 to 3,3',5'-triiodothyronine (rT3) by a selective inner-ring (5) deiodination. The selenocysteine (Sec) residue in the active site of ID-3 is believed indispensable for efficient inner-ring deiodination as confirmed by its substitution with cysteine causing a reduction of catalytic efficiency. Nonetheless the structures and the working mechanism of the deiodinases are still incomplete. For these reasons, with the aim to gain knowledge on the chemical mechanism of ID-3, in the last decade different selenium containing models able to reproduce the catalytic functions of ID-3 have been extensively developed. In this poster we present the potential energy surfaces, obtained at density functional theory level on the deiodination mechanism, for different naphthyl-based bio inspired complexes with a different combination of selenium or sulphur atoms.

This work has been financially supported by Università della Calabria and FP7-PEOPLE-2011-IRSES, Project No.295172

INO-P8

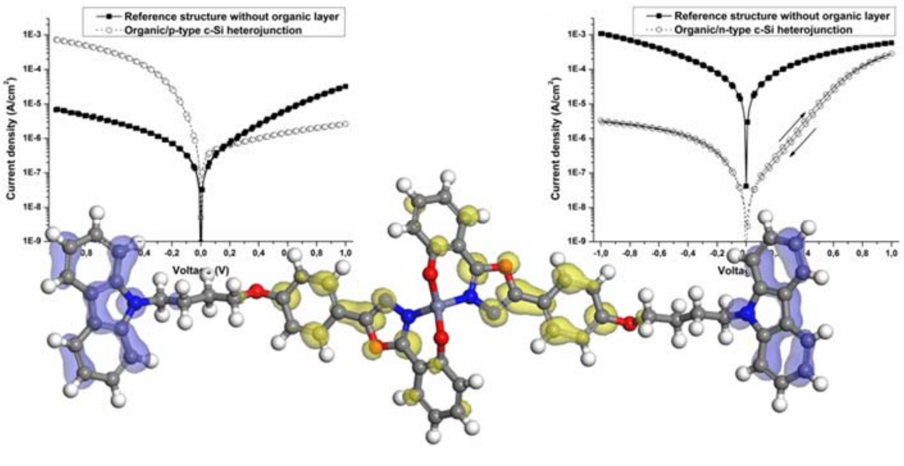
Mononuclear Zn(II) complex based on oxadiazole/carbazole structure

Simona Concilio[a], *Stefano Piotto*[b], *Lucia Sessa*[a], *Valeria Bugatti*[a], *Heinz C. Neitzert*[a], *Giovanni Landi*[a], *and Pio Iannelli*[b]

[a] *Department of Industrial Engineering (DIIn), University of Salerno, Via Giovanni Paolo II 132, 84084 Fisciano (Salerno), Italy*
[b] *Department of Pharmacy (DIFARMA), University of Salerno, Via Giovanni Paolo II 132, 84084 Fisciano (Salerno), Italy*

sconcilio@unisa.it

A mononuclear Zn(II) complex containing two carbazole/oxadiazole moieties, $Zn(OC)_2$, was synthesized and characterized by means of elemental and thermal analyses and infrared spectroscopy. Current–voltage measurements of $Ag/Zn(OC)_2/p$-Si and $Ag/Zn(OC)_2/n$-Si heterostructures have been performed and compared to that of reference structures with the same metal contacts but without the insertion of the $Zn(OC)_2$ layer. Good rectification behavior has been observed for both hetero-diodes, independent of the silicon substrate doping type, confirming that the metal–organic layer can act both as electron or hole-conductor. $Zn(OC)_2$ complex displayed blue photo-luminescence in solution and in film.



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INO-P9

Contributo Ritirato

INO-P10

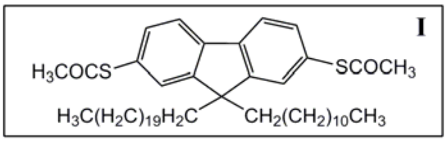
Bifunctional ligands as capping agent for gold nanoparticles: synthesis and characterizations

Laura Fontana[a], Ilaria Fratoddi[a,b], Iole Venditti[a], Maria Vittoria Russo[a,c]

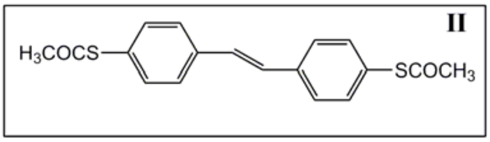
a Dpt. of Chemistry, University of Rome Sapienza, P.le A. Moro 5, 00185 Rome, Italy
b Center for Nanotechnology for Engineering (CNIS), University of Rome Sapienza, P.le A. Moro 5, 00185 Rome, Italy
c Center for Protection of Environment and Cultural Heritages (CIABC) University of Rome Sapienza, P.le A. Moro 5, 00185 Rome, Italy

laura.fontana@uniroma1.it

Among the materials that have attracted recent interest in science there are the noble metal nanoparticles which show extremely interesting properties that make them excellent candidates for applications ranging from catalysis, biotechnology, optoelectronics.[1-3] In this paper we present the latest results on the preparation of gold nanoparticles (AuNPs) stabilized with synthesized bifunctional ligands characterized by an extended π -conjugated system: 9,9-didodecil-2,7-bis(tioacetyl)fluorene(I) and trans-4,4'-bis(tioacetyl)stilbene (II).



I



II

We obtained in this way nanoparticles with diameter less than 10 nm, deeply characterized to obtain both morphological and structural information.[4,5]

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INO-P11

Studio dell'inattesa reattività tra H-Si(100) e molecole con gruppi ancoranti saturi sotto irraggiamento con luce bianca

Marco Carboni[a], *Andrea Giacomo Marrani*[a], *Robertino Zanoni*[a]

a Dipartimento di Chimica, Università La Sapienza, P.le A. Moro 5, 00185, Roma, Italia

m.carboni@uniroma1.it

Le superfici di Si cristallino funzionalizzate con derivati del ferrocene hanno dimostrato da anni di essere buone candidate per applicazioni in elettronica molecolare, mostrando una risposta redox modulabile attraverso la scelta opportuna dei gruppi ancoranti su Si. Il meccanismo finora proposto per l'adesione su H-Si(100) tramite illuminazione con luce bianca prevede la presenza di una insaturazione nel gruppo ancorante della molecola (es. vinil- ed etinilferrocene) [1], mentre non esistono teorie capaci di spiegare il chemisorbimento fotoindotto di un idrocarburo saturo a H-Si(100). Questo lavoro [2] getta luce sull'effettivo meccanismo di reazione tra H-Si(100) e catene idrocarburiche sature, investigando l'ancoraggio di alchil-ferroceni su superfici di H-Si(100) attraverso irraggiamento con luce bianca. I risultati ottenuti da misure XPS, elettrochimiche e microscopiche e da calcoli DFT sono sorprendenti, in quanto mostrano l'effettiva formazione di legami covalenti Si-C, ma solo per specie aromatiche. Un meccanismo di reazione viene proposto, che coinvolge l'effetto di iperconiugazione come possibile fattore che esalta la reattività di uno specifico atomo di C della catena ancorante satura sotto illuminazione con luce bianca.

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INO-P12

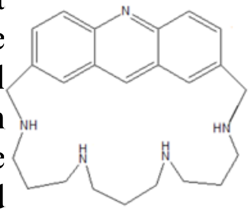
Optical and electrochemical characterization of acridine ligands for sensoristic applications.

Andrea Bencini[a], Francesca Bettazzi[a], Luca Conti[a], Claudia Giorgi[a], Ilaria Palchetti[a], Barbara Valtancoli[a], Diego Voccia[a].

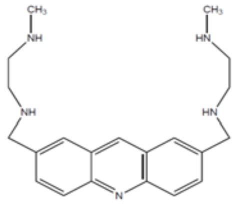
[a] *Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3, 50019, Sesto Fiorentino-Florence (FI), Italy.*

luca.conti@unifi.it

Arsenic and selenium play an important role in several environmental and health issues; while arsenic is an important contaminant of water, selenium instead is an element present in trace amounts in most environmental and biological systems, indispensable in humans at trace levels, but extremely toxic when taken in excessive doses. It is therefore evident how important would be to develop a simple and effective methodology for the environmental monitoring of both of these species. Our main goal, is to develop selective and sensitive optical and electrochemical sensors modified with new acridine ligands[1], Acry333 and Acryopen (Figure), for the determination of the anionic species SeO_4^{2-}, SeO_3^{2-}, AsO_4^{3-}, AsO_3^{3-}. For this purpose we have studied the ligand-anion interaction, through potentiometric and ^{1}H-NMR measurements and investigated the electrochemical and optical behavior of the ligand-anion complex both through voltammetry[2-3]and fluorescence, respectively. Due to the specific chelating ability of these ligands, the developed optical and electrochemical sensors would be extremely promising in terms of selectivity and sensitivity in the determination of these toxic elements.



Acry 333



AcryOpen

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INO-P13

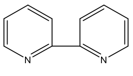
New Group VI metal (Mo, W) based electrocatalysts for reduction of CO_2

Luca Nencini, Federico Franco, Claudio Cometto, Fabrizio Sordello, Carlo Nervi, Roberto Gobetto, Claudio Minero

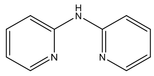
Dipartimento di Chimica, Università di Torino, Via Pietro Giuria 7, 10125, Torino, Italia

luca.nencini@unito.it

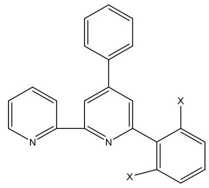
Whereas the majority of the reported studies is mainly focused on the catalytic activity of Group VII metal-based molecular systems (Mn(I)[1], Re(I))[2], much less attention has been paid on the possible usage of complexes with Group VI transition metals (Cr, Mo and W) as electrocatalysts for CO_2 reduction, although many examples from biology and organometallic science could support this idea[3].



bipy



dpa



bipy-PhX$_2$ (X = H, OCH$_3$)

For this reason, we synthesized some tetracarbonyl Group VI metal-based coordination compounds containing polypyridyl ligands, [$M^0(CO)_4(L)$] (M=Mo, W; L=2,2'-bipyridine and derivatives; 2,2'-dipyridylamine). Unlike the other structurally similar Group VII metal based counterparts, the complexes under study are characterized by zero-valent metal centers with the presence of a CO molecule instead of an anionic ligand (Cl^- or others). This issue could imply new interesting mechanistic insights about the catalytic process. The electrocatalytic activity of these compounds was tested by means of such electrochemical techniques, as cyclic voltammetry and bulk electrolysis, performing the experiments either under Ar atmosphere and in CO_2 saturation conditions. Our results revealed that some activity is present towards CO_2 as a substrate, even though at very negative potentials, being close to the values for the direct CO_2 reduction (about -2.0 V vs SCE). Further investigation on the identity of the reaction products, together with the understanding of the mechanistic details of the catalytic process are still in progress.

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INO-P14

Novel Re(I) based catalysts for CO_2 Photo- and Electrocatalytic reduction at low overpotential

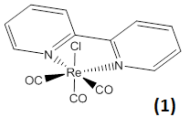
Federico Franco, *Claudio Cometto, Cunfa Sun, Luca Nencini, Fabrizio Sordello, Claudio Garino, Roberto Gobetto, Carlo Nervi, Claudio Minero*

Department of Chemistry and NIS, University of Turin, via P. Giuria 7, 10125 Torino, Italy

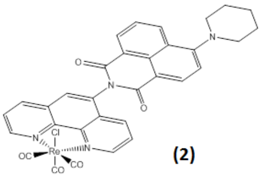
federico.franco@unito.it

Our research mainly focused on the synthesis of a series of novel Re(I)-carbonyl diimine complexes, to be used as catalysts for both photo- and electroreduction of CO_2. In more detail, a new class of catalysts is characterized by the presence of common polypyridyl ligands covalently attached to the highly fluorescent PNI cromophore (N-(diimine)-4-(1-piperidinyl) naphthalene-1,8-dicarboximide), which revealed to be able to provide a huge excited state lifetime enhancement in a Re(I) charge-transfer complex [1]. This feature may play a role in the process of photocatalytic CO_2 reduction.

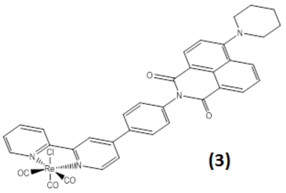
The electrochemical behaviour of the synthesized organometallic compounds **2-3** was studied either under inert atmosphere and in presence of CO_2, in order to test their electrocatalytic activities. A direct comparison with the activity of $Re(CO)_3(bipy)Cl$ (**1**), already known as an efficient molecular catalyst, is reported [2]. Controlled-potential electrolysis measurements in homogeneous solution under continuous CO_2 flow (in the figure below) revealed that the PNI-containing Re(I) complexes **2-3** have sluggish kinetics towards CO_2 as a substrate, but, at the same time, they can operate at substantially lower overpotential (-1.96 V vs Fc/Fc^+ couple) than **1**.



(1)



(2)



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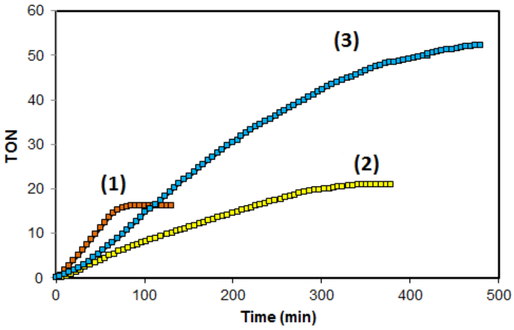

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INO-P15

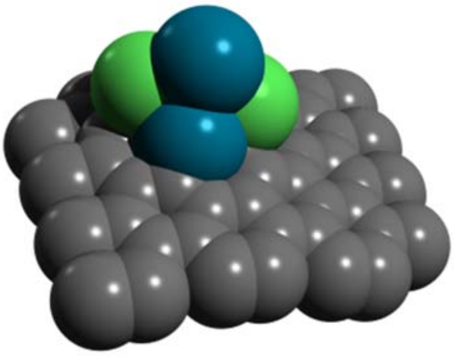
Studio computazionale sull'accrescimento di cluster di Pd, Ni, Pt, Re su un foglio di Grafene

Antonio Prestianni, Francesco Ferrante, Dario Duca

Dipartimento di Fisica e Chimica, Università degli Studi di Palermo, Viale delle Scienze, Parco d'Orleáns II, Ed. 17, 90128, Palermo, Italia

antonio.prestianni@unipa.it

Negli ultimi anni i processi di conversione di biomassa in combustibili liquidi e gassosi sono divenuti di cruciale importanza. L'obbiettivo principale è quello di ridurre lo sfruttamento di combustibili fossili fornendo energia, direttamente fruibile, a basso impatto ambientale. L'APR (Aqueous Phase Reforming)[1] è un processo a consumo energetico contenuto e di conseguenza tra i più promettenti e competitivi nella produzione di combustibili ecosostenibili come idrogeno e idrocarburi semplici a basso peso molecolare. In questo contesto la catalisi eterogenea riveste un ruolo di primaria importanza, soprattutto per quel che riguarda la razionalizzazione e l'ottimizzazione dei processi sopra menzionati. I catalizzatori costituiti da nano-particelle supportate su substrati carboniosi sembrano mostrare buone *performance* catalitiche a costi sia in termini economici che ambientali soddisfacenti. In questo lavoro, mediante un approccio DFT periodico, sono ottenute informazioni relative all'accrescimento di cluster metallici e bimetallici Pd/Ni, Pt/Re su un foglio di grafene, sia come elementi puri, sia in lega a diversa composizione. Lo *screening* delle diverse strutture e le stabilità relative hanno permesso di determinare quali sistemi risultano, almeno da un punto di vista prettamente teorico, maggiormente probabili, permettendo così di avviare lo *step* successivo ossia lo studio teorico dei processi reattivi in processi di tipo APR.



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INO-P16

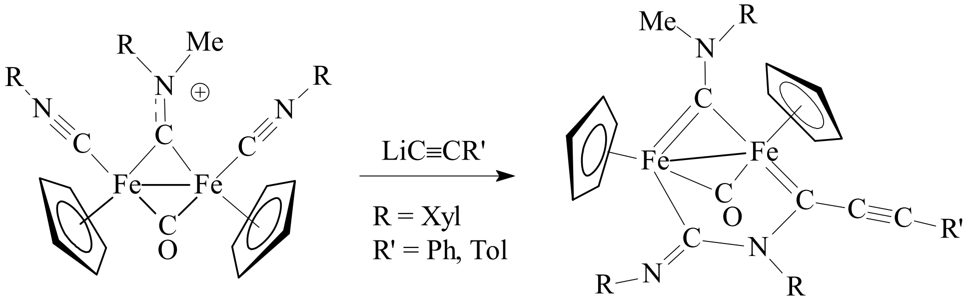
Iron mediated isocyanides assembly

F. Marchetti[a], *R. Mazzoni*[b], *S. Zacchini*[b], *V. Zanotti,*

a Dipartimento di Chimica Dipartimento di Chimica e Chimica Industriale,
Università di Pisa, Via Risorgimento 35, I-56126 Pisa, Italy
b Dipartimento di Chimica Industriale "Toso Montanari" Università di Bologna, viale Risorgimento 4, I-40136 Bologna, Italy

valerio.zanotti@unibo.it

Increasing attention to sustainability and the need for new catalysts based on more cost-effective and benign transition metal compounds has produced an exponentially grown of interest toward iron mediated bond forming reactions. In this research field diiron complexes can play a distinctive role in that they combine the advantages associated to iron with those due to the presence of two adjacent metal centres. [1]



Here, focus is on coupling of isocyanide ligands in diiron complexes promoted by acetilyde nucleophilic addition. The reactions, (one example is shown in the following scheme), leads to the formation of C-C and C-N bonds and the assembly of an organic fragment, which remains coordinated in the form of bridging ligand.

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INO-P17

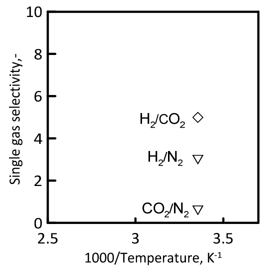
Microporous FAU Y-type membranes.

Teresa F. Mastropietro[a], *Teresa Poerio*[b], *Pasquale F. Zito*[a], *Adele Brunetti*[b],
Enrico Drioli[a,b], *Giuseppe Barbieri*[b]

a Department of Environmental and Territorial Engineering and Chemical Engineering,
University of Calabria, Via P. Bucci, 87036, Rende, Italy
b National Research Council, Institute for Membrane Technology (ITM–CNR) c/o University
of Calabria, Via P. Bucci,87036, Rende, Italy

teresafina.mastropietro@gmail.com

Owing to their intrinsic well-defined microporous structures and their superior thermal stability and solvent resistance, zeolites membranes are ideal candidates for application in membrane-based separation processes and as membrane reactors. [1] Various high-performance zeolite membranes have been prepared in laboratory conditions. However, more convenient and reproducible synthesis routes are required for large-scale manufacture. Furthermore, defect-free, continuous zeolite layers are necessary for application in gas separation processes, since defects constitute non selective permeation pathways that deplete the membrane performances. In the course of our research project, different synthetic approaches have been explored for the preparation of FAU-type membranes on tubular α -Al_2O_3 supports and the effects of various parameters on the ultimate membrane quality and performance have been evaluated, including i) Seeding procedure; ii) Pre-hydrothermal treatment; iii) Synthesis solution composition; iv) Ion-exchange; v) Functionalization of the support. The as-synthesized membranes have been characterization by XRD, EDX, SEM. N_2, CO_2 and H_2 single/mixed gas (dry and humidified) permeation tests at different temperatures have been carried out to estimate the mass transport properties of the membranes.



GAS	Ideal Selectivity, -	Knudsen Selectivity, -
CO_2/N_2	0.8	0.56
H_2/N_2	5.5	2.65
H_2/CO_2	7.1	4.7

Research partially funded by FP7/2007-2013 under DEMCAMER project (NMP3-LA-2011-262840).

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INO-P18

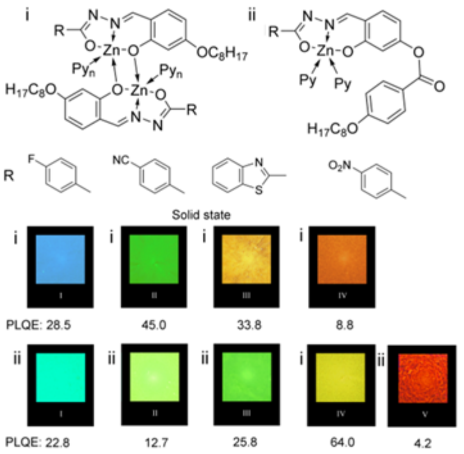
Mono- and dinuclear Zn^{II} complexes with high solid state PL quantum yield

Fabio Borbone [a], *Ugo Caruso* [a], *Mauro Causà* [b], *Sandra Fusco* [a], *Barbara Panunzi* [c], *Antonio Roviello* [a], *Rafi Shikler* [d], *Angela Tuzi* [a]

a Dipartimento di Scienze Chimiche, Università di Napoli Federico II, Via Cintia, 80126, Napoli, Italy
b Dipartimento di Ingegneria Chimica, dei Materiali e delle Produzioni Industriali, Università di Napoli Federico II, Piazzale V. Tecchio 80, 80125 Napoli, Italy
c Dipartimento di Agraria, Università di Napoli Federico II, via Università 100, 80055 Portici (Napoli) Italy
d Department of Electrical and Computer Engineering, Ben-Gurion University of the Negev, POB 653 Beer-Sheva 84105 Israel

fabio.borbone@unina.it

A series of N-salicylidene-N’-aroylhydrazine tridentate chelating molecules was synthesized to obtain neutral complexes by reaction with Zn^{II} acetate and pyridine as further ligand. Ligands and complexes were characterized by mass spectrometry and standard spectroscopic techniques (^{1}H-NMR, UV-Visible, photoluminescence and FT-IR). The structure of the complexes were solved by single crystals X-Ray analysis, both for mononuclear and dinuclear species. A nematogenic phase behavior was detected for ligands only. Photoluminescence spectra were recorded both in solution and in solid state. All the complexes show a noteworthy PL emission in the solid state which is tunable by varying the N-substituent on the hydrazine group or through the mononuclear or dinuclear arrangement (in a special case). Medium to very high PL quantum yields were recorded on the crystalline complexes. Both periodic and molecular DFT calculations were performed to rationalize the absorbance of these complexes at “one particle” level.



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INO-P19

Growth of HKUST-1 on functionalized graphene layers.

María Victoria-Rodríguez, Fabio Rimoldi, Lucia Carlucci

Dipartimento di Chimica, Università degli Studi di Milano, Via C. Golgi 19 ,20133, Milano, Italy

maria.victoria@unimi.it, lucia.carlucci@unimi.it

Metal Organic Frameworks (MOFs) are porous crystalline materials showing 1, 2 and 3 dimensional extended frameworks that are sustained by coordinative chemical bonds between organic ligands and metal cations/clusters. Among all the characterized MOFs, HKUST-1 or $[Cu_3(BTC)_2(H_2O)_3]_n$ (H_3BTC = benzene-1,3,5-tricarboxylic acid) is one of the most studied [1]. Recently it has been noticed that HKUST-1 is also a good system for methane storage [2].

Even MOFs can act as gas storage on their own, they have been also combined with other materials to create composites in order to improve their properties. These composites have been mainly prepared with other materials such as silica, carbon nanotubes, graphite oxide or other carbon types [3]. Graphene is a single layer (2D) of sp^2 carbon atoms arranged with a honeycomb structure. Due to its properties (high-resistance, high thermal and electrical conductivity) it has gained a lot of interest in recent years. In particular, the development of composite materials with improved properties as well as the organic functionalization of the graphene layers are of increasing interest. Here we report our results on the growth of HKUST-1 in the presence of benzoic acid functionalized graphene. [4]

Authors acknowledge financial support from Regione Lombardia (Project: NASEMS, Concert_EN-046).

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INO-P20

Copper (II) metallocycles as anions receptors.

Further studies on their synthesis, spectroscopic and spectrometric characterization in solution

Rossana Galassi[a], *Camille S. Oumarou*[a], *Alfredo Burini*[a], *Massimiliano Lupacchini*[a], *Stefania Pucciarelli*[b]

a School of Science and Technology, Università di Camerino, Via Sant'Agostino 1, 62032, Camerino, Italia
b School of Biosciences and Biotechnology, University of Camerino, Via Gentile III da Varano, 1, 62032 Camerino, Italy

camillesimon.oumarou@unicam.it

Halide-centered hexanuclear copper(II) pyrazolate complexes, such as [trans-$Cu_6\{(3,5-CF_3)_2pz\}_6(OH)_6X]^-$, X= Cl, Br, I can be isolated in a good yield from the redox reaction of the trinuclear copper(I) pyrazolate complex [μ-$Cu_3\{(3,5-CF_3)_2pz\}_3$] with a halide source such as Ph_3PAuCl, $[Bu_4N]X$, X= Cl, Br or I and $PPN(NO_2)$ where PPN is $(Ph_3P)_2N$ [1]. We report in this work a new route for the synthesis of the [trans-$Cu_6\{(3,5-CF_3)_2pz\}_6(OH)_6X$] starting from the neutral 3,5-$(CF_3)_2pzH$. The reactions showed lower yields but fast conversion to the corresponding halide centered metallocycles. A water centered metallocycle was obtained too. The nature of the molecule inside the cavity was discussed by IR spectroscopy, X-ray structural data and by determining the rate constant of the water exchange reaction in acetone solution. The mechanism likely involves the formation of pyrazoles self-aggregates by intermolecular hydrogen bonding. From data analysis, we can assume that the cavity is very affine for chloride and bromide but scarcely selective, while is slightly less affine for iodide.

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INO-P21

Supramolecular Chemistry and photophysical Properties of a New Gold (I) Cyclic Trinuclear Complex, [Au(μ-C^2,N^3-1-vinylimidazole)]$_3$

R. Galassi[a], *A. Burini*[a], *C. S. Oumarou*[a], *V. N. Nesterov*[b], *M. A. Omary*[b]

a Dipartimento di Scienze Chimica, Università di Camerino, Via Sant Agostino, 1, 62032 Camerino, Italia
b Department of Chemistry, University of North Texas, Denton, TX 76203, USA

camillesimon.oumarou@unicam.it

In the past years several cyclic trinuclear complexes (CTCs) have been synthetized and characterized on the basis of the capacity of d^{10} transition metal ions to give bicoordinated linear compounds. This intriguing class of compounds display π-acid/π-base properties that can be finely tuned by : the nature of the metal, the substituents on the ligand or the ligand itself.[1] These complexes are attractive building blocks to obtain supramolecular compounds showing interesting photopysical properties [2] or heterobimetallic cyclic trinuclear complexes with potential use in mixed-metal catalysis.[3] Here we report the synthesis of a novel gold(I) CTC, [Au(μ-C^2,N^3-1-vinylimidazole)]$_3$, and the study of some photophysical properties of its supramolecular derivatives obtained by the intercalation of metal ions in between the metallocycles.

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INO-P22

Solid State NMR spectra and GIPAW plane-wave investigation of hydrogen storage materials

Roberto Gobetto, Federico Franco, Michele Chierotti, Carlo Nervi, Marcello Baricco

Department of Chemistry and NIS, University of Turin, via P. Giuria 7, 10125 Torino, Italy

roberto.gobetto@unito.it

An integrated experimental-theoretical approach for the SSNMR investigation of a series of Group I and II metal hydrides and borohydrides, such as NaH, LiH, $NaBH_4$, MgH_2, CaH_2, $Ca(BH_4)_2$ and $LiBH_4$, is reported, mainly focusing on the computation of the ^1H, ^{23}Na, ^{11}B, and ^6Li SSNMR parameters by means of the GIPAW method for these systems, thus aiming to check the reliability of the approach for modelling of NMR spectra. Periodic lattice calculations were performed by using the plane-wave method, as implemented in the Quantum Espresso package (v. 4.3.2). Projector Augmented Wave (PAW), including the Gauge-Including Projected Augmented-Wave (GIPAW) method [1] for SSNMR calculations was used, using both Rappe-Rabe-Kaxiras-Joannopoulos (RRKJ) ultrasoft pseudopotentials (PP) and new developed pseudopotentials.

This new set of PAW PP was validated by comparison not only with experimental data, but also with computed data achieved by employing others sets of PP already available. In particular, the predicted SSNMR ^1H, ^{23}Na, and ^6Li chemical shift values obtained by using PAW PP are analogous to those derived by employing the standard PP, whereas the former allows a substantial improvement of the ^{11}B chemical shift estimation. Moreover, our computed results reproduce the ^{11}B MAS experimental spectrum of commercial $Ca(BH_4)_2$, distinguishing the two phases (α and β) contained in it [2].

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INO-P23

SOD mimic activity and redox property of Cerium-doped Bioglasses

L.Menabue[a], *F.Benedetti*[b], *P.Luches*[b], *G.Lusvardi*[a], *V.Nicolini*[a], *G.Malavasi*[a], *S.Valeri*[b], ,

a Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia,
Via G.Campi 183, 41125, Modena, Italia

b Dipartimento di Fisica, Informatica e Matematica, Università di Modena e Reggio Emilia,
Via G.Campi 213, 41125, Modena, Italia

ledi.menabue@unimore.it

The ability of nanoceria to switch between oxidation states is great because of the high number of surface oxygen vancancies[1] and previous studies established an ability comparable to that of biological antioxidant[1]; in particular the ability to mimic superoxide dismutase and catalase has been demonstrated[1][2]. We are aimed at verify if these properties are maintained also for CeO_2 –doped bioglasses. We have synthesized 45S5 Hench's –based bioglass doped with different percentage of CeO_2, up to 5.3%mol, then they were put in a solution of 0.1 mol H_2O_2 for a time in the range 1h- 7d. After treatment and filtering the remaining solution has been titrated to check the concentration of H_2O_2. The UV-vis spectra carried out on the reacted glasses (Fig. 1) show the shift of the maximum toward a higher λ value as compared to as-quenched glasses, used as control suggesting that the oxidation of Ce^{3+} on the glass surface to Ce^{4+} occurred on the glass. This behavior indicates that the antioxidant property of ceria is still present in Ce-doped bioglasses, moreover after 1h of contact the reduction of H_2O_2 is observed.

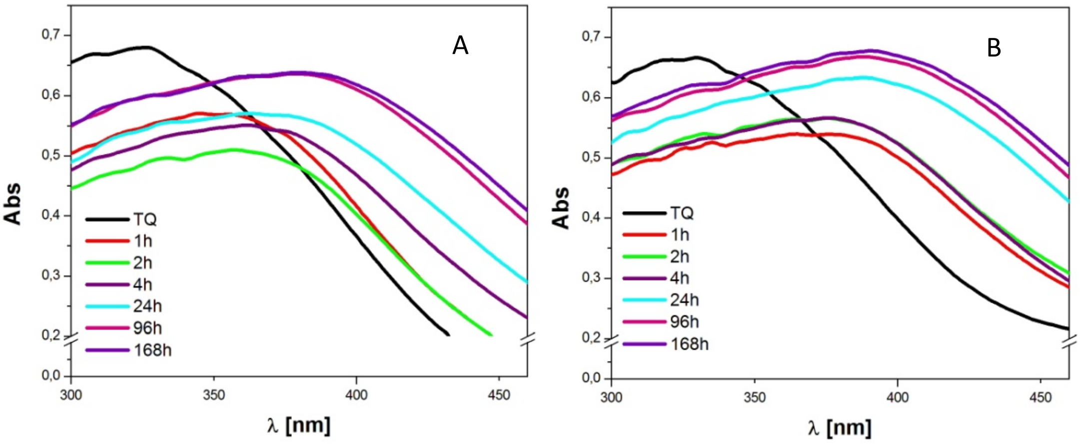

Fig.1 UV-vis spectrum of 45S5 Hench's bioglass doped with 3.6% (A) and 5.3% (B) mol of CeO_2 after different time of contact with 0.1M H_2O_2

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INO-P24

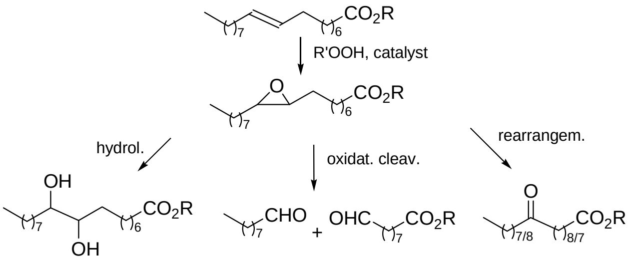
Catalytic oxidation of fatty acid methyl esters by oxovanadium complexes

Martina Maya Cecchini, Marcello Crucianelli, Francesco De Angelis, Samantha Reale

Dipartimento di Scienze Fisiche e Chimiche, Università dell'Aquila, Via Vetoio-Coppito 2, I-67100 L'Aquila

marcello.crucianelli@univaq.it

Fatty acid methyl esters (FAMEs) represent a class of chemicals playing a central role, especially as epoxide derivatives, in the production of a wide series of important industrial products and materials. In particular, derivatives of FAME epoxides find applications in several fields such as in the manufacture of lubricants, plasticizers in polymers, wood impregnation, cosmetics, pharmaceuticals and so on. Currently, at the industrial level, the epoxides of FAMEs are generally obtained in homogeneous phase *via* the Prilezhaev reaction, using *in situ* generated peracetic or performic acids. Many catalytic systems based on different metals, using milder oxidants, both under homogeneous and heterogeneous conditions, have been developed in recent years for the epoxidation of vegetable oils and their derivatives, with the aim to study and avoid disadvantages of industrial process.[1]



Selected routes for FAMEs oxidation

Despite its extensive use as an activator of peroxidic oxidants in the oxyfunctionalization of C=C double bonds, the use of oxovanadium systems, in this stimulating field, has never been adequately described. Moved by these considerations, and also by our experience in catalyzed oxidation reactions of organic substrates, we report here on our recent results in an in-depth study of the behavior of oxovanadium(IV) complexes in the oxidation of selected FAME substrates, by using different peroxides under mild reaction conditions.

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INO-P25

Pyran based chromophores for DSSC

Cira Maglione, [a] *Antonio Carella,* [a] *Roberto Centore,* [a] *Daniele Colonna,* [b] *Aldo Di Carlo.* [b]

[a] *Dipartimento di Scienze Chimiche, Università d Napoli Federico II, Complesso Universitario di Monte Sant'Angelo, Via Cintia ,80126, Napoli, Italia*
[b] *Centre for Hybrid and Organic Solar Energy (CHOSE)*
Dipartimento di Ingegneria Elettronica
Università degli studi di Roma Tor Vergata, Via del Politecnico 1, 00133, Roma, Italia

cira.maglione@unina.it

Dye sensitized solar cells (DSSC) represent one of the most interesting photovoltaic emerging technology.[1] As compared to traditional silicon based solar cells, DSSC offer several advantages, like a simplified production process, the use of relatively cheap materials, the possibility of building photovoltaic module on flexible substrates. Moreover, the possibility of using dyes with absorb in different part of the visible spectrum, make possible to realize photovoltaic modules of different and estetichally appealing colors.

Though up to now, the most efficient photosensitizers are based on organo-metallic complexes of Ruthenium, metal free absorbing dyes are anyway highly desired because they feature tipically higher light absorptivity, a more facile synthesis and they are relatively cheaper.[2]

In this context, we investigated the properties of a set of novel dyes, and their application, as photosensitizers in DSSC. The dyes are based on a pyrane core, simmetrically linked to carbazolic electron donor mojeties. The pyrane core can be functionalized with different electron acceptor groups, tuning the absorption wavelenghts so that a large part of the visible spectrum can be covered. They are characterized by large molar estinction coefficient ε, up to 10^5 $l \cdot mol^{-1} \cdot cm^{-1}$. They were used as photosensitizers in classical DSSC based on a TiO_2 photoanode and I^-/I_3^- redox couple, in a methoxypropionitrile based electrolite. Interesting power conversion efficiencies up to 2% were found.

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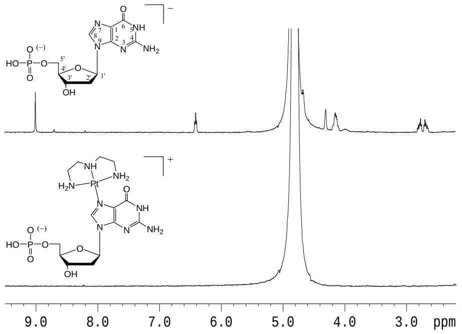
INO-P26

Effect of metalation on the adsorption of nucleotides on hydroxyapatite

Michele Benedetti,[a] *Chiara R. Girelli,*[a] *Federica De Castro,*[a] *Daniela Antonucci,*[a] *Marco Lelli,*[b] *Norberto Roveri,*[b] *and Francesco P. Fanizzi.*[a]

[a] *University of Salento - Department of Biological and Environmental Sciences and Technologies - Via Monteroni, 73100 - Lecce, Italy.*
[b] *University of Bologna - Department of Chemistry "G. Ciamician" - Via Selmi 2, 40126 - Bologna Italy.*

michele.benedetti@unisalento.it



In this work we report evidences of the importance of the residual charge of a nucleotide derivative for the absorption on hydroxyapatite nanocrystals (nHAP), in water solution. In particular we focalized our attention on model molecules with a variable number of phosphates, based on metalated and not metalated nucleotide derivatives, and on their eventual adsorption on hydroxiapatite nanoparticles evidenced by ^{1}H NMR analysis (see figure). This interest is justified because molecules bearing phosphate groups have a variety of pharmacological, biological and technological applications.[1,2] We demonstrated that a cationic or neutral charge on a nucleotide derivative produces a chemical adsorption absent or strongly reduced, instead strong adsorption on biomimetic nHAP is observed, in the presence of a net negative charge. At neutral pH, the presence of phosphates seems not a sufficient prerequisite to guarantee adsorption and the number of phosphate residues on a molecule produces only secondary effects, on the modulation of the adsorption efficiency. These aspects seem of particular interest, in relation to the adsorption, transport and delivery of drugs, in specific tissues and/or cell compartments, with a possible modulation of the pharmacological activity and control of eventual side effects.

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INO-P27

Preparation, Characterization and Optical properties of a Dendritic Dye Sensitizer-TiO_2 hybrid material

Elisa Moretti[*a], *Loretta Storaro*[a], *Manuela Aversa*[a], *Alberto Scrivanti*[a], *Aldo Talon*[a], *Riccardo Marin*[a], *Stefano Polizzi*[§a], *Juan Antonio Cecilia*[b] *and Enrique Rodríguez-Castellón*[b]

[a]*INSTM-Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari Venezia, Via Torino 155/b, 30172 Venezia, Italy.*
[§] *Centro di Microscopia Elettronica "Giovanni Stevanato", Università Ca' Foscari Venezia, Italy.*
[b]*Departamento de Química Inorgánica, Cristalografía y Mineralogía (Unidad Asociada al ICP-CSIC), Facultad de Ciencias, Universidad de Málaga, Campus de Teatinos, E-29071 Málaga, Spain.*

elisa.moretti@unive.it

Here we report the synthesis of a new triphenylamine-based dye having a dendritic structure and a preliminary study of its potential use as sensitizer for TiO_2.

We investigated the optical properties of the dye-titania composite material showing that the dye performs more efficiently on a pure anatase TiO_2 than on the commercial Degussa P25. The synthesized organic molecule and the hybrid material, obtained by impregnation of the chromophore on the two different inorganic matrices, were characterized by ^1H NMR, XPS, XRD, SEM and TEM. X-Ray diffraction confirmed that the synthesized TiO_2 is composed of pure anatase phase [1], whereas the commercial Degussa P25 contains a 20% of rutile phase. SEM and TEM micrographs showed that the building blocks of the porous structure are nanoparticles of 20-30 nm in size. N_2 physisorption measurements indicate that the two porous structures present a similar specific surface area, with the area of pure anatase sample somewhat larger than that of the P25 one.

Optical measurements showed that the absorption of the dye in the pure anatase sample is more efficient than that in P25, extending the spectral region and resulting potentially useful for conversion of photons into electrical current in a solar cell [2], making this metal-free organic dye a promising candidate for Dye-Sensitized Solar Cells DSSCs.

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INO-P28

ε and β-Fe_2O_3 nanomaterials: structure, morphology and magnetic properties

Giorgio Carraro,[a] *Davide Barreca,*[b] *A. Gasparotto,*[a]
Chiara Maccato,[a] *César de Julián Fernández,*[c] *and Andrea Caneschi*[d]

a Dip.to di Scienze Chimiche, Università di Padova ed INSTM, Padova, Italia
b IENI-CNR - Dip.to di Chimica, Università di Padova and INSTM,
Padova, Italia
c IMEM-CNR, Parco Area delle Scienze, Parma, Italy
d Dip.to di Chimica, Università di Firenze ed INSTM, Sesto Fiorentino (FI), Italia.

giorgio.carraro@unipd.it

Si(100)-supported Fe_2O_3 nanomaterials were fabricated by chemical vapor deposition at temperatures between 400 and 550°C. Interestingly, the choice of the reaction atmosphere played a key role in determining the crystal phase, yielding the scarcely studied β- and ε-Fe_2O_3 polymorphs under O_2 or O_2+H_2O reaction environments, respectively.[1] Correspondingly, the observed morphology underwent a progressive evolution from interconnected nanopyramids to vertically aligned nanorods. The present work provides an insight into the β- and ε-Fe_2O_3 nano-organization by a systematic analysis of their structure/morphology as a function of growth conditions. In particular, a thorough multi-technique investigation demonstrated a high structural and compositional homogeneity throughout the whole nanodeposit thickness.

In addition, β- and ε-Fe_2O_3 magnetic properties have been studied. ε-Fe_2O_3 showed a hard magnetic behaviour with a giant coercitivity field also at room temperature, whereas β-Fe_2O_3 presented antiferro/paramagnetic characteristics. Remarkably, the magnetic properties of the obtained nanosystems were directly influenced by the system morphological organization and structural orientations.[2]

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INO-P29

Cu_xO-TiO_2 (x = 1, 2) nanomaterials by CVD: promising anodes for thin film lithium batteries

D. Barreca,[a] G. Carraro,[b] A. Gasparotto,[b] C. Maccato,[b] M. Cruz-Yusta,[c] J. L. Gómez-Camer,[c] C. Sada,[d] J. Morales,[c] L. Sánchez[c]

a Dip.to di Scienze Chimiche, Università di Padova and INSTM, Padova, Italia
b IENI-CNR and Dip.to di Scienze Chimiche,
Università di Padova and INSTM, Padova, Italia
c Dep.to de Química Inorgánica e Ingeniería Química -
Universidad de Córdoba, Córdoba, Spain;
d Dip.to di Fisica ed Astronomia-Università di Padova, Padova, Italy.

giorgio.carraro@unipd.it

Cu_xO-TiO_2 (x = 1, 2) nanocomposites represent appealing materials in view of various functional applications, such as catalysis, gas sensing, and photo-activated hydrogen production.[1] In the present work, supported Cu_xO-TiO_2 nanosystems are prepared for the use in anodes for Li-ion batteries. In particular, the adopted preparation strategy consists in a two-step chemical vapor deposition (CVD) route. First, CVD of Cu_xO nanomaterials was carried out on polycrystalline Ti starting from $Cu(hfa)_2$•TMEDA (hfa = 1,1,1,5,5,5 - hexafluoro - 2,4 - pentanedionate; TMEDA = *N*,*N*,*N'*,*N'* - tetramethylethylenediamine).[1,2] In a second step, the deposition of TiO_2 nanoparticles was performed using $Ti(O\text{-}^iPr)_2(dpm)_2$ ($O\text{-}^iPr$ = isopropoxy; dpm = 2,2,6,6 - tetramethyl - 3,5 - heptanedionate) as molecular precursor. The over-dispersion of TiO_2 on copper oxides was tailored in order to improve the anode electrochemical efficiency.[2] Notably, the proposed strategy enabled the tailoring of the system phase composition and nano-organization, with an intimate contact between Cu_xO and TiO_2, resulting in attractive electrochemical properties.

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INO-P30

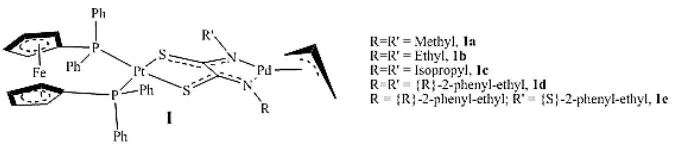
Chiral, achiral and pseudochiral heterotrimetalic complexes showing unusual fluxional behaviour

A.Giannetto I.Ielo, A.Saccà, G.Bruno, S.Lanza

Dipartimento di Scienze Chimiche, Università di Messina Via F Stagno D'Alcontres, 31 98166, Messina, Italy

IIelo@unime.it

Heterobimetallic metalloligands [(dppf, κ-P,P Pt) Pt(dialkyldithiooxamidate κ- S,S Pt]Cl react with [Pd(η^3-allyl)Cl_2]$_2$ giving rise to the following heterotrimetallic complexes **1**



NOESY experiments performed on various alkyl substituted type **1** complexes invariably show sin/anti exchange in the allyl moiety, in agreement with the allyl pseudorotation witch follows palladium-carbon bond rupture (η^3-η^1- η^3 mechanism). In a series of similar complexes the allyl isomerization was found to be the result of palladium-nitrogen bond rupture, so that only sin-sin/anti-anti exchange appeared in the NOESY 2D spectra.[1] However, in type **1** complexes geminal groups, if any, of alkyl substituents appear to be enantiotopic in the proton spectrum at room temperature; this fact seems to be in contrast with the Pd-C bond rupture as the sole cause of allyl motion, since in such a case geminal groups should have been diastereotopic. Thus, a chloroform solution of **1b**, whose ^{1}H NMR spectrum at rt showed only one sharp quartet featuring –CH_2- geminal protons, was gradually cooled till to 218 K. As a result, the sharp quartet coalesced at 253 K and changed at 218 K into 16 lines which were in agreement with an ABX_3 spin pattern. This means that in type **1** complexes allyl isomerization takes place at low temperature likely the T shaped intermediates after the Pd-N bond rupture (sin-sin/anti-anti exchange), and that at a by far higher temperature the η^3-η^1- η^3 mechanism becomes operating as well. With the aim to evidence both sin-sin/anti-anti and sin/anti exchange in the same 2D NOESY spectrum, complexes **1d** and **1e** were synthesized. In **1d** alkyl substituents are homochiral groups and therefore CH_2 terminal allyl protons are diastereotopic, and then sin protons, as well as the anti ones, should exchange into one another. In **1e** the binucleating dithiooxamide bears two enantiomorphic alkyl groups. As a consequence, **1e** does exist as an equimolar mixture of diastereomers, being palladium atom a pseudochiral centre. Thus, allyl pseudorotation should exchange sin protons of a diastereomer in the sin protons of the other one. Of course the same is true for the anti protons. Actually, 2D NOESY spectra of both **1d** and **1e** provide quite tangled results and do not exclude that the Pt-P bond rupture could be the source of the apparent rotation of allyl cuspid.

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INO-P31

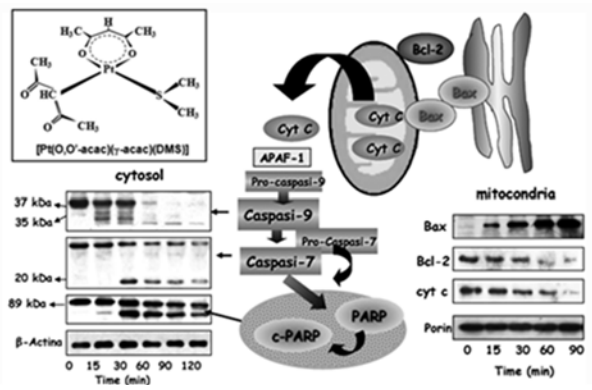
Antitumor activity *in vivo* of [Pt(*O,O′*-acac)(γ-acac)(DMS)] in malignant pleural mesothelioma

C. Vetrugno[a], A. Muscella[a], L. Cossa[b], S. Marsigliante[a], S.A. De Pascali[a], F.P. Fanizzi[a]

a Dipartimento di Scienze e Tecnologie Biologiche ed Ambientali, Università del Salento, Prov.le Lecce-Monteroni, 73100, Lecce, Italy
b Neuropathology Unit, Institute of Experimental Neurology and Division of Neuroscience, IRCCS San Raffaele Scientific Institute, Italy

fp.fanizzi@unisalento.it

Malignant pleural mesothelioma is an aggressive malignancy highly resistant to chemotherapy. The most effective treatment is the combination of multi-folate inhibitors and cisplatin, but still the median survival is only 12 months, and response rates are approximately 40% [1]. Recently, a new Pt(II) complex, [Pt(*O,O′*-acac)(γ-acac)(DMS)], showed strong *in vitro* and *in vivo* antiproliferative activity and reduced toxicity on breast cancer [2]. In this work we studied the efficacy and the action mechanism of [Pt(*O,O′*-acac)(γ-acac)(DMS)] and cisplatin treatment both in ZL55 human mesothelioma cells line *in vitro* and in a murine xenograft model *in vivo*. [Pt(*O,O′*-acac)(γ-acac)(DMS)] was more effective than cisplatin producing apoptosis characterized by: (a) mitochondria depolarization, (b) increase of bax expression and decrease of Bcl-2 expression, (c) activation of caspase-7 and -9, (d) generation of reactive oxygen species. Finally, the treatment of ZL55 solid tumor-bearing nude mice with [Pt(*O,O′*-acac)(γ-acac)(DMS)] significantly inhibited tumor growth *in vivo*, causing minimal systemic toxicity.



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INO-P32

New Organotin(IV) Compounds: Structural Basis for Antiproliferative Activity and Selectivity.

P. Sabatino[a], *M.A. Girasolo*[b], *A. Attanzio*[b], *L. Tesoriere*[b]

[a] *Dipartimento di Chimica "G. Ciamician", Alma Mater Studiorum, via F. Selmi 2, 40126, Bologna, Italy*
[b] *Dipartimento di Scienze e Tecnologie Molecolari e Biomolecolari, Università degli Studi di Palermo, Viale delle Scienze, pad. 16, Parco d'Orleans, 90128 Palermo, Italy*

piera.sabatino@unibo.it

Table 1
Calculated IC_{50} (μM) values[a] for anti-proliferative activity of organotin(IV) complexes against different human cell lines.

	$IC_{50} \pm SD$		
Compound	HepG2	MCF-7	HeLa
$Me_2SnCl_2(dbtp)$ **(1)**	nd[b]	nd[b]	nd[b]
$Me_2SnCl_2(dbtp)_2$ **(2)**	nd[b]	nd[b]	nd[b]
$Et_2SnCl_2(dbtp)$ **(3)**	>50	12 ± 1.40	>50
$Et_2SnCl_2(dbtp)_2$ **(4)**	>50	15 ± 1.10	>50
$Et_2SnCl_2(dptp)$ **(5)**	20 ± 1.50	7.5 ± 0.60	20 ± 1.50
$Bu_2SnCl_2(dbtp)_2$ **(6)**	1.0 ± 0.11	0.3 ± 0.02	1.2 ± 0.09
$Bu_2SnCl_2(dptp)$ **(7)**	0.6 ± 0.03	0.7 ± 0.05	1.6 ± 0.08
$Ph_2SnCl_2(dbtp)$ **(8)**	4.0 ± 0.30	4.8 ± 0.05	7.0 ± 0.40
$Ph_2SnCl_2(EtOH)_2(dptp)_2$ **(9)**	3.0 ± 0.25	3.8 ± 0.40	7.5 ± 0.50
cisplatin	65 ± 2	10 ± 1	17.5 ± 1.0

Organotin(IV) compounds, besides their use in industry and agriculture, are becoming increasingly important in health care, although the mechanism underlying their anti-cancer effects is still not completely understood[1]. New organotin(IV) compounds of 5,7-ditertbutyl-1,2,4-triazolo[1,5-a]pyrimidine (**dbtp**) and 5,7-diphenyl-1,2,4-triazolo[1,5-a]pyrimidine (**dptp**) were synthesized and characterized by FT-IR and ^{119}Sn Mössbauer in the solid state and by ^1H and ^{13}C NMR spectroscopy in solution [2]. Three of them have also been investigated by X-ray diffraction studies. All compounds were tested towards their cytotoxic activity by MTT test on three tumor cell lines, HepG2 (human hepatocellular carcinoma), HeLa (human cervix adenocarcinoma) and MCF-7 (human breast cancer), Table 1. Except for **1** and **2**, which were ineffective, all compounds significantly showed a dose-dependent anti-proliferative effect towards the three cell lines. By calculated IC_{50} values, cytotoxicity of the complexes followed the order ^{n}Bu > Ph > Et > Me for all the selected tumor cells. Complexes **4** and **9** contain hexacoordinated tin atoms [2], while **7** is a five-coordinated species with a distorted trigonal bipyramidal structure [3]. Conformational mobility of the cytotoxic complexes can sum up to the ligands ability to form H-bonds and aromatic interactions and play an important role in molecular recognition processes. Activity or inactivity of organotin(IV) compounds with monodentate N-donors seems to be the result of an interplay of favorable steric, enantiomeric and conformational factors in addition to the nature of the organotin(IV) ligands

[1]A. Davies, M. Gielen, K.H. Pannell, E.R.T. Tiekink, Tin Chemistry: Fundamentals, Frontiers, and Applications, John Wiley & Sons, Chichester, U. K., 2008.
[2]M.A.Girasolo, L.Canfora, P.Sabatino, D.Schillaci, E.Foresti, S.Rubino, G.Ruisi, G.Stocco, *J.Inorg.Biochem.* 2012, **106**, 156-163.
[3]M.A.Girasolo, A.Attanzio, P.Sabatino, L.Tesoriere, S.Rubino, G.C.Stocco, Inorg.Chim.Acta 2014, in press.

INO-P33

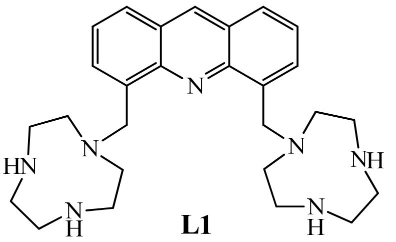
New acridine based ligands for metal ion binding and fluorescence sensing

Francesco Bartoli[a], *Andrea Bencini*[a], *Alessandra Garau,*[b] *Claudia Giorgi*[a], *Vito Lippolis,*[b] *Barbara Valtancoli,*[a]

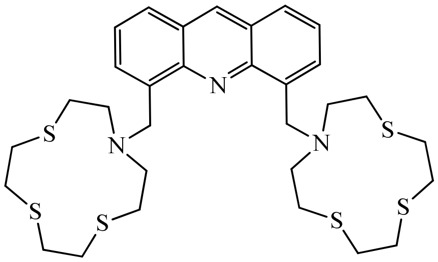
[a]*Dipartimento di Chimica "Ugo Schiff", Università di Firenze, Via della Lastruccia, 50019, Sesto Fiorentino, Italy*
[b] *Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari, Cittadella Universitaria – S.S. 554 bivio per Sestu, 09042 Monserrato, Cagliari Italy*

Francesco.Bartoli@unifi.it

There is a growing interest for new fluorescent ligands capable to bind selected metal ions, due to their potential use for metal cation sensing in biological or environmental matrices.[1] In this context, we have synthesized two new chelating agents containing an acridine fluorophore and two 1,4,7-triazonane (**L1**) or 1,4,7-trithia-10-azacyclododecane (**L2**) units as binding site for metals. Metal binding was analyzed by coupling potentiometric titrations and UV-vis and fluorimetric measurements.



L1



L2

Ligand **L1** is able to selectively sense in aqueous media Zn(II) over transition, post-transition, alkali and alkaline metal cations, thanks to a marked increase of the emission observed upon Zn(II) binding. The emission is not only determined by metal binding, but also by pH, the Zn(II) complex being strongly emissive at neutral or slightly acidic pH values. **L2** is able to sense Cd(II) and presents a different pH dependence of the emission of the complexes. These results will be discussed considering the different binding ability of the chelating sites of **L1** and **L2** not only for metal cations but also for acidic protons.

[1] A.Bencini, V.Lippolis *Coord. chem. rev.*, 2012, **256**, 149-169

Chimica Organica

Keynote

ORG-K1

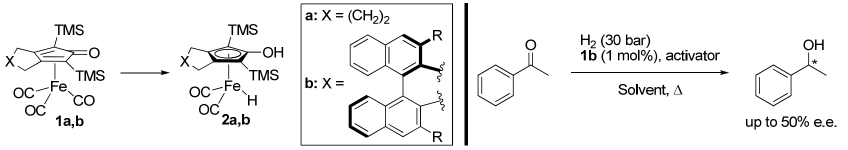
Towards a new class of chiral Fe-catalysts for the enantioselective hydrogenation of ketones

L. Pignataro,[a,b] *P. Gajewski,*[a,d] *C. Gennari,*[a,b] *R. Ferraccioli,*[b] *S. Vailati Facchini,*[c] *U. Piarulli,*[c] *M. Renom Carrasco,*[a,d] *L. Lefort,*[d] *J. G. de Vries*[e]

[a]*Università degli Studi di Milano, Dipartimento di Chimica, Milano, Italy*
[b]*CNR-Istituto di Scienze e Tecnologie Molecolari (ISTM), Milano, Italy*
[c]*Università degli Studi dell'Insubria, Dipartimento di Scienza e Alta Tecnologia, Como, Italy*
[d]*DSM Innovative Synthesis BV, Geleen, The Netherlands*
[e]*Leibniz-Institut für Katalyse an der Universität Rostock, Rostock, Germany*

luca.pignataro@unimi.it

Asymmetric catalysis is the most efficient strategy for producing enantiopure compounds, and the enantioselective reduction of double bonds (hydrogenation in particular) is one of its most well-developed applications. Compared to other transition metals, Fe is significantly less exploited for the homogeneous catalysis of double bond reductions. However, given the far lower cost and greater abundance of Fe over the more precious metals, in recent years there has been a growing interest for developing efficient and selective homogeneous Fe-catalysts.[1] Despite these efforts, only a few efficient enantioselective reduction methodologies based on Fe-catalysis have been developed so far. To fill this gap, we are developing new chiral catalysts for the enantioselective hydrogenation of ketones. We took inspiration from the Knölker-Casey catalyst **2a**,[2] an achiral Cp-Fe(II) hydride that can be generated *in situ* from the air-stable Fe(0)-cyclopentadienone precursor **1a**.[3] Catalyst **2a** can promote the hydrogenation of ketones and imines with very high efficiency (up to 3,800 TON). Chiral cyclopentadienone complexes **1b** were obtained by replacing the six-membered fused ring of **1a** with a BINOL-derived chiral moiety.



Complexes **2b**, formed *in situ* from **1b** using known procedures,[3] showed ability to promote the hydrogenation of acetophenone with good conversions (96%) and promising enantioselectivity (up to 55% e.e.). The synthesis of improved, second-generation catalysts is currently underway.

1. M. Darwish, M. Wills, *Catal. Sci. Technol.* **2012**, *2*, 243-255.
2. A. Quintard, J. Rodriguez, *Angew. Chem. Int. Ed.* **2014**, *53*, 4044-4055.
3. S. Fleischer, S. Zhou, K. Junge, M. Beller, *Angew. Chem. Int. Ed.* **2013**, *52*, 5120-5124.

This work was funded by the European Commission [EID-ITN Network 'REDUCTO', contract n. PITN-GA-2012-316371]. L.P. thanks the Dipartimento di Chimica, Università di Milano, for financial support (Piano di sviluppo dell'Ateneo—anno 2014—Linea B.1—grants for young researchers).

ORG-K2

Nanostructured polymer based platforms for tissue engineering

Luigi Ambrosio

Department of Chemical Science & Materials Technology,
National Research Council
P.le A. Moro 7, 00185 Roma, Italy

direttore.dsctm@cnr.it

In biological and medical applications, the capability of controlling physical and chemical interactions at the level of elementary natural components, from proteins to cells, is necessary to offer a more efficient exploration, manipulation, and application of living systems. In this context, micro or nano-structured polymers in the form of nanoparticles, nano-fibers and nano-composites have gained increasing interest in regenerative medicine because they often mimic the physical features of natural extracellular matrix (ECM) at the sub-micro and nano-scale level. By their manipulation via nanotechnologies, they currently represent an interesting tool to reproduce the features of native cell microenvironment which determine tissue specificity and architecture of tissues. In this context, many nano-inspired processes and tools have been recently studied to acquire better knowledge on the natural evolution of healthy or pathological tissues in 3D scaffolds, and to discover new technological solutions to improve conventional strategies in tissue engineering. Among them, Electrohydrodynamic Techniques (EDT) currently allow to revisit the traditional processing techniques for scaffold design by utilizing electrostatic forces as the driving force to assembly fibers and/or particles from an electrically charged polymer solution. By a careful selection of materials and processing conditions, they offer the opportunity to finely control characteristic shapes and sizes from micro to sub-micrometric scale and to incorporate biopolymers and bioactive molecules such as proteins or growth factor. The design of different nanostructure are made by electrospinning and/or electrospraying technique and rapid prototyping is proposed to develop active platforms to support the regeneration of different tissues such bone, nerve and skeletal muscle.

V Guarino, A. Gloria, M.G. Raucci, R. De Santis and L. Ambrosio ". Inter Mat Rev 2012

ORG-K3

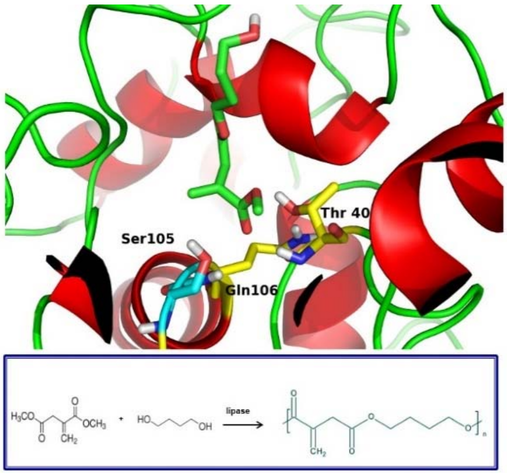
Enzymes in organic synthesis: towards a rational design of biocatalyzed reactions.

Valerio Ferrario, Cynthia Ebert, Lucia Gardossi.

Dipartimento di Scienze Chimiche e Farmaceutiche, Università degli Studi di Trieste.
Piazzale Europa 1, 34127, Trieste, Italia

gardossi@units.it

The integration of chemistry and bio-transformations has already set robust basis for bio-based chemistry and new generations of efficient biorefineries. However the accomplishment of sustainable but also competitive innovation requires the full exploitation of catalytic and selectivity potential of enzymes. Organic chemistry, physical organic chemistry and computational chemistry provide the tools for the understanding of molecular basis of enzyme action on unnatural substrates along with enzyme behavior under extreme non-conventional conditions. This rational route has been explored within the FP7 IRENE project that has also opened new perspectives towards the rational design of substrate and catalytic promiscuity within enzyme scaffolds. Rational strategies, in antithesis with "molecular evolution" strategies, stems on the fundamental knowledge of how reactions take place in the "pre-organized environment" of the enzyme active site. Examples will be illustrated that include the rational planning for the synthesis of chiral synthons, fine chemicals but also functionalized polyesters (see figure above).



[1] Ferrario V., Ebert C., Knapic L., Fattor D., Basso A., Spizzo P., Gardossi L. *Adv. Synth. Catal*. 2011, **353,** 2466 – 2480.
[2] Ferrario V., Braiuca P., Tessaro P., Knapic L., Gruber C., Pleiss J., Ebert C., Eichhorn E., Gardossi L. *J. Biomol. Struct. Dyn.*", 2012, **30**, 74-88.
[3] Ferrario V., Ebert C., Svendsen A., Besenmatter W., Gardossi L. *J. Mol. Cat. B*: *Enzymatic,* 2014, **101,** 7–15.

ORG-K4

Studying protein dynamics with an eye to molecular design

Giorgio Colombo

Istituto di Chimica del Riconoscimento Molecolare, CNR
Via Mario Bianco 9, 20131 MILANO (ITALY)

giorgio.colombo@icrm.cnr.it

In this study, we will present recent results on the development of computational strategies for the discovery of new inhibitors of protein-protein interactions with drug-like properties, and for the study of the functional dynamics and allosteric signal propagation mechanisms in proteins.

In the first part, a computational analysis of signal propagation mechanisms and long-range communication pathways in the molecular chaperone Hsp90 will be described. The analysis is carried out using molecular dynamics (MD) simulations of the full-length Hsp90 dimer, combined with essential dynamics, correlated motions analysis and a signal propagation model. We elucidate the mechanisms of signal propagation and determine hot spot residues involved in the inter-domain communication pathways from the nucleotide-binding site to the C-terminal domain interface. Interestingly, different communication mechanisms are triggered by different ligands. This information is then used to select for new allosteric modulators of the chaperone. The new molecules show the ability to allosterically inhibit the chaperone’s functional motions.

In the second part, we will discuss new methods to investigate the interaction properties of proteins, and in particular the prediction of antibody-binding sites. To this end, we have developed an integrated analysis of the dynamical and energetic properties of antigens, to identify non-optimized, low-intensity energetic interaction-networks in the protein structure isolated in solution. Analyzing the results on isolated proteins and benchmarking against antibody-complexes, the method successfully identifies binding sites located on the protein surface and accessible by putative binding partners.

Finally we will discuss the implication of these methods in drug and vaccine discovery.

ORG-K5

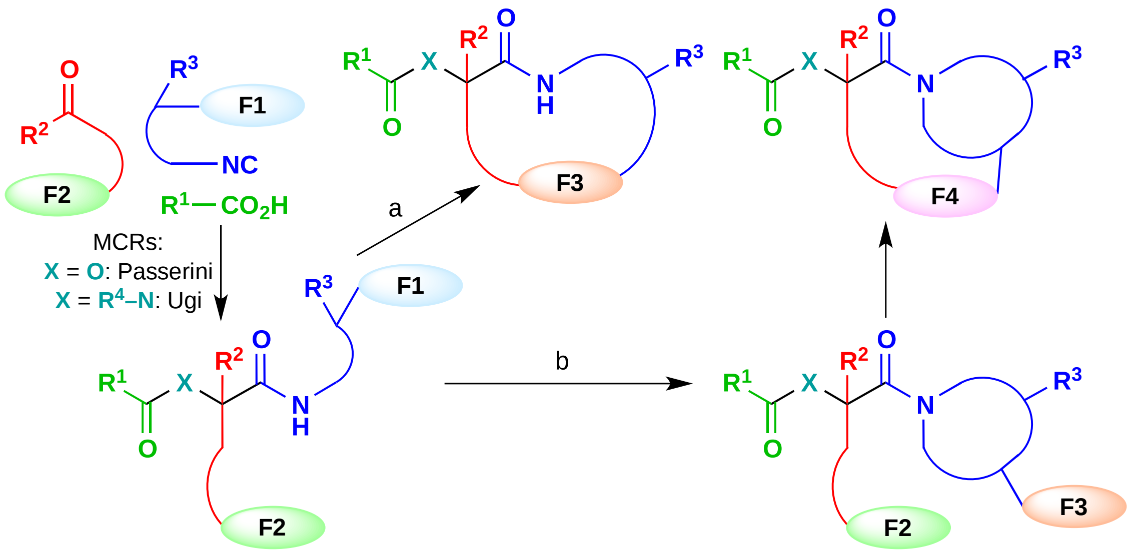
Combining multicomponent with organometal reactions: a valuable synergism

Renata Riva

Dipartimento di Chimica e Chimica Industriale, Università di Genova, Via Dodecaneso 31, 16146, Genova, I

riva@chimica.unige.it

Multicomponent reactions (MCRs), in particular those based on isocyanides (Passerini and Ugi reactions), offer a very convergent entry to highly functionalized acyclic derivatives. The presence of additional functional groups, properly placed on the starting materials, can be used both for further single (**a**) or multiple (**b**) chemical transformations, as separate steps or as one-pot sequences.
This strategy allows to build very complex heterocyclic scaffolds that may find interesting applications as biologically relevant structures or as new materials with photochromic properties.
Within this field a main solution is represented by transition metals promoted cyclizations. The most significant results will be presented.



ORG-K6

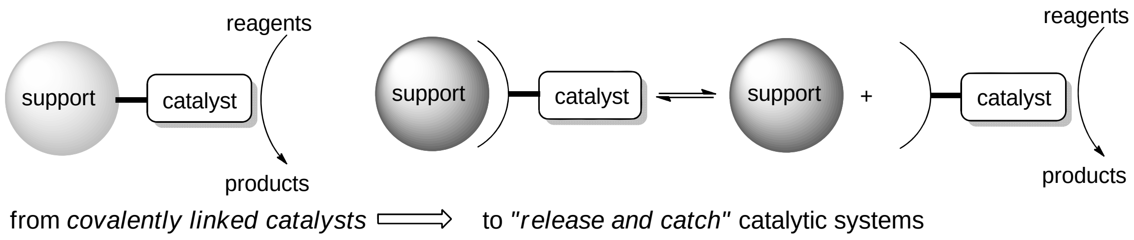
From covalently linked catalysts to “release and catch” catalytic systems

Michelangelo Gruttadauria, Francesco Giacalone, Renato Noto

Dipartimento di Scienze e Tecnologie Biologiche Chimiche e Farmaceutiche (STEBICEF), Sezione di Chimica, Università di Palermo, Viale delle Scienze, Ed. 17, 90128, Palermo, Italia

michelangelo.gruttadauria@unipa.it

Recovery and reuse of catalytic systems is a key issue in modern chemistry. Several strategies for catalyst recycling have been explored [1-2]. First, the active catalyst can be covalently linked to some kind of support. A second type of recycling methodology is biphasic catalysis. The third type of recovering strategy is the use of noncovalently supported catalysts. An improvement of the latter strategy is the development of a “release and catch” or “boomerang” catalytic system. A “release and catch” catalytic system is prepared by noncovalent immobilization of the catalytic moiety on a suitable support, but differently from the usual non-covalently supported catalyst, the catalytic moiety is released in solution during the course of the reaction and it is recaptured at the end of the process. Here we presents our recent results starting from covalently linked catalysts to “release and catch” catalytic systems [3].



[1] Catalytic Methods in Asymmetric Synthesis: Advanced Materials, Techniques, and Applications; M. Gruttadauria and F. Giacalone, Eds., John Wiley & Sons, 2011.
[2] Recoverable and Recyclable Catalysts; M. Benaglia, Ed., Wiley, 2009.
[3] M. Gruttadauria, F. Giacalone and R. Noto *Green Chem.*, 2013, **15**, 2608-2618.

ORG-K7

Green Solvents in Organic Synthesis

Ugo Azzena, Massimo Carraro, Ashenafi Damtew Mamuye, Irene Murgia, Luisa Pisano

Dipartimento di Chimica e Farmacia, Università di Sassari, Via Vienna 2 , 07100, Sassari, Italy

ugo@uniss.it

Solvents play a fundamental role in a variety of manufacturing and industrial services and chemical processes. Meanwhile, they greatly contribute to the environmental impact of human activities with specific problems concerning, *inter alia*, their toxicity, volatility and contribution to greenhouse effect, thus requiring significant efforts dedicated to their recovery, purification and recycle.

Accordingly, the quest for alternative reaction media endowed with environmental friendly characteristics, *i.e.*, Green Solvents, is a topic of current interest in contemporary synthetic organic chemistry,[1-4] with life cycle assessments being recognized as fundamental issues to evaluate the application of a solvent to a given reaction (or set of reactions).[5]

In this keynote, we will also present recent results from our laboratory concerning the employment of low impact ethereal solvents, namely cyclopentyl methyl ether and 2-methyltetrahydrofuran, in reaction involving the generation and reaction of polar organometallic reagents as well as the protection of carbonyl compounds under Dean-Stark reaction conditions.[6]

[1] J. M. DeSimone, *Science*, 2002, **297**, 799-803.
[2] R. A. Sheldon, *Green Chem.*, 2005, **7**, 267-278.
[3] P. G. Jessop, *Green Chem.*, 2011, **13**, 1391-1398.
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[5] J. H. Clark and S. T. Tavener *Org. Process Res. Dev.*, 2007, **11**, 149-155.
[6] With the financial support of Regione Autonoma della Sardegna (L. 07/09/2007, CRP-59740) and Fondazione Banco di Sardegna (contributo 2013.1273).

Chimica Organica

Medaglie

ORG-M1

Medaglia Mangini

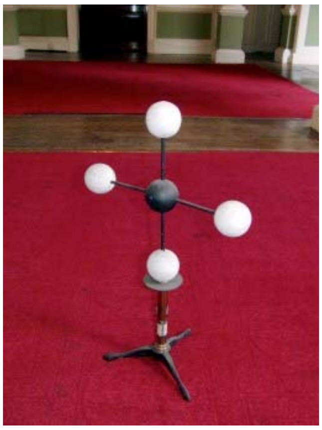
From physical organic chemistry to cheminformatics

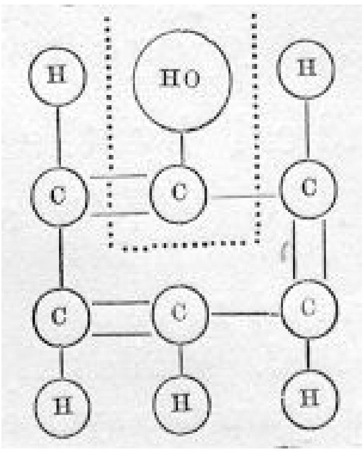
Gabriele Cruciani

Dipartimento di Chimica, Biologia e Biotecnologia, Università di Perugia, Via Elce di sotto 8, 06123, Perugia, Italia

gabriele.cruciani@unipg.it

According to some researchers, and this is also my personal opinion, the explosion of chemistry in the 19th century was due to the capability of the chemists to describe chemistry by using simple and effective models. Starting from the first attempt of August von Hofmann (ca. 1860) to model methane, to the model of phenol from Brown, until the first link of activity with molecular structure by Frazer in 1868, the chemists always tried to use mathematical or physical models, obeying certain specified conditions, to understand a chemical, physical or biological system to which they are analogous in some way.





Is this momentum forever lost? Are we developing appropriate models for the new challenges of the 21st century?

The paper will present an evolution of chemical models biased by industrial applications and problems, showing how the figure of the chemist may be still pivotal, from old fashioned drug design to the new omics disciplines.

ORG-M2

Medaglia Ciamician

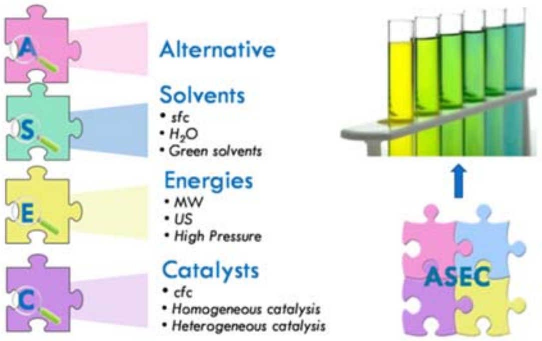
Green opportunities from the ASEC (Alternative Solvents, Energies and Catalysts) paradigm

Manuela Oliverio

Dipartimento di Scienze della Salute, Università degli Studi Magna Græcia - Catanzaro

m.oliverio@unicz.it

In the last two decades, the environmental issues that are linked to the chemical and other associated industries, have become increasingly pertinent in the scientific community. The need to improve process conditions and economics incorporating green chemistry into the synthesis of fine chemicals has ever more importance for the pharmaceuticals industry.



This work will deal with a new philosophy driving chemistry toward sustainability. The ASEC (Alternative Solvents, Energy and Catalyst) paradigm has been our strategy for the review of several important organic reactions in a more environmental-friendly way.[1] The goals of the ASEC paradigm are both to develop simple, reliable new protocols of pharmaceutical and chemical products and to suggest an eco-friendly option to be employed by companies that will be able to reduce the cost of processes, handling and disposal of waste and energy consumption. As an example of the application of ASEC paradigm to pharmaceutical chemistry two sustainable routes toward semi-synthetic oleuropein derivatives[2] and a novel class of Donepezil analogues will be discussed[3].

(1) (a) M. Oliverio et al. *ACS Sustainable Chem. Eng.*, **2014**, *2*, 1228-1233; (b) M. Oliverio et al. *RSC Adv.*, **2013**, *3*, 2548-2552; (c) M.Oliverio et al. *Aust. J. Chem.*, **2011**, *64*, 1522-1529; (d) A. Procopio et al. *Green Chem.*, **2011**, *13*, 436-443; (e) Procopio et al. *ChemSusChem*,**2008**, *1*, 916-919.
(2) A. Procopio et al.. *J. Agric. Food Chem.*, **2009**, 57, 11161–11167.
(3) M. Oliverio, et al. *Molecules*, **2014,** *19*, 5599-5610

ORG-M3

Medaglia Quilico

Fungal and Plant Phytotoxins: an adventure forty years long

Antonio Evidente

Dipartimento di Scienze Chimiche, Università di Napoli Federico II, Complesso Universitario Monte S. Angelo, Via Cintia 4, 80126 Napoli;

evidente@unina.it

The damages caused by pathogenic micro-organisms, weeds and insects to the main agrarian crops, ornamental and forest plants, with consequent heavy economical and environmental losses, as well as the risks for human and animal health have prompted studies to find efficient long term and eco-friendly alternative control methods. An innovative approach, started some decades ago through the collaboration between chemists of natural compounds and plant pathologists, physiologists and genetists, is based on the use of natural compounds with activity against these plant enemies. The microorganisms and plants possess a big fantasy to biosynthesize secondary metabolites with different and original carbon skeleton. Although a large number of metabolites were discovered until now, micro-organisms and plants remain the main source of new bioactive compounds. Extensive studies were carried out on the fungal phytotoxins, secondary metabolites that play a major role in the development of the plant disease symptoms. Recently, the study was also extended to phytotoxins produced by allelopathic plants. Phytotoxins, assayed at very low concentration, showed other very interesting activities as microbial antagonisms and hormone like. So that, several new bioactive metabolites, belonging to different classes of natural compounds, were isolated from phytopathogenic fungi and allelophatic plants, showing potential applications in agriculture as fungicides, bacteriocides, herbicides and insecticides. Some fungal phytotoxins surprisingly also showed a strong anticancer activity associated with an original mode of action. These phytotoxins were object of an intensive collaboration with biologists aimed to find natural compounds with a probable leading role in cancer drug discovery resulting in a large number of clinically useful agents.

This seminar will be an overview covering forty years the activity on the isolation and chemical and biological characterization of several fungal and plants bioactive metabolites also discussing, in some cases, their structure-activity relationships, mode of action and their potential applications in agriculture and/or medicine.

ORG-M4

Medaglia Piria

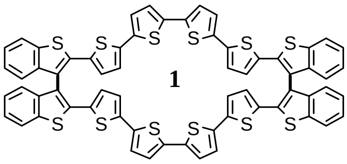
Inherently chiral, electroactive, macrocyclic oligoheteroarenes: D_n symmetric ellipses and triangles

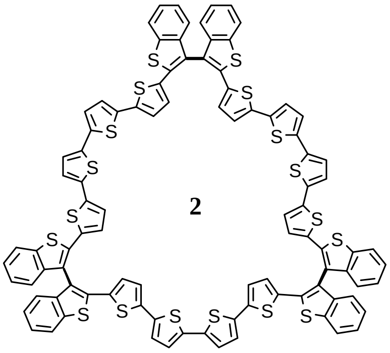
<u>F. Sannicolò</u>[a], T. Benincori[b], P. R. Mussini[a], S. Arnaboldi[a], E. Quartapelle Procopio[a], R. Martinazz [a], M. Panigati[a], S. Abbate[c], G. Longhi[c], E. Castiglioni[c], R. Cirill[d], S. Rizzo[e], M. Pierini[f]

a Dip. di Chimica and C.I.Ma.I.Na, Univ. di Milano, via Golgi 19, 20133 Milano, Italy
b Dip. di Scienza e Alta Tecnologia, Univ. dell'Insubria, via Valleggio 11, 22100, Como, Italy
c Dip. di Medicina Molecolare e Traslazionale, Univ. di Brescia, Viale Europa 11, 25121, Brescia, Italy
d Dip. del Farmaco, Ist. Superiore di Sanità, Viale Regina Elena, 299, 00161, Roma, Italy
e Ist. di Scienze e Tecnologie Molecolari, CNR, via Golgi 19, 20133, Milano, Italy
[f] Univ. di Roma "La Sapienza", Dip. di Chimica e Tecnologie del Farmaco, Piazza Aldo Moro 5, 20100 Roma, Italy

francesco.sannicolo@unimi.it

Linear conjugated oligo-thiophenes of variable length and different substitution pattern are ubiquitous in technologically advanced opto-electronic devices, though limitations in application derive from insolubility, scarce processability and chain-ends effects. Chirality is associated to these systems by attaching chiral pendants to the chain. The communication describes an easy access to inherently chiral macrocyclic oligothiophenes in which chirality is produced by a torsion in the conjugated backbone.[1] The most abundant macrocycles, displaying the general structure **1** and **2** are constituted by 12 and 18 fully conjugated thiophene units. Combination of chirality with electroactivity makes these molecules unique in the current literature. These oligothiophenes, which are stable and soluble in most organic solvents, show outstanding chiroptical properties, high Circularly Polarized Luminescence effects and an exceptional enantiorecognition ability.





[1] F. Sannicolò, S. Arnaboldi, T. Benincori, V. Bonometti, R. Cirilli, L. Dunsch, W. Kutner, G. Longhi, P. R. Mussini, M. Panigati, M. Pierini, S. Rizzo, *Angew. Chem. Int. Ed.* 2014, **53**, 2623-2627.

Work supported by Fondazione Cariplo (reg. No. 2011-0417).

Chimica Organica

Premi

ORG-R1

Premio alla ricerca "Chimica organica nei suoi aspetti di applicazione industriale"

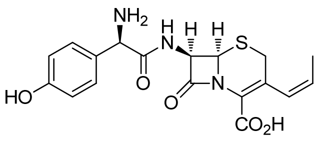
20 Anni di Sintesi di Principi Attivi

Vittorio Farina

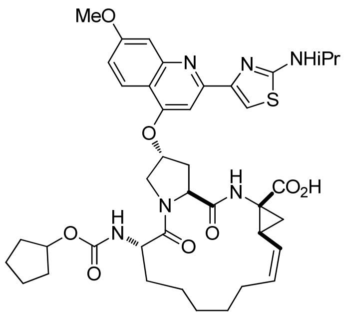
API Small Molecule Development, Janssen Pharmaceutica, Turnhoutseweg 30, 2340 Beerse, Belgio

vfarina@its.jnj.com

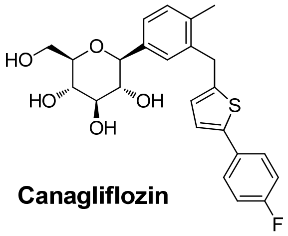
Il seminario passera' in rassegna le problematiche affrontate durante lo sviluppo di processi industriali in relazione a tre farmaci (Cefprozil [1], Ciluprevir [2] e Canagliflozin [3]) sviluppati presso tre ditte farmaceutiche diverse (BMS, Boehringer-Ingelheim e Janssen) durante un arco di 20 anni.



Cefprozil



Ciluprevir



Canagliflozin

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[1] V. Farina, con Sébastien Lemaire *Org. Lett.*, 2012, **14**, 1480, *e dati non pubblicati*.
[2] V. Farina, con Chutian Shu *Org. Lett.* 2008, **10**, 303.
[3] V. Farina, con Joydeep Kant *J. Org. Chem.* 1994, **59**, 4956.

ORG-R2

Premio alla ricerca "Chimica organica nei suoi aspetti sintetici"

The many aspects of Peptide Nucleic Acids as tools for diagnostics and therapy

Emanuela Licandro

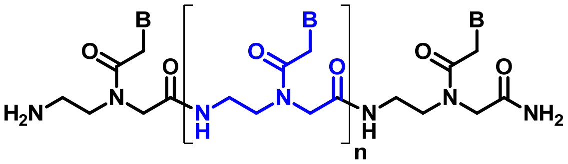
Dipartimento di Chimica, Università degli Studi di Milano, Via C. Golgi 19 , 20133, Milano

emanuela.licandro@unimi.it

PNA are a remarkable example of a simple, neutral structure able to act as a perfect mimic of native nucleic acid structures in terms of molecular recognition properties. PNA are made of a pseudopeptide backbone, in which the ribose phosphodiester backbone of DNA and RNA is replaced by units of *N*-(2-aminoethyl)glycine, on which the nucleobases are inserted. Therefore, they can bind to target natural DNA or RNA with high sequence specificity and affinity and are excellent candidates in diagnostics and biodrug theraphy.

We have contributed to this research topic by tailoring the structure of selected sequences of PNA to specific objectives with unconventional functionalities such as luminescent dirhenium complexes or magnetic nanoparticles (MNPs).

The insertion of the luminescent rhenium complexes has a twofold aim: allowing the traceability of PNAs within the organism by optical imaging, and facilitating cell penetration. The conjugation of PNA to MNPs can be exploited both as contrast agents for magnetic resonance imaging (MRI) and as sources of local overheating for hyperthermia treatment.



A PNA oligomer

[1] C. Mari, M. Panigati, L. D'Alfonso, I. Zanoni, D. Donghi, L. Sironi, M. Collini, S. Maiorana, C. Baldoli, G. D'Alfonso, E. Licandro, *Organometallics*, **2012**, *31*, 5918−5928.

[2] G. Prencipe, S. Maiorana, P. Verderio, M. Colombo, P. Fermo, E. Caneva, D. Prosperi, E. Licandro, *Chem. Commun*, **2009**, 6017–6019.

ORG-R3

Premio alla ricerca "Chimica organica nei suoi aspetti meccanicistici e teorici"

"The Great Beauty" of Organolithium Chemistry: A Land Still Worth Exploring

Vito Capriati

Dipartimento di Farmacia-Scienze del Farmaco, Università di Bari "Aldo Moro",
Consorzio C.I.N.M.P.I.S., Via E. Orabona 4, I-70125, Bari, Italy

vito.capriati@uniba.it

Organolithium compounds form the largest single group of synthetically useful organometallic compounds, and not a day goes by without the announcement of a new, versatile RLi species, or a novel aspect of reactivity of an older one.[1] Organolithiums are indeed reputed to exhibit an astonishing array of self-assembled structures and a careful exploitation of the *structure-reactivity relationship* can coax them to follow different and unusual pathways. The nature of the reaction medium, the mode of organolithium addition, the temperature, the concentration, and the presence of additives, influencing both *aggregation* and *solvation*, may in turn contribute to a fine-tuning of the reactivity, thereby allowing "optimization" of organolithium reactions.[1] In this lecture, some recent selected examples of our work[2] will be illustrated showing how different experimental conditions and known aggregation states can affect the *reactivity* and the *stereochemical behavior* of functionalized organolithium compounds. The promising employment of Deep Eutectic Solvents, that is eutectic mixtures comprising a hydrogen-bond donor (e.g., glycerol, urea, or water) and a simple halide salt (e.g., choline chloride) as new, green, bio-renewable reaction media for the highly reactive organolithium compounds will be also discussed.[3]

Acknowledgments: Programma Operativo Nazionale Ricerca e Competitività 2007-2013 (PON01_00862).

[1] a) *Lithium Compounds in Organic Synthesis – From Fundamentals to Applications*, ed. R. Luisi and V. Capriati, Wiley-VCH, 2014; b) V. Capriati, F. M. Perna and A. Salomone, *Dalton Trans.* 2014, DOI: 10.1039/C4DT01004C, Frontier article.
[2] a) D. I. Coppi, A. Salomone, F. M. Perna and V. Capriati, *Chem. Comm.* 2011, **47**, 9918–9920; b) D. I. Coppi, A. Salomone, F. M. Perna and V. Capriati, *Angew. Chem. Int. Ed.* 2012, **51**, 7532–7536; c) R. Mansueto, V. Mallardo, F. M. Perna, A. Salomone and V. Capriati, *Chem. Comm.* 2013, **49**, 10160–10162; d) R. Mansueto, F. M. Perna, A. Salomone, S. Florio and V. Capriati, *Chem. Comm.* 2013, **49**, 4911–4913; e) A. Salomone, F. M. Perna, A. Falcicchio, S. O. Nilsson Lill, A. Moliterni, R. Michel, S. Florio, D. Stalke and V. Capriati, *Chem. Sci.*, 2014, **5**, 528–538.
[3] V. Mallardo, R. Rizzi, F. C. Sassone, R. Mansueto, F. M. Perna, A. Salomone and V. Capriati, *Chem. Comm.* 2014, DOI: 10.1039/C4CC03149K.

ORG-R4

Premio alla ricerca "Chimica organica nei suoi aspetti di determinazione strutturale e interazioni molecolari"

A shortcut to complexity: cooperation within functional nanoparticles

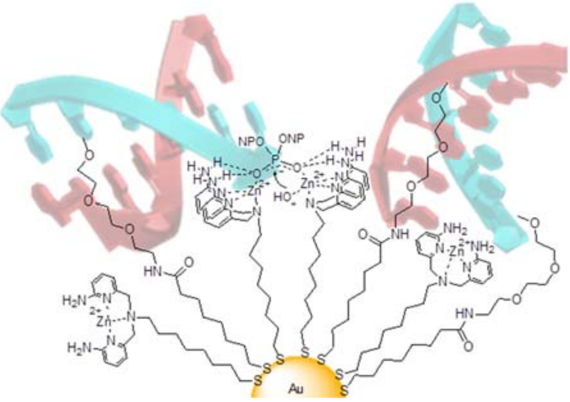
Fabrizio Mancin

Dipartimento di Scienze Chimiche, Università di Padova, Via Marzolo 1, Padova, Italia

fabrizio.mancin@unipd.it

The assembly of simple building block in large structures allowed Nature to create chemical systems capable to perform complex and sophisticate functions. Approaching such a complexity by chemical design and synthesis is still out of our reach. However, nanoparticles protected by a monolayer of organic molecules may offer an accessible shortcut to the realization of complex systems. The functional group organization in the monolayer can be exploited to achieve cooperative and collective effects, including molecular recognition, catalysis and sensing. The talk will illustrate our results on the use of different nanoparticles as templates to direct the self-organization of supramolecular systems.

Silica nanoparticles functionalization with ligands for metal ions and fluorescent dyes provided fluorescent chemosensors. This approach allows the straightforward optimization and regulation of the sensor performance, the creation of recognition sites, the differentiation of the components tasks, and the modulation of the interaction with biological systems.[1]



Gold nanoparticles functionalizated with Zn(II) were studied as multivalent catalysts for the hydrolysis of phosphate diesters, included DNA (Figure), where reactivity can be controlled by the monolayer features.[2]

Finally, recognition ability of monolayer protected gold nanoparticles has been exploited to introduce "NMR chemosensing", a new method for the detection and identification of organic molecules based on the use of NMR spectrometry and nanoparticles. After target recognition, the nanoparticle labels it by magnetization transfer while the signals of the other species present are cancelled by a diffusion filter. [3]

1) *Chem. Eur. J.*, **2007**, *8*, 2238-2245; *Org. Lett.*, **2012**, *14*, 2984-2987.
2) *J. Am. Chem. Soc.* **2008**, *130*, 15744-15745, *J. Am. Chem. Soc.* **2014**, *136*, 15744-15745.
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Chimica Organica

Oral

ORG-O1

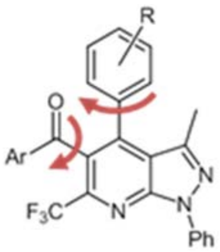
Atropisomers of 4-arylpyrazolo-pyridine. Conformational analysis and absolute configuration

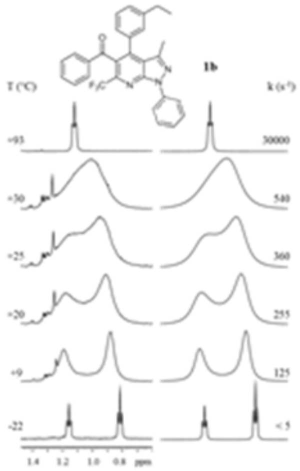
S. Perumal[a], P. Gunasekaran[a], J. C. Menendez[b], M. Mancinelli[c], S. Ranieri[c], A. Mazzanti[c]

a Department of Organic Chemistry, School of Chemistry, Madurai Kamaraj University,
Madurai – 625 021, Tamil Nadu, India
b Departamento de Química Orgánica y Farmacéutica, Facultad de Farmacia, Universidad
Complutense, 28040 Madrid, Spain
c Department of Industrial Chemistry "Toso Montanari", University of Bologna,
Viale Risorgimento 4, 40136 - Bologna, Italy

andrea.mazzanti@unibo.it , subbu.perum@gmail.com

In this work the stereodynamic behavior of a series of pyrazolo-pyridine[1] derivatives was studied. The restricted rotations of the aryl substituent in position 4 of the heteroaromatic ring and of the benzoyl group in position 5 generate conformational enantiomers or conformational diastereoisomers depending on the local symmetry of the aryl substituent in position 4. The energy barrier for the rotation of the 5-benzoyl group and for the 4-aromatic ring were measured by dynamic NMR and rationalized by DFT calculations[2].





[1] Gunasekaran, P.; Indumathi S.; Perumal S. *RSC Advances*, **2013**, 3, 8318–8325.
[2] *a)* Casarini D., Lunazzi L., Mazzanti A., *Eur. J. Org. Chem.* **2010**, 2035–2056. *b)* Bogdan N., Grosu I., Benoît G., Toupet L., Ramondenc Y., Condamine E., Dumitrescu I. S., Plé G., *Org. Lett.* **2006**, 8, 2619–2622.

ORG-O2

Metal catalyzed reactions for (+)-a*R*,11*S*-myricanol total synthesis

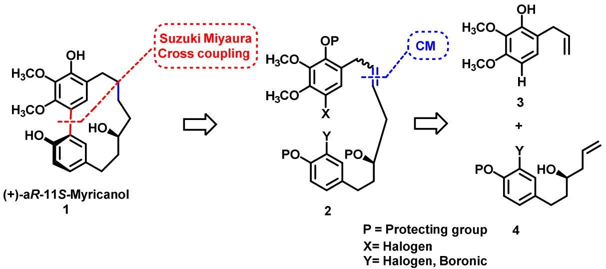
Antonella Bochicchio[1], *Lucia Chiummiento*[1], *Maria Funicello*[1], *Paolo Lupattelli*[1], *Gilles Hanquet*[2], *Sabine Choppin*[2] *and Françoise Colobert*[2]

[1] *Dipartimento di Scienze, Università della Basilicata*
Via dell'Ateneo Lucano10, 85100 Potenza, Italia.
[2] *CNRS-Université de Strasbourg, UMR 7509, Equipe SynCat*

Rue Becquerel 25, 67087 Strasbourg Cedex 02, France.

antonella.bochicchio@unibas.it

We are interesting in the bioactive diarylheptanoids[1] and especially in the stereoselective synthesis of (+)-a*R*,11*S*-myricanol **1**.(Scheme 1)



Scheme 1

This cyclic diarylheptanoid extracted from *Myrica cerifera* (86% e.e.) potently reduces tau protein levels in cells (anti Alzheimer effect).[2] We envisioned to controle the axial chirality using an atropodiastereoselective Suzuki-Miyaura reaction[3] on compound **2**. The linear diarylheptanoid and its analogues could be obtained by cross metathesis reaction[4] between **3** and the homoallylic alcohol **4** on which the central chirality could be achieved from the chemistry of asymmetric sulfoxide.[5]

[1]. Lv, H.; She, G. *Rec. Nat. Prod.* **2012**, *6:4*, 321-333.
[2]. Jones, J. R., Lebar, M. D.; Jinwal, U. K.; Abisambra, J. F.; Koren, J.; III; Blair, L.; O'Leary, J. C.; Davey, Z.; Trotter, J.; Johnson, A. G.; Weeber, E.; Eckman, C. B.; Baker, B. J.; Dickey, C. A. *J. Nat. Prod.* **2011**, *74*, 38–44.
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ORG-O3

Organocatalytic Tandem Methodologies for Asymmetric Synthesis of Cyclic Molecules

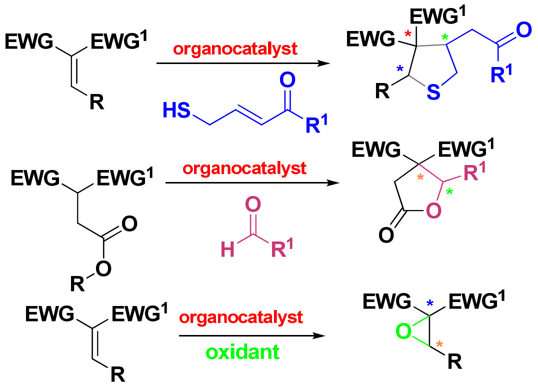
Sara Meninno[a], Alessandra Lattanzi[*,a]

[a] *Dipartimento di Chimica, Università di Salerno, Via Giovanni Paolo II, 84084, Fisciano, Italy*

smeninno@unisa.it

Ring-forming reactions allow access to a range of natural products and biologically important molecules. The development of cascade reactions to synthesize carbo- and heterocyclic compounds of different ring sizes, in a single operation, is a topic of intense investigation.[1] They have several inherent advantages over multistep syntheses, including time- and cost-savings, atom economy, environmental friendliness. Asymmetric organocatalysis has introduced new perspectives with regard to the design and application of one-pot stereoselective processes. The covalent organocatalysis, such as aminocatalysis, has been more extensively used in stereoselective one-pot syntheses of cyclic molecules compared to non-covalent catalysis such as hydrogen bonding catalysis/ion-pairing. Important promoters of the second category of transformations are cinchona thioureas and squaramides, diaryl prolinols, etc.

In this communication, our recent results on the development of tandem non-covalent organocatalytic methodologies, in particular focused on the synthesis of cyclic molecules having quaternary stereogenic centers, will be illustrated.[2]



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ORG-O4

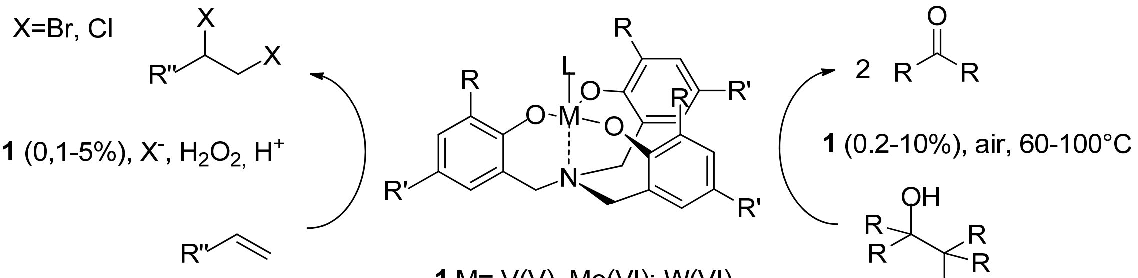
Aminotriphenolate Metal Complexes for Effective Catalytic Oxidations

Emanuele Amadio, Elena Badetti, Cristiano Zonta, Giulia Licini

Dipartimento di Scienze Chimiche, Università di Padova, Via Marzolo, 1, 35131, Padova, Italy

giulia.licini@unipd.it

Recently aminotriphenolate metal complexes **1**[1] have been reported to effectively catalyse important reactions like polymerizations,[2] olefin metathesis,[3] CO_2/epoxide cycloadditions,[4] and oxygen transfer processes.[5] Here we will report on their use in catalytic oxidative processes like haloperoxidations and aerobic carbon-carbon oxidative cleavage of vicinal diols and hydroxyethers, model compounds of lignin.



1 M= V(V), Mo(VI); W(VI)

[1] M. Mba, C. Zonta, G. Licini *Dalton. Trans.*, 2009, 5265.
[2] J. Chmura, M. G. Davidson, C. J. Frankis, M. D. Jones and M. D. Lunn, *Chem. Commun.*, 2008, 1293.
[3] K. Jyothish, W. Zhang, *Angew. Chem., Int. Ed.*, 2011, **50**, 8478.
[4] C. J. Whiteoak, N. Kielland, V. Laserna, E. C. Escudero-Adán, E. Martin, A. W. Kleij *J. Am. Chem. Soc.*, 2013, **155**, 1228.
[5] C. Zonta and G. Licini *Chem. Eur. J.* 2013, **19**, 9438 and references therein.

ORG-O5

Thiahelicene Phosphoruos Derivatives

Davide Dova[a]*, Silvia Cauteruccio*[a]*, Lucia Viglianti*[a]*, Andrea Genoni*[a]*, Manuel Orlandi*[a]*, Claudia Graiff*[b]*, Patrizia R. Mussini*[a]*, Emanuela Licandro*[a]

a Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, I-20133, Milano, Italia
b Dipartimento di Chimica, Università degli Studi di Parma, Viale delle Scienze 17/A, 43100, Parma, Italia

davide.dova@unimi.it

Tetrathia[7]helicenes (7-TH) are polyconjugated π-systems in which four thiophene rings are *ortho*-fused to alternating arene rings to generate a non planar and chiral helix, which allows the existence and the separation of the *M* and *P* antipodes. Exploiting our well-established know-how in the synthesis and functionalization of 7-TH derivatives, we have recently focused our attention on the study of new 7-TH phosphorous derivatives as potential chiral ligands in asymmetric organometallic catalysis[1] and organocatalysis.[2]

Based on the promising results obtained in these studies, new classes of 7-TH phosphorous derivatives, whose structures are reported in Figure 1, have been synthesized, and their chiroptical, structural, electronic and electrochemical properties have been investigated.

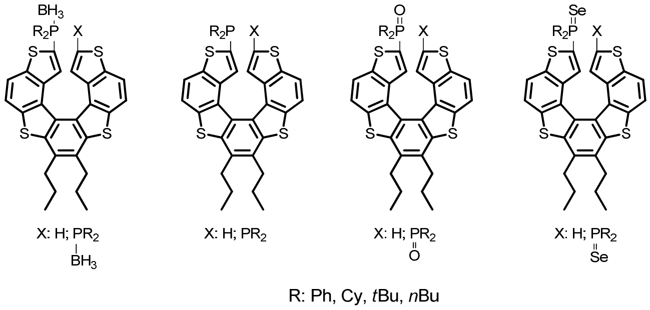


Figure 1.

[1] a) S. Cauteruccio, S. Maiorana, E. Licandro, et al. *Eur. J. Org. Chem.* **2011**, 5649; b) S. Cauteruccio, A. Bossi, D. Dova, A. Dreuw, E. Licandro, A. S. K. Hashmi, *Inorg. Chem.* **2013**, *52*, 7995.

[2] S. Cauteruccio, D. Dova, M. Benaglia, A. Genoni, M. Orlandi, E. Licandro, *Eur. J. Org. Chem.* **2014**, 2694.

ORG-O6

Biocompatible Sugar-Based BODIPY Derivatives: Synthesis, Photophysical Properties and Biological Studies

Teresa Papalia[a], Anna Barattucci[b], Paola Bonaccorsi,[b]Fausto Puntoriero[b], Maria Teresa Sciortino[c] and Sebastiano Campagna[b,]

a Dipartimento di Scienze del Farmaco e dei Prodotti per la Salute, Università di Messina, Villaggio SS. Annunziata, 98166, Messina, Italy
b Dipartimento di Scienze Chimiche, Università di Messina, Viale F. Stagno D'Alcontres 31, 98166, Messina, Italy
c Dipartimento di Scienze Biologiche e Ambientali, Università di Messina, Viale F. Stagno D'Alcontres 31, 98166, Messina, Italy

tpapalia@unime.it

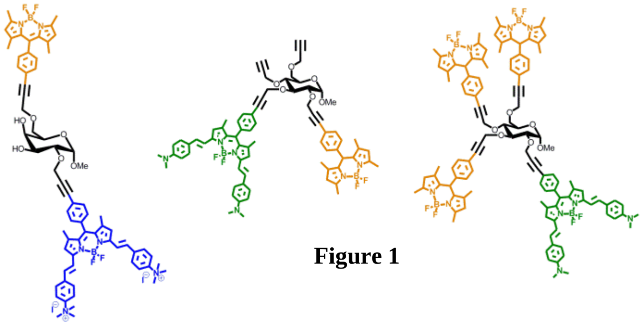


Figure 1

The synthesis and spectroscopic properties of a family of new biocompatible bodipy-based fluorescent dyes bearing sugar residues will be described. The key step of the synthesis was the coupling, by a copper-free Sonogashira reaction, of iodoaryl-substituted BODIPY frameworks with suitably functionalized sugar residues. Efficient FRET platforms, featuring semiflexible sugar spacers between two different BODIPY dyes, were obtained in good yields (Figure 1).[1] The biological results, for some of the BODIPY-based dyes, in cellular internalization experiments will be also discussed (Figure 2).[2]

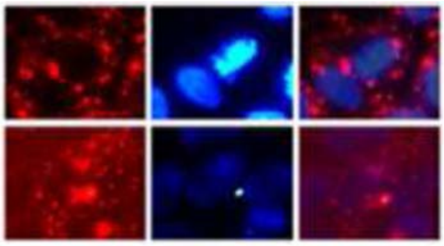


Figure 2

[1] P. Bonaccorsi, M. C. Aversa, A. Barattucci, T. Papalia, F. Puntoriero and S. Campagna *Chem Commun*, 2012; **48**, 10550-10552.
[2] T. Papalia, G. Siracusano, I. Colao, A. Barattucci, M. C. Aversa, S. Serroni, G. Zappalà, S. Campagna, M. T. Sciortino, F. Puntoriero and P. Bonaccorsi *Dyes and Pigments*, 2014, accepted.

ORG-O7

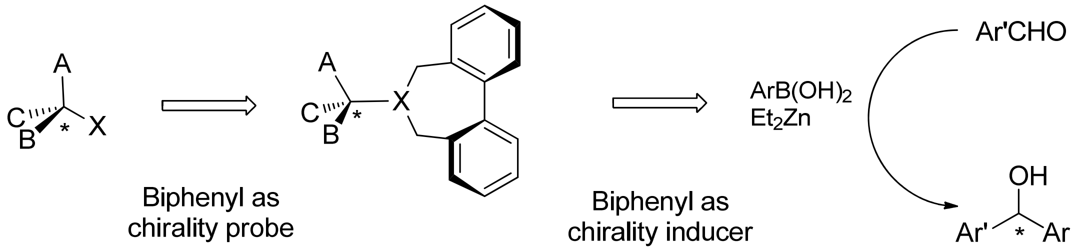
Flexible Biphenyls: from Chiral Sensing to Chiral Induction

Stefano Superchi, Laura Pisani, Stefania Vergura, Patrizia Scafato

Dipartimento di Scienze, Università della Basilicata, Via Ateneo Lucano 10, 85100, Potenza, Italy

stefano.superchi@unibas.it

Flexible biphenyls can provide a suitable probe for detection of absolute configuration of chiral molecules by chiroptical spectroscopies. In fact, when such atropisomerically flexible moiety is covalently liked to a chiral molecule a central to axial chirality transfer occurs and the biphenyl system assumes a preferred torsion depending on the absolute configuration of the derivatized molecule. Such torsion can be easily detected by either ECD and/or ORD spectroscopy, therefore just looking at the ECD spectrum of the biphenyl derivate or at its OR sign it is possible to arrive at determining the absolute configuration of the molecule under investigation. Such approach proved to be reliable for chiral non racemic diols,[1a] carboxylic acids,[1b] and amines. The same central to axial chirality transfer mechanism makes these flexible biphenyls suitable *tropos* moieties[2] for designing efficient ligands for asymmetric catalysis.[3] The use of such non-atropisomerically stable biphenyls as sensors for chirality detection and inducers in asymmetric synthesis will be described.



[1] (a) S. Superchi, D. Casarini, A. Laurita, A. Bavoso and C. Rosini *Angew. Chem. Int. Ed. Engl.*, 2001, **40**, 451-454. (b) S. Superchi, R. Bisaccia, D. Casarini, A. Laurita and C. Rosini *J. Am. Chem. Soc.*, 2006, **128**, 6893-6902.
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ORG-O8

α,ε-Hybrid Foldamers Containing 1,2,3-Triazole Rings

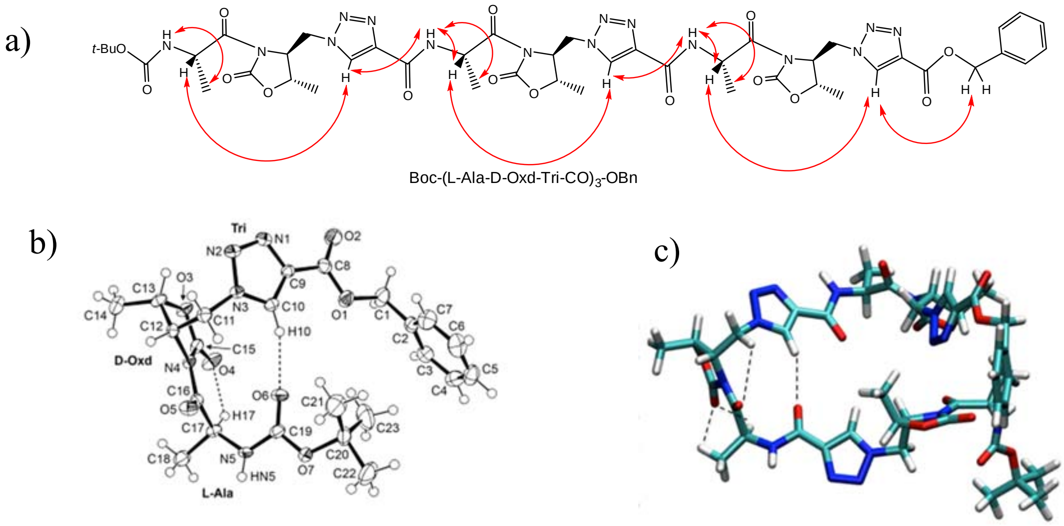
Lorenzo Milli[a], *Nicola Castellucci*[a], *Claudia Tomasini* [a]*

Dipartimento di Chimica "G. Ciamician", Alma Mater Studiorum Università di Bologna, Via Selmi 2, 40126, Bologna, Italia

lorenzo.milli.88@gmail.com

Two epimeric series of foldamers characterized by the presence of a repeating α,ε-dipeptide unit have been prepared and analyzed by ^{1}H NMR and ECD spectroscopies together with X-ray diffraction. The first series contains L-Ala and D-4-carboxy-5-methyl-oxazolidin-2-one (D-Oxd). The other series contains L-Ala and L-Oxd. The L,D series of oligomers forms ordered β-turn foldamers, characterized by a 3_{11} pattern. The L,L series is not ordered.

These new foldamers containing the L-Ala-D-Oxd-Tri-CO motif may be introduced in any peptide sequence requiring the presence of a stable β-turn conformations.



a) ROESY spectrum of Boc-(L-Ala-D-Oxd-Tri)$_3$-OBn; b) Ortep-3 plot of Boc-L-Ala-D-Oxd-Tri-OBn; c) Most stable conformation of Boc-(L-Ala-D-Oxd-Tri)$_3$-OBn by molecular dynamics.

[1] L. Milli, M. Larocca, M. Tedesco, N. Castellucci, E. Ghibaudi, A. Cornia, M. Calvaresi, F. Zerbetto, C. Tomasini, *J. Org. Chem.*, submitted

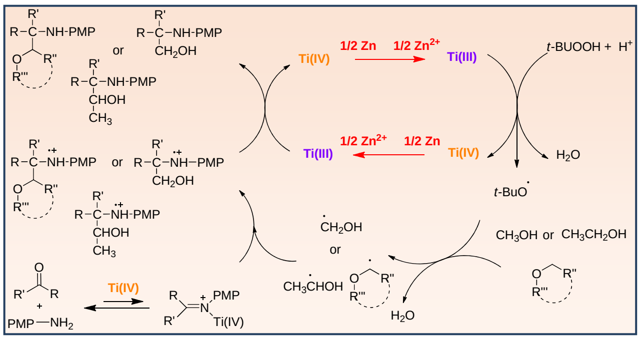
ORG-O9

One-Pot Multicomponent Free-Radical Reactions Mediated by Titanium Salts

Bianca Rossi[a], *Nadia Pastori*[a], *Lucio Melone*[a], *Elena Tallarita*[a], *Gabriele Candiani*[a], *Carlo Punta*[a]

a Dipartimento di Chimica, Materiali, Ingegneria Chimica "Giulio Natta", Politecnico di Milano, P.zza Leonardo da Vinci, 20133, Milano, Italy

bianca.rossi@polimi.it



Nucleophilic radical addition to the carbon atom of imine derivatives has proved to be a valuable alternative for the synthesis of a wide range of polyfunctional molecules. [1]

Particularly interesting is the role of $TiCl_4$-Zn/*t*-BuOOH catalytic system to promote free-Radical Multicomponent Reactions. As shown in the reaction mechanism proposed, Titanium promotes the imine formation in situ and activates its reactivity. Here we report three applications:

a) Synthesis of *β*-amino alcohols via Nucleophilic radical hydroxymethylation of ketimines [2]; b) *β*-aminoalkylation of ethers[3]; c) Nucleophilic radical hydroxyalkylation of ketimines with ethanol[3]. Preliminary results show the possible application of this reaction for the grafting of polymers bearing primary amino groups, as polyethyleneimine and chitosan, to be used as non-viral vectors for gene delivery.[4]

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ORG-O10

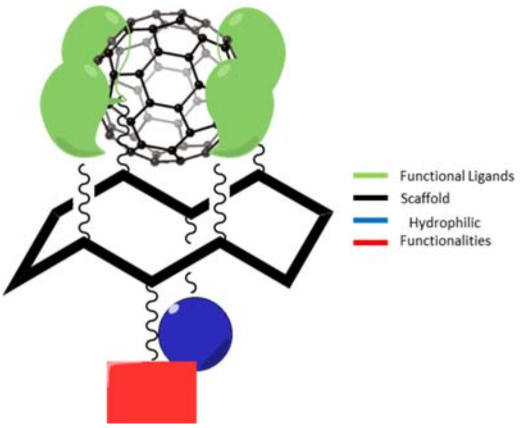
Solubilization of Fullerene C_{60} in Water by a Cyclic Decapeptide

Silvia Bartocci[a], *Michele Maggini*[a], *Miriam Mba*[a]

a Dipartimento di Scienze Chimiche, Università degli Studi di Padova
Via Marzolo 1, 35131, Padova, Italia

silvia.bartocci@unipd.it

After the discovery of Fullerene in 1985 [1], the number of applications of this molecule in materials chemistry or biomedicine that exploit its unique physical and chemical properties have grown up exponentially. However, making this carbon sphere soluble in aqueous media to fully exploit all its potential is still a big challenge. Many hydrophilic derivatives have been obtained using a covalent functionalization that is not trivial and often can modify the fullerene properties. The most successful strategy is a non-covalent approach in which fullerene is carried into water by an hydrophilic carrier upon formation of a supramolecular nanocomposite/host-guest complex [2]; in this way any modification of the structure and properties of fullerene is avoided. In this communication we report the use of a novel water-soluble cyclic decapeptide to obtain stable solutions of fullerene C_{60} in water.



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ORG-O11

Study of the Ugi and Ugi-Smiles reaction mechanism by Electrospray Mass Spectrometry (ESI-MS)

C. Iacobucci [a], *S. Reale*[a], *J-F Gal*[b], *F. De Angelis* [a]

a Dipartimento di Scienze Fisiche e Chimiche, Università dell'Aquila, Via Vetoio-Coppito II, 67100, L'Aquila, Italia
b Institut de Chimie de Nice, Université Nice Sophia Antipolis, CNRS-UMR 7272, Parc Valrose, 06108 Nice Cedex 2, France

francesco.deangelis@univaq.it

ESI-MS has spread greatly in the last few years as an effective technique for mechanistic studies of organic reactions, since it allows to investigate in the gas-phase key-species with short lifetimes at very low concentration.
The Ugi reaction, one of the most prominent multicomponent reaction in organic synthesis, still is under debate concerning its reaction mechanism. To date, two mechanistic proposals are the most accredited for this reaction: i) the original pathway introduced by Ugi himself; ii) a more recent proposal which points to a delayed isocyanide insertion. Only two papers deal to some extent with the Ugi mechanism: one is a study from a theoretic point of view[1], while the other gives some experimental evidence by ESI-MS investigation, which we present now as well, but by using charged tagged reagents which, because of their nature, will introduce a charged bias into the reaction mechanism itself [2].
Thus, we report here on our results on the study of both the Ugi and the Ugi-Smiles reactions by ESI-MS, by way of a strategy which does not require charge-tagged reagents. Strong evidences for the Ugi and Ugi-Smiles reaction mechanism have been collected. Crucial intermediates have been intercepted and structurally characterized by ESI-MS and MS/MS. All the data are clearly in favour of the original hypothesis by Ugi of a *via* nitrilium-ion mechanism.

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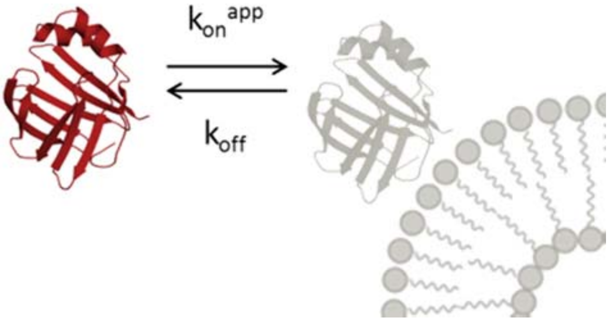
ORG-O12

Equilibrium partitioning of fatty acid binding proteins to liposomal nanoparticles

Michael Assfalg, Alberto Ceccon, Mariapina D'Onofrio, Henriette Molinari

Dipartimento di Biotecnologie, Università di Verona, Strada Le Grazie 15 , 37134, Verona, Italia

michael.assfalg@univr.it



The characterization of the adsorption of water-soluble proteins onto lipid surfaces is of high interest in several scientific fields, including biochemistry, nanotechnology, materials science.

Proteins and lipid layers have mutual influence on their structure and dynamics, but the details of these modifications are difficult to grasp experimentally.

We recently focused on the development of novel magnetic resonance methods for the investigation of protein-lipid surface binding equilibria.

Fatty acid binding proteins (FABP) were chosen as model polypeptides due to their recently assessed membranotropic behavior [1] and their well-characterized structural and dynamic properties in solution. Protein samples were presented with unilamellar lipid nanovesicles of different chemical compositions. We exploited the chemical exchange saturation transfer mechanism to obtain kinetic and dynamic information about the protein-lipid interactions, both at low resolution at an atomic level of detail [2,3].

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ORG-O13

Gemini guests drive the self-assembling of calixarene-based capsules in water

Carmela Bonaccorso, Carmelo Sgarlata, Giuseppe Arena, Domenico Sciotto

Dipartimento di Schienze Chimiche, Università di degli Studi di Catania,
Viale Andrea Doria 6, Cap. 95125, Catania, Italia

bonaccorsoc@gmail.com

Non-covalent, weak interactions have been widely exploited to drive the assembly of molecules into nanometer-sized supramolecular structures in solution. In organic media, a variety of strategies has been used to build molecular containers that assemble through noncovalent interactions, such as hydrogen bonds or metal–ligand interactions. On the other hand, the design of water-compatible non-covalent containers is a great challenge, and methods to obtain an active control on the encapsulation or transport of drugs or other relevant molecules are topics of interest.

We have recently shown that a gemini guest, having both aromatic units and negative charges, triggers the self-assembling of a homodimeric capsule in the presence of calixarenes in aqueous solution.[1] Water-soluble homodimeric capsules result from the electrostatic and hydrophobic interactions between the calixarene receptors and gemini guests having the charged ends separated by alkyl chains of various length. The formation of the supramolecular capsules occurs through concerted hydrophobic and electrostatic interactions between the charged and aromatic groups of the guests and the host as indicated by ^{1}H NMR, ITC, ROESY and DOSY NMR data. The different size of the guests may strongly affect the stability of the capsule.

The surprising features of these host–guest systems disclose new paths for the design of more efficient capsules in highly competitive media such as water.

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ORG-O14

Identification of new potential antiinflammatory and anticancer agents with a dihydropyrimidinone core

Stefania Terracciano[a], *Maria Strocchia*[a], *Gianluigi Lauro*[a], *Maria Giovanna Chini*[a], *Raffaele Riccio*[a], *Ines Bruno*[a] *and Giuseppe Bifulco*[a]

a Department of Pharmacy, University of Salerno, via Giovanni Paolo II, 132, 84084 Fisciano, Italy

sterracciano@unisa.it

In recent years, our research group has been deeply involved in the discovery of new anti-inflammatory and/or anti-cancer compounds able to interfere with strategic biological targets. Among these, our attention has been addressed on the microsomal prostaglandin E_2 (PGE) synthase-1 (mPGES-1), an inducible enzyme involved in the biosynthesis of PGE_2, which represents an attractive target for the development of a new wave generation of anti-inflammatory drugs. [1] The other target under investigation is the heat shock protein 90 (Hsp90), a molecular chaperone which plays an essential role in many cellular processes including cell cycle control, cell survival and other signaling pathways. [2] In our on-going project to find new molecular platforms able to interfere with these interesting targets, we focused our attention on the synthesis and biological evaluation of 1,4-dihydropyridinone (1,4-DHPM) molecules [3]. Nowadays it is clear that the 1,4-DHPM represents a privileged scaffold since, when appropriately substituted, it can selectively modulate diverse receptors, channels and enzymes responsible for a wide range of pharmacological effects.

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ORG-O15

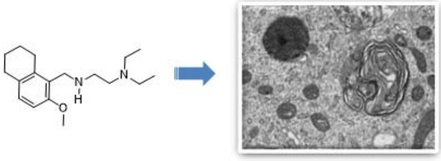
Phospholipidosis induced by cationic amphiphilic drugs: the organic chemistry perspective

Laura Goracci, Martina Ceccarelli, Aurora Valeri, Sandra Buratta

[a] *Department of Chemistry, Biology and Biotechnology, University of Perugia, Via Elce di Sotto 8, 06123, Perugia, Italy*

laura.goracci@unipg.it

Phospholipidosis (PLD) induced by drugs is a lipid storage disorder characterized by an accumulation of phospholipids and the inducing drugs in lysosomes, forming multilamellar vesicles. Lysosomes represent the first line of cell defense, thus in the last ten years the FDA has been investigating whether or not PLD should be considered a toxic effect. Nowadays, more than 50 marketed drugs are known to induce PLD.[1] Cationic amphiphilic drugs represent the main class of PLD inducers and, although the mechanism of PLD induction is still uncertain, their amphiphilic nature plays a key role in phospholipid accumulation. In the last years, a great effort has been made to predict PLD induction risk, but little is known about the chemical features typical of PLD inducers. Moreover, drugs are metabolized in the body, and the metabolism products can increase or decrease the PLD risk.[2] In the present study, a deeper investigation on the relationship between the chemical structure of compounds and their PLD effect is reported, showing that chemistry might play an important role not only for mechanism elucidation but also for PLD risk prediction.



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ORG-O16

Synthetic receptors for carbohydrates: essentials for an effective recognition

Oscar Francesconi[a], *Matteo Gentili*[a], *Cristina Nativi*[a], *Stefano Roelens*[b]

a University of Florence, Dept. of Chemistry, I-50019 Sesto Fiorentino, Florence (Italy)
b Istituto di Metodologie Chimiche (IMC), Consiglio Nazionale delle Ricerche (CNR), Dept. of Chemistry, I-50019 Sesto Fiorentino, Florence (Italy)

oscar.francesconi@unifi.it

Molecular recognition of carbohydrates attracted an increasing interest in the last decades.[1] The impetus for research in this field is largely provided by the prominence of carbohydrate recognition events in biological processes.[2] A molecular level understanding of the mechanism underlying these processes is a main goal pursued by current research. Synthetic receptors able to selectively recognize specific carbohydrates of biological interest through non covalent interactions, mimicking the natural lectins, have been used to explain the structural and chemical requirements for an effective recognition. In recent literature cage receptors proved to be a successful class of structures for recognition of carbohydrates, even in water.[3] Because only a few synthetic receptors have been reported to recognize carbohydrate in water, the search for new architectures is a target of primary interest. We have recently developed an aminopyrrolic bicyclic cage receptor able to specifically recognize β-glucopyranoside, mainly through H-bonding and CH-π interaction.[4] In order to better understand the key recognition elements of this architecture, we dissected its structure and investigated the role and the significance of its constituting elements.[5] In this communication we present the results of a systematic study that revealed the essential features required for an effective recognition.

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ORG-O17

Ru(III) complexes for anticancer therapy: the importance of being nucleolipidic

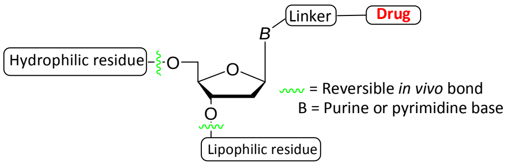
Daniela Montesarchio[a], *Domenica Musumeci*[a], *Claudia Riccardi*[a], *Carlo Irace*[b],
Gerardino D'Errico[a], *Luigi Paduano*[a]

[a]*Dipartimento di Scienze Chimiche, Università di Napoli Federico II, Via Cintia 21, I-80126, Napoli, Italy*
[b]*Dipartimento di Farmacia, Università di Napoli Federico II, Via D. Montesano 49, I-80131, Napoli, Italy*

daniela.montesarchio@unina.it

Ruthenium complexes are drawing increasing attention as second generation metal-based chemotherapeutics, with NAMI-A and KP1019 currently in Phase II clinical trials.[1] Our recent interests have been focused on the synthesis and characterization of new amphiphilic derivatives of nucleosides (nucleolipids), as core scaffolds tightly binding Ru(III) salts and able to self-assemble in aq. solutions into nanocarriers efficiently transporting the metal ions in cell. Using ribo- and deoxyribonucleosides as synthetic platforms, a library of Ru(III) complexes decorated with diverse hydrophilic and lipophilic chains has been produced.[2] Co-aggregated with biocompatible lipids, all these Ru(III)-containing pro-drugs proved to be stable under physiological conditions. Detailed microstructural characterization, carried out through DLS, EPR and SANS analyses, allowed to determine their stability, size and shape.

Tested on a panel of human or non human cells, all the studied Ru(III) complexes showed potent anticancer activity, sensibly higher than NAMI-A-like analogs.[2]



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ORG-O18

Phytotoxins by *Diaporthe* spp. as potential herbicides to biological control of *Carthamus lanatus*

Marco Evidente[a], *Anna Andolfi*[a], *Angela Boari*[b], *Alessio Cimmino*[a], *Maurizio Vurro*[b], *Gavin Ash*[c], *Antonio Evidente*[a]

[a]*Dipartimento di Scienze Chimiche, Università di Napoli Federico II, Complesso Universitario Monte S. Angelo, Via Cintia 4, 80126 Napoli;*
[b]*Istituto di Scienze delle Produzioni Alimentari, Consiglio Nazionale delle Ricerche, Via Amendola 122/O, 70125 Bari, Italy;*
[c]*Graham Centre for Agricolture Innovation (an Alliance between Charles Sturt University an NSW DPI), WaggaWagga, Australia.*

marco.evidente@unina.it

Diaporthe gulyae has been proposed as a mycoerbicide for the biological control of the invasive species *Carthamus lanatus L.* ssp. *lanatus* (saffron thistle) (Ash et al., 2010) which was introduced from the Mediterranean region and quickly spread in cultivated areas and pastures in Australia (Shorten, 2013). The symptoms of the disease suggested the involvement of phytotoxins produced by the fungus, and thus their production was investigated in *vitro.* This study led to isolation and chemical and biological characterization of a new geranylhydroquinone, named phomentrioloxin (1*R*,2*R*,3*R*,4*R*)-3-methoxy-6-(7-methyl-3-methylene-oct-6-en-1-ynyl)-cyclohex-5-ene-1,2,4-triol (Cimmino et al., 2012). A successive study on structure-activity relationships, carried out on seven derivatives obtained by chemical modifications of the main functional groups of the toxin, allowed to obtain interesting results on the phytotoxic, antimicrobial and zootoxic activities of these derivatives (Cimmino et al., 2013).

In the present communication the isolation and chemical and biological characterization of other bioactive metabolites produced by *D. gulyae* grown in different conditions will be discussed. Indeed, when grown in static liquid conditions or in a fermenter, the fungus showed a metabolic profile significantly different by that obtained in shaken conditions, then producing many metabolites belonging to different classes of natural compounds. Furthermore, possible biosynthetic pathways of these metabolites will be discussed.

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ORG-O19

Stereocontrolled synthesis of azasugars

Paolo Bovicelli,[a] *Ergys Dema,*[b] *Emanuela Mandic',*[b] *Giuliana Righi,*[a] *Gabriele Rinaldi,*[b] *Carla Sappino,*[b] *Marco Zeqireja*[b]

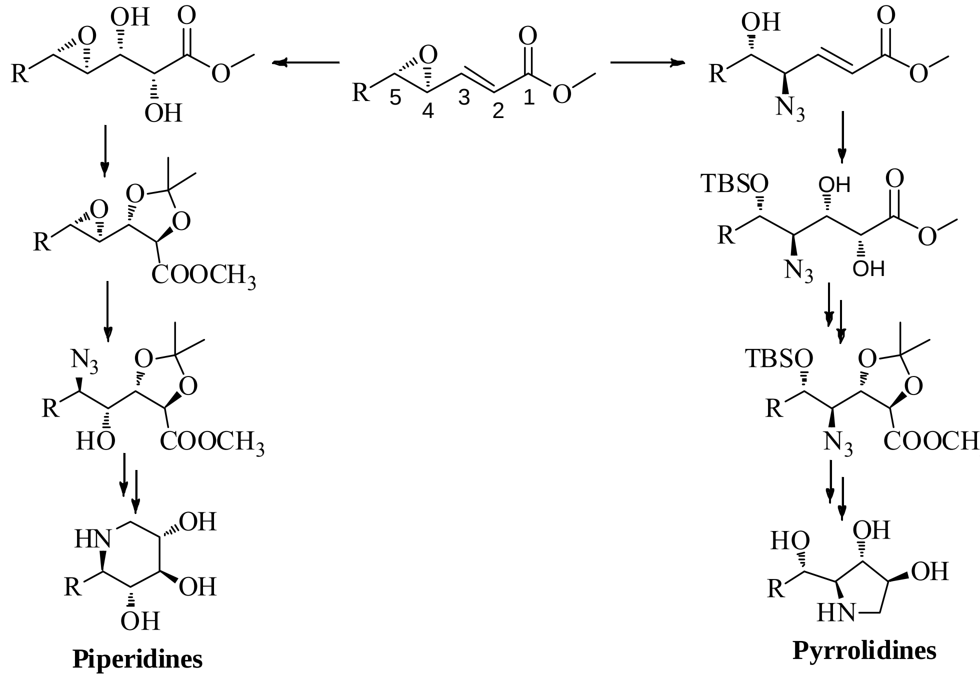
a C.N.R. - IBMN c/o Dipartimento di Chimica, Sapienza Università di Roma
b Dipartimento di Chimica, Sapienza Università di Roma,
P.le Aldo Moro, 5 00185 Roma

emanuela.mandic@gmail.com

Azasugars, carbohydrate analogues in which the endocyclic oxygen atom is replaced by a nitrogen, are today the most attractive class of sugar mimics because of their interesting glycosidase and glycosyltransferase inhibitor activity and therefore their high therapeutic potential in a wide range of diseases (1).

The key step in our divergent synthesis is the asymmetric dihydroxylation reaction on optically active *trans* α,β-unsaturated epoxyesters and their derivatives, recently studied by our research group (2), which allows to obtain four adjacent chiral centres with full stereochemistry control.

A subsequent epoxyde ring opening reaction by a regioselective azide attack in C-4 or C-5 position leads respectively to pyrrolidine or piperidine azasugars (when R = CH_2OP) and bicyclic alkaloids (when R = $(CH_2)_nOP$).



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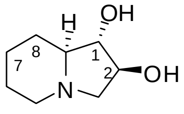
ORG-O20

Sintesi di composti indolizidinici poliossidrilati mirati all'attività proapoptotica

Carolina Vurchio[a], *Franca M. Cordero*[a], *Alberto Brandi*[a]

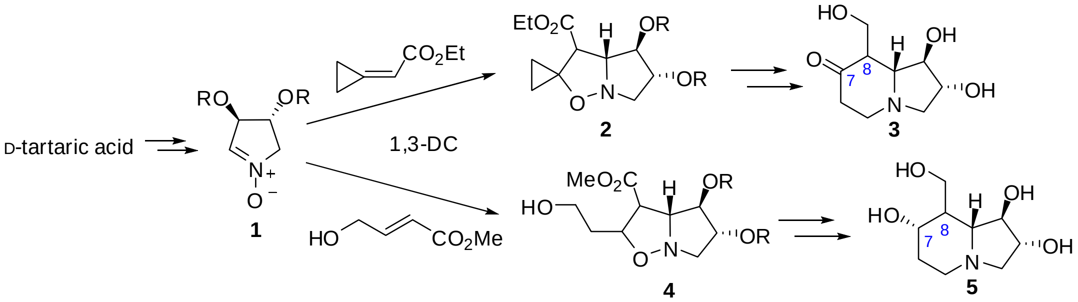
a Dipartimento di Chimica "Ugo Schiff", Università di Firenze, Via della Lastruccia 13, 50019, Sesto Fiorentino (FI), Italia.

carolina.vurchio@unifi.it



(–)-Lentiginosina

È stato recentemente dimostrato che la (–)-lentiginosina, appartenente alla classe degli imminozuccheri, possiede una interessante attività proapoptotica nei confronti di varie linee cellulari tumorali e una bassa citotossicità.[1] In quest'ultimi anni, sono stati sintetizzati nuovi derivati della (–)-lentiginosina funzionalizzati sull'anello a sei termini con gruppi ossidrilici, atomi di alogeno, biomarkers e anelli aromatici.[2] Studi biologici hanno provato che molti di questi nuovi composti mantengono l'attività biologica del capostipite aprendo nuove strade per approfondire e studiare il meccanismo dell'attività proapoptotica non ancora conosciuto. Studi mirati a sviluppare nuove metodologie sintetiche sono in corso al fine di ottenere i nuovi derivati **3** e **5** a loro volta ulteriormente funzionalizzabili e creare così una vera e propria libreria di derivati della (–)-lentiginosina. Attraverso reazioni di cicloaddizione 1,3-dipolare tra la pirrolidina-*N*-ossido **1** derivata dall'acido D-tartarico e dipolarifili opportunamente sostituiti è stato possibile ottenere composti a struttura indolizidinica mediante differenti reazioni di elaborazione dei cicloaddotti intermedi **2** e **4**. In questa comunicazione saranno presentati i risultati ottenuti nel corso dello sviluppo del progetto, relativi sia all'aspetto sintetico (vedi schema) che biologico.



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ORG-O21

Gold nanoparticles as drug carriers

Boccalon Mariangela[a], *Bidoggia Silvia*[a], *Franchi Paola*[b], *Lucarini Marco*[b],
Pengo Paolo,[a] *Pasquato Lucia*[a]

a Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Trieste, Via Licio Giorgieri 1, 34127, Trieste, Italy
b Dipartimento di Chimica "G. Ciamician", Università di Bologna, Via San Giacomo 11, 40126, Bologna, Italy

mboccalon@units.it

Gold nanoparticles (AuNPs) provide non-toxic carriers for drug and gene delivery applications. In these systems, the gold core imparts stability to the assembly, while the monolayer allows tuning of surface properties such as charge and hydrophobicity.[1] Surely hydrophobic interactions and charge complementarity between the small molecule guest and the hosting monolayer play important roles, but the effect of the monolayer structure and morphology in dictating the affinity towards putative drugs is only little explored. In the recent year we have studied the role of the gold core diameter[2] and the type of the monolayer in the entrapment of small hydrophobic drug using ESR technique.[3]

Here we report the comparison of the entrapment of small hydrophobic drugs in three type of AuNPs with different monolayer. We found that fluorinated monolayer shows a greater hydrophobicity compare to the analogous hydrogenated monolayer and a significant boost of the affinity constants when the poorly solvated and more "open" fluorinated monolayers, instead of the more compact hydrogenated ones, served as hosts. This increase in binding affinity was observed towards both fluorinated and hydrogenated guests. We also found that increasing the conformational freedom of the fluorinated region of the monolayer is beneficial in increasing the binding affinities towards both fluorinated and hydrogenated guests. These data as well as the data on the release of model drugs will be presented.

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ORG-O22

PNA probes for nanoparticle-enhanced ultrasensitive DNA detection in photonic crystal fiber sensors

Alex Manicardi[a], *Alessandro Bertucci*[a], *Alessandro Candiani*[b], *Annamaria Cucinotta*[b], *Stefano Selleri*[b], *Roberto Corradini*[a]

a Dipartimento di Chimica, Università di Parma, Parco Area delle Scienze 17/1, 43124,Parma, Italy
b Dipartimento di Ingenieria dell'informazione, Università di Parma, Parco Area delle Scienze 181/A, 43124, Parma, Italy

alex.manicardi@unipr.it

Biophotonics and optofluidic devices represent a highly attractive field of interest integrating ICT technology with biological systems and bioprobes. Label-free DNA detection can be achieved using this approach, but PCR-free detection should be an ultimate goal for rapid and point-of care diagnostics [1]. Photonic Crystal Fibers (PCFs), have the unique feature of presenting a cross-section defined by air-hole arrays, allowing to modulate light transmission as a result of the sensing process [2]. We have developed methodologies allowing to functionalize optical fibers with peptide nucleic acid (PNA) probes [3]. In this paper we describe the use of PCF fibers containing Bragg grating, internally modified with a PNA probe as an optofluidic device for the detection of unamplified DNA; sensing was achieved by measuring the shift in the wavelength of the reflected IR light. Enhancement of optical read-out was obtained using a sandwich scheme with gold nanoparticles, enabling to achieve statistically significant, label-free, and amplification-free detection of target DNA. Computer simulations of the fiber optics based on Finite Element Method (FEM) were used to rationally describe the sensor response.

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ORG-O23

Synthesis of polycation dendrimers for gene delivery

Silvana Alfei, Marco Pocci, Francesco Lucchesini, Vincenzo Bertini

Dipartimento di Farmacia, Università di Genova,
Via Brigata Salerno,13 16147, Genova, Italia

alfei@difar.unige.it

Gene therapy requires the delivering of genetic materials to the interior of a target cell through specific vectors which can be viral or nonviral. Nonviral synthetic vectors [1] are considered a very promising, safer alternative to the viral ones which are used at present in the majority of clinics, but suffer from drawbacks such as immune response, recombination of viruses, limitation of the size of the genetic material to be internalized.

Synthetic nonviral vectors are cationic lipids or polymers able to electrostatically bind the negative charged genetic material to form nanostructured complexes smaller than 100 nm.

In this field we turned our attention to dendrimers, for their well-defined nanostructured architecture, high symmetry, narrow polydispersity and possible introduction of selected different functional groups at the periphery. Polyester-based dendrimers bearing hydroxy end-groups derived from 2,2-*bis*(hydroxymethyl)propanoic acid (**1**) appeared to us particularly attractive due to their low toxicity *in vivo* and possibility of functionalization.

In this communication we report the synthesis of dendrimers derived from **1** developed to the fifth generation, their functionalization with proper amino acids forming polycationic systems able to bind genetic material, and their NMR characterization. A relevant synthetic work concerns the not simple introduction on the dendrimers surface of arginine moieties, whose interest is enhanced by the fact that residues of the guanidine-type can favor the internalization of synthetic polymers into cells [2,3].

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ORG-O24

Decoration of Carbon Nanotubes with Fluorescent Probes for Applications in Drug Delivery Systems

Fedeli S.,[a] *Brandi A.,*[a] *Cicchi S.,*[a] *Chiarugi P.,*[b] *Giannoni E.,*[b] *Paoli P.*[b]

a Dipartimento di Chimica "Ugo Schiff", Via della Lastruccia 3-13, 50019 Sesto Fiorentino, Italy

b Dipartimento Scienze Biomediche Sperimentali e Cliniche, Viale Morgagni 50, 50134 Firenze, Italy

stefano.fedeli@unifi.it

As first step of the development of a carbon nanotubes (CNTs) based drug delivery system (Figure 1), we have synthesized CNTs decorated with fluorescent molecules. In a drug delivery system is fundamental the presence of a fluorescent probe to reveal its internalization inside the cells. Concerning the fluorescent molecule, we have synthesized and characterized new derivatives of a class of fluorescent probes known as "Bodipy". The stability and the high fluorescence of these molecules are proven, as well as the tunability of their absorption and fluorescence wavelengths. Various Bodipy probes have been tested. The decoration of the nanotubes surface was performed through a covalent approach (3 steps): (1) the CNTs were preliminary functionalized by treatment with an alkyne derivative, (2) the Bodipy molecule were synthesized bearing an azide (N_3) function, (3) the coupling between the CNT and the Bodipy molecule was obtained through a simple "click" reaction. The CNTs were characterized by spectrofluorimetric analysis, their internalization inside cells was evaluated by confocal microscopies and cytofluorimetric studies.

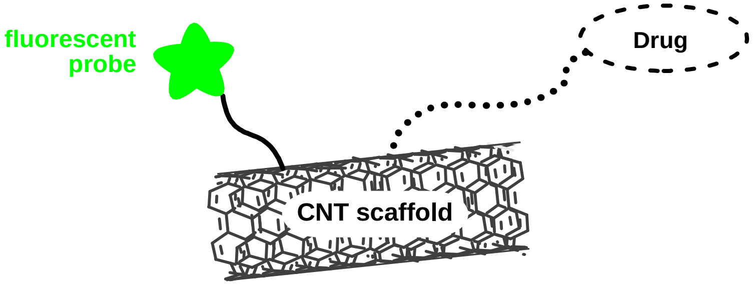


Figure 1. Scheme of the drug delivery system

ORG-O25

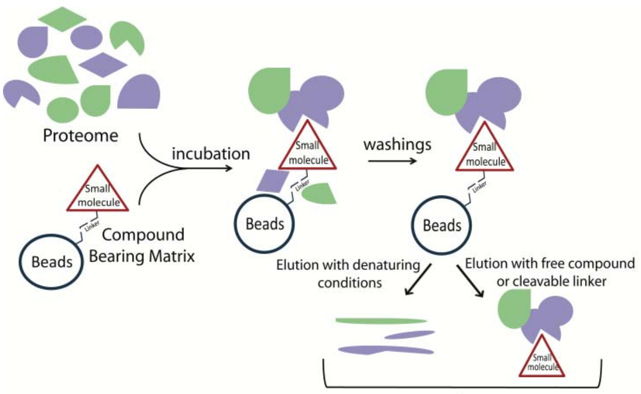
Functional Proteomics discloses the biological targets of natural compounds.

Maria Chiara Monti[a], *Chiara Cassiano*[a], *Angela Capolupo*[a], *Angela Zampella*[b], *Roberta Palladino*[a], *Federica del Gaudio*[a], *Alessandra Tosco*[a], *Raffaele Riccio*[a], *Agostino Casapullo*[a]

a Dipartimento di Farmacia, Università di Salerno, Via Giovanni Paolo II 132 , 84084, Fisciano, Salerno, Italia
b Dipartimento di Farmacia, Università degli Studi di Napoli "Federico II", Via Montesanto, 80131, Napoli, Italia

mcmonti@unisa.it

Natural products have gained a central role in the drug discovery process due to their peculiar structural features and the high bioactivity, often mediated by interaction with multiple targets at low concentrations. The therapeutic potential of the most promising compounds can be determined by preclinical and clinical trial, even if the discovery of their mode of action remains one of the main questions affecting the chemical biology. Aiming the identification of bioactive compounds biological interactors, the mass spectrometry-based affinity purification approaches (AP-MS) have been recently applied to fish out of a complex biological system –such as a cellular lysate or a tissue – the macromolecular partners specifically binding to the small compound immobilized on a solid support. In the last two years, we have applied this methodology gaining successful results in the characterization of the interaction profile of several interesting bioactive molecule, such as Oleochantal, Heteronemin and Theonellasterone.[1,2]



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ORG-O26

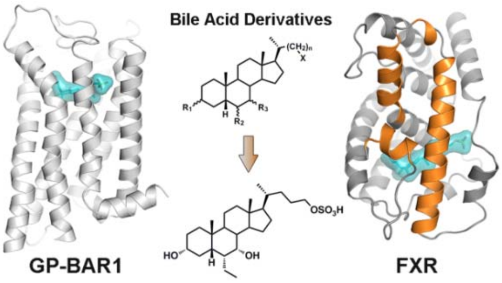
Potent Dual Agonists of Nuclear and Membrane Bile Acid Receptors

Valentina Sepe[a], *Claudio D'Amore*[b], *Francesco Saverio Di Leva*[c], *Barbara Renga*[b], *Maria Valeria D'Auria*[a], *Vittorio Limongelli*[a], *Stefano Fiorucci*[b], *Angela Zampella*[a]

a Department of Pharmacy, University of Naples "Federico II", Via D. Montesano, 49, 80131, Naples, Italy
b Department of Clinical and Experimental Medicine, University of Perugia, Via Gambuli, 1, 06132, Perugia, Italy
c Department of Drug Discovery and Development, Istituto Italiano di tecnologia, Via Morego, 30, 16163, Genova, Italy

valentina.sepe@unina.it

Considered for many years as the final product of cholesterol catabolism, bile acids are experiencing a new life, being recognized as key elements of endocrine functions, related to homeostasis of cholesterol levels, control of lipid and carbohydrate metabolism, regulation on immune system. Bile acids exert their effects by interacting with membrane G-protein coupled receptors, including the bile acid receptor GP-BAR1, and nuclear receptors, such as the farnesoid X receptor (FXR). GP-BAR1/FXR dual agonists represent innovative strategy for the treatment of entero-endocrine disorders.



In this communication, we report the design, total synthesis and *in vitro*/*in vivo* pharmacological evaluation of a new generation of dual bile acid receptor agonists.

We elucidate also the binding mode of the most potent dual agonists in the two receptors. So this study provides the molecular bases of ligand/receptor interaction, useful for designing novel dual agonists.

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ORG-O27

Improving the versatility of ligand-receptor interaction studies by NMR

Cristina Airoldi[a], *Francesco Nicotra*[a]

a Dipartimento di Biotecnologie e Bioscienze, Università degli Studi di Milano-Bicocca,
P.zza della Scienza 2 ,20126, Milano, Italia

cristina.airoldi@unimib.it

Receptor-ligand interaction studies allow obtaining structural information essential for the comprehension of biological phenomena. This knowledge is necessary also for the rational design of new molecules able to interact and modulate the activity of bio-macromolecules of pharmacological and biomedical interest.

Nevertheless, the application of very consolidated techniques, such as STD and trNOESY experiment, for some samples may be far from trivial and require specific experimental setups.

Typical cases are the screening of ligands present in complex mixtures, such as natural extracts from plants,[1] or non-homogenous samples, such as systems containing membrane proteins,[2] nanoparticles,[3] amyloid aggregates,[1] cells[2] and, in general, biocompatible materials employed for tissue regeneration.[4]

In this communication we will briefly review our results concerning molecular recognition studies performed on this kind of systems.

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ORG-O28

Innovative Conjugated Donor-Acceptor Isatin-based Monomers and Polymers for BHJ Solar Cells

Andrea Nitti,[a] *Dario Pasini*[a]

[a] *Department of Chemistry, University of Pavia, Viale Taramelli 10, 27100, Pavia, Italy.*

andrea.nitti01@universitadipavia.it

Conjugated polymers combining electron-donating (Donor) and electron-withdrawing (Acceptor) units are widely addressed targets for efficient Bulk HeteroJunction (BHJ) architectures. New polymeric materials based on natural dyes and pigments for BHJ solar cells have recently attracted considerable attention [1]. Their availability and the possibility of their chemical tuning to design new families of π-conjugated donor-acceptor building blocks with tailored photochemical and electrochemical properties are very appealing, in order to construct advanced polymeric semiconducting architectures. The natural dye isatin (1H-indole-2,3-dione) and its derivatives are commercially available and their chemistry has been subject of many studies over last 50 years, demonstrating their synthetic versatility [2], which has been widely utilized in drug design. Their use in materials science, however, is still in its infancy. The purpose of our project consist in the synthesis of new isatin-based Donor-Acceptor building blocks and their polymerization to obtain conjugated D-A copolymers employed in organic photovoltaic devices with BHJ architecture. Our results in the synthesis of novel D-A copolymers incorporating benzodithiophene (BDT) and fluorinated aromatic units as the acceptors will also be presented. BDT derivatives have been successfully used for tuning of the band gap and energy levels when combined with several accepting units in D–A polymers [3].

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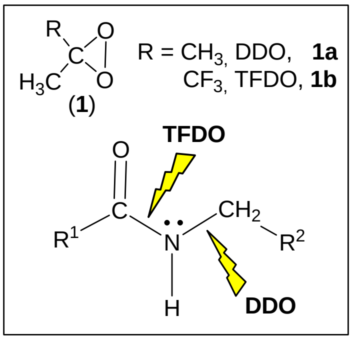
ORG-O29

Amides and Dioxiranes: intriguing reactive partners. Experimental and Theoretical Investigations

Cosimo Annese[a], *Lucia D'Accolti*[b], *Caterina Fusco*[a], *Giulia Licini*[c], *Cristiano Zonta*[c]

a CNR-ICCOM, UOS Bari, Via Orabona 4, 70126 Bari, Italy
b Dipartimento di Chimica, Università di Bari "A. Moro", Via Orabona 4, 70126 Bari, Italy
c Dipartimento di Scienze Chimiche, Università di Padova, Via Marzolo 1, 35131, Padova, Italy

annese@ba.iccom.cnr.it



The reactivity of amides in the oxidation with dioxiranes (**1**) has so far gone unnoticed. If the amide bonds of peptides are generally reluctant to dioxirane oxidation, lactams of various ring size undergo oxidative cleavage by the powerful **1b** affording ω-nitroacids.[1] This method is clean, efficient, and represents an attractive alternative to few established routes to such valuable bi-functional compounds. Conversely, the less potent **1a** reacts with lactams yielding imides or ω-carbamoyl acids, with this being an exceptional case of different selectivity exhibited by the two dioxiranes.

Extension to target amide compounds revealed that the change in selectivity is less stringent, yet the oxidation outcome depends on the chemical environment surrounding the amide bond.

These findings prompted us to reinvestigate, with the aid of theoretical chemistry,[2] some mechanistic aspects concerning the O-insertion into the N-H and C-H bond by both dioxiranes **1**.

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ORG-O30

Stereochemical determination of highly flexible systems by quantitative NMR-derived interproton distances combined with quantum mechanical calculations of ^{13}C chemical shifts

Simone Di Micco[a], *Angela Zampella*[b], *Maria Valeria D'Auria*[b], *Carmen Festa*[b], *Simona De Marino*[b], *Raffaele Riccio*[a], *Craig P. Butts*[c], *Giuseppe Bifulco*[a]

a Dipartimento di Farmacia, Università di Salerno, via Giovanni Paolo II 132, 84084 Fisciano (SA), Italy
b Dipartimento di Farmacia, Università di Napoli "Federico II", via D. Montesano 49, 80131 Napoli, Italy
c Department of Chemistry, University of Bristol, Cantocks Close, BS8 1TS Bristol, United Kingdom

sdimicco@unisa.it

Experimental interproton distances derived from a quantitative and accurate NOEs analysis [1] has been recently proposed as method for the relative configuration assignment of organic compounds. This method has been developed for the stereochemical assignments of rigid molecules, as the NOE analysis is complicated by multiple conformer equilibriums. We recently demonstrated that integrating the quantitative NOE-based protocol with the quantum mechanical calculation of ^{13}C chemical shifts leads to a better discrimination of stereochemical configurations of a rigid natural product [2]. In the present contribution, we have extended our integrated approach [3] to the more challenging stereochemical configurations of two new conformationally flexible oxygenated polyketides, plakilactone G (**1**) and H (**2**), isolated from a Fiji collection of the marine sponge *Plakinastrella mamillaris*.

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ORG-O31

Nanoparticles assisted NMR: from sensing to chromatography

M-V. Salvia, B. Perrone, S. Springhetti, F. Ramadori, F. Mancin, F. Rastrelli

Dipartimento di Scienze Chimiche, Università degli Studi di Padova,
Via Marzolo 1, 35131, Padova, Italy

federico.rastrelli@unipd.it

Nanoparticles (NPs) protected by a monolayer of organic molecules offer a straightforward route to the construction of complex chemical systems, ranging from catalysts and sensors to theranostic agents and artificial vaccines [1].

It is well known that monolayers of organic molecules coating gold NPs can effectively interact with small molecules via non-covalent interactions. We show here that such a feature can be exploited to label and detect the interacting molecules either by magnetization transfer [2] or by a perturbation of their diffusion coefficient. When the interaction is weak, the spins located on the NPs monolayer can be used as a magnetization source to be selectively transferred to the interacting analytes via NOE. In such a way, only the signals of the interacting species are found in the final spectrum. As opposite, when the interactions are strong, a variation of the analytes diffusion coefficient is observed, which generally results in better separation within diffusion-ordered spectra (DOSY). We have tested this method with several combinations of monolayer-protected nanoparticles and different mixtures of analytes, namely benzene derivatives, aromatic anions, and primary ammonium salts. Eventually, the emerging picture is one wherein the interactions of the analytes with NPs monolayers closely parallel those of a stationary phase in a chromatographic medium. We finally put our sensing protocol at test in a situation as challenging as the analysis of drug metabolites in urines [2]. In this respect, the encouraging results obtained seem to address the classic but still actual problem of realizing systems that can detect organic molecules in water, where most receptors fail to recognize their targets.

Financial support from ERC-StG 2010 Project MOSAIC (259014) is acknowledged

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ORG-O32

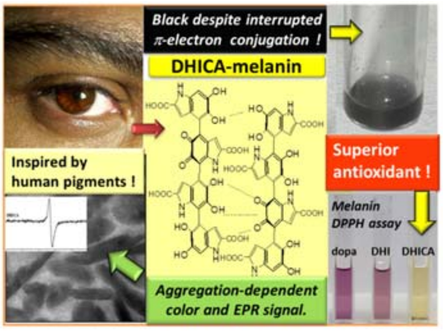
Tailoring synthetic melanins for technological applications: lessons from Nature

Lucia Panzella[a], *Gennaro Gentile*[b], *Gerardino D'Errico*[a], *Nicola Fyodor Della Vecchia*[a], *Maria Emanuela Errico*[b], *Alessandra Napolitano*[a], *Cosimo Carfagna*[b], *Marco d'Ischia*[a]

a Dipartimento di Scienze Chimiche, Università di Napoli "Federico II", Via Cintia 4, I-80126, Napoli, Italia
b CNR, Istituto di Chimica e Tecnologia dei Polimeri, via Campi Flegrei 34, I-80078 Pozzuoli (NA), Italy

panzella@unina.it

Eumelanins, the key photoprotective agents of human skin and eyes, are produced *in vivo* by the enzymatic oxidation of L-dopa via 5,6-dihydroxyindole-2-carboxylic acid (DHICA). However, when carried out *in vitro* under biomimetic conditions, the reaction leads to 5,6-dihydroxyindole (DHI) as the major (>90%) eumelanin building block. Thus, the fundamental issue is: why did Nature select DHICA as the key melanin constituent? Herein, we show that synthetic DHICA melanin is a far superior free radical scavenger compared to DHI and dopa melanins. Integrated spectral investigations revealed that DHICA melanin exhibits peculiar structural properties associated to a conformationally-interrupted π-electron network leading to atypical optical, paramagnetic and aggregation properties.[1] These results settle a long lasting *conundrum* in human pigment synthesis and provide unprecedented clues to tailor eumelanin properties for novel technological and biomedical applications.



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ORG-O33

Funzionalizzazione di materiali melanici

M. Mastropasqua Talamo[a,b], *M.Ambrico*[b], *P. F. Ambrico*[b], *A. Cardone*[c], *S. R. Cicco*[c], *N. F. Della Vecchia*[d], *A. Napolitano*[d], *P. Manini*[d], *M. d'Ischia*[d], *G.M. Farinola*[a,c]

a Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro", v. Orabona 4, 70126, Bari Italy
b CNR-IMIP – UOS di Bari, v. Orabona 4, 70126, Bari Italy
c CNR-ICCOM – UOS di Bari, v. Orabona 4, 70126, Bari Italy
d Dipartimento di Scienze Chimiche, Università degli Studi di Napoli, v. Cintia 4, 80126, Napoli, Italy

maurizio.mastropasquatalamo@uniba.it

Le melanine sono polimeri molto diffusi in natura, con la principale funzione di pigmenti fotoprotettori. La presenza di melanina anche in tessuti non esposti alla luce suggerisce tuttavia possibili altri ruoli e funzioni.[1] Recentemente le melanine sono emerse come materiali per bioelettronica, grazie ad una unica combinazione di proprietà chimico-fisiche tra cui la conducibilità ibrida elettronica-protonica, fortemente influenzata dal grado di idratazione.[2] Tuttavia la scarsa solubilità delle melanine nella maggior parte dei solventi è uno dei maggiori ostacoli al processing per la loro integrazione in dispositivi.[3] Opportune funzionalizzazioni permettono sia di modulare le proprietà elettroniche delle melanine che di conferire loro caratteristiche di solubilità per l'impiego nell'elettronica organica.

In questo contributo si riportano due diversi approcci chimici per la modificazione di materiali melanici. Nel primo caso sarà mostrata una strategia di copolimerizzazione della dopamina con opportuni co-monomeri (ammine aromatiche come la 3-amino-tirosina e la *p*-fenilendiamina) al fine di modulare le proprietà elettriche del materiale.[4] Nel secondo sarà presentata una melanina solubile in acqua, derivante da un 5,6-diidrossi-indolo funzionalizzato con catena oligoetilenglicolica.

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ORG-O34

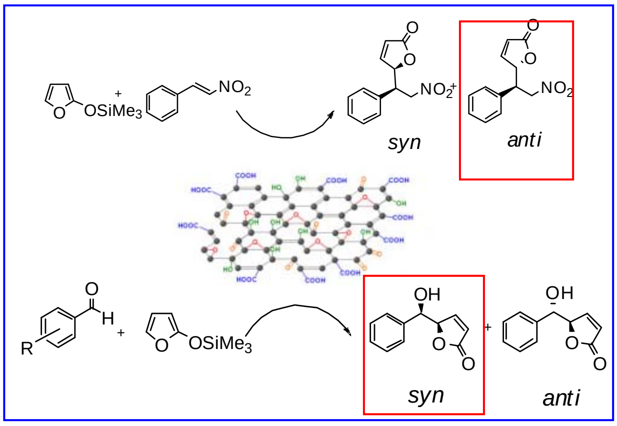
Carbocatalysis: New frontiers for organic chemistry and material technology

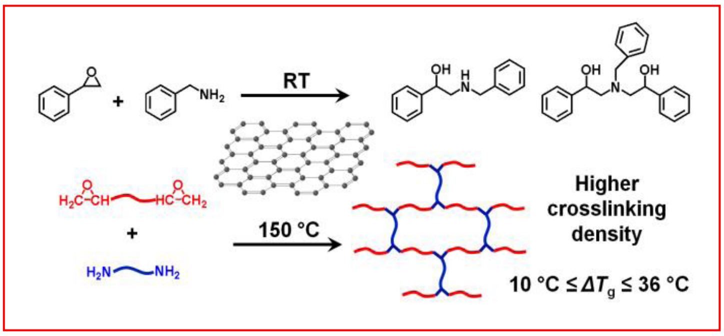
Maria Rosaria Acocella[a], *Marco Mauro*[a], *Gaetano Guerra*[a]

a Dipartimento di Chimica e Biologia, Università degli Studi di Salerno, Via Giovanni Paolo II, 132, 84084 , Fisciano (Salerno)ITALIA

rosyaco@hotmail.it

Graphite oxide and exfoliated GO have been used to efficiently promote organic transformations such as Mukaiyama-Michael,[1] aldol reactions[2] and epoxide ring opening reactions in solvent free conditions. For the first time, the GO catalysts are not only chemically selective but also able to control the stereoselective pathway of the reactions. The ability of graphene oxide to promote ring opening reaction was further extended to epoxy resin polymerization[3] becoming a great chance for new application of Carbocatalysis in nanocomposites thermosets polymer-based.





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ORG-O35

Molecular nano-hybrids based on bis-functionalized polyoxometalates

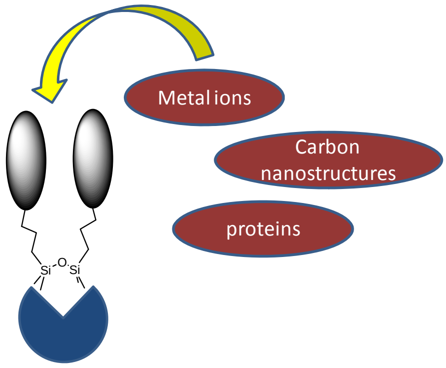
M. Carraro, [a] G. Modugno, [a] M. Bonchio [a]

[a] *Dipartimento di Scienze Chimiche, Università degli Studi di Padova, e ITM-CNR*
Via Marzolo 1, 35131 Padova, Italy

mauro.carraro@unipd.it

Hybrid organic-inorganic molecular species can be very appealing for the development of novel nanodevices and nanostructured materials. Among inorganic scaffolds, divacant polyoxometalates (POM) are robust and molecular polyanionic metal-oxides that can be conveniently exploited for anchoring two organic pendants in a tweezer-type arrangement.[1]

An brief overview on bis-functionalized POMs will thus be presented, including examples in the field of metal ion sensing and catalysis.[2,3] Recent results obtained with a bis-pyrene tweezer, demonstrating the possibility to prepare carbon nanostructures-based materials with different morphologies, will be finally presented.[4]



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ORG-O36

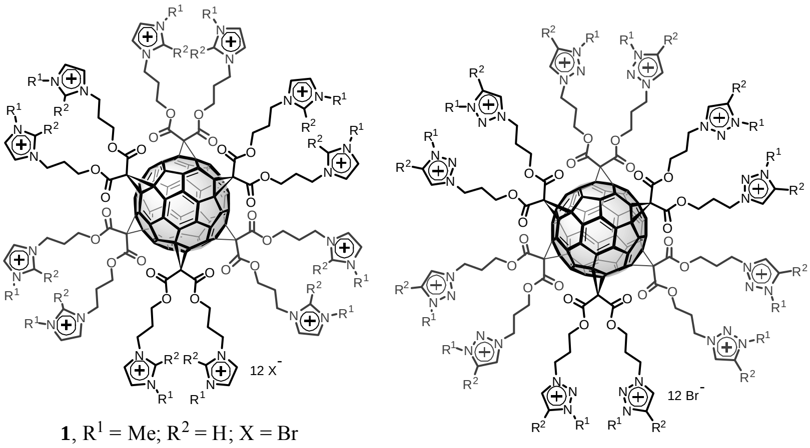
Nuovi ibridi [60]fullerene-liquido ionico

Vincenzo Campisciano[a], Francesco Giacalone[a], Michelangelo Gruttadauria[a]

[a] Dipartimento di Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche (STEBICEF)-Sezione di Chimica, Università degli Studi di Palermo, Viale delle Scienze s/n - Edificio 17, 90128, Palermo

vincenzo.campisciano@unipa.it

Recentemente i liquidi ionici (*ILs*) hanno trovato impiego in unione a diverse nanoforme di carbonio,[1,2] ma tra queste il fullerene C_{60} è quello che meno è stato studiato per quanto riguarda la funzionalizzazione covalente con liquidi ionici. Di fatto, è stato riportato solo un esempio riguardante la sintesi e lo studio del profilo di solubilità di sali di imidazolio di derivati fulleropirrolidinici.[3] Si è dunque pensato di preparare diversi sistemi ibridi fullerene-*IL* (la Figura 1 riporta alcuni esempi di tali composti) ricorrendo a differenti strategie sintetiche. I nuovi derivati di C_{60} ottenuti, oltre a possedere elevate solubilità in solventi polari (acqua e metanolo), hanno grandi potenzialità dal punto di vista applicativo. Il composto **1** è stato impiegato come supporto molecolare per nanoparticelle di palladio e il sistema catalitico risultante è stato testato con successo nella catalisi delle reazioni di Suzuki e di Heck con un carico dello 0,1 % in moli.



1, R^1 = Me; R^2 = H; X = Br
2, R^1 = Me; R^2 = Me; X = Br
3, R^1 = Bu; R^2 = H; X = Br
4, R^1 = Bu; R^2 = H; X = Cl

5, R^1 = Bn; R^2 = Ph

Figura 1

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ORG-O37

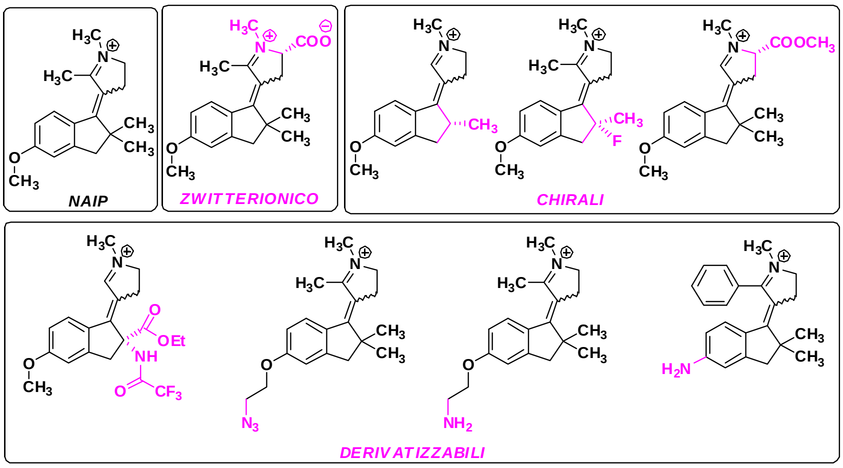
Sintesi di Interruttori Molecolari Biomimetici Fotoisomerizzabili

Marco Paolino[a], *Stefania Fusi*[a], *Vinicio Zanirato*[b], *Massimo Olivucci*[a,c]

a Dipartimento di Biotecnologie Chimica e Farmacia, Università degli studi di Siena, Via A. Moro 2, 53100, Siena, Italia
b Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Ferrara, Via Fossato di Mortara 17-19, I-44100, Ferrara, Italia
c Chemistry Department, Bowling Green State University, Bowling Green, Ohio 43403, USA

paomar@oneonline.it

Gli interruttori molecolari fotoisomerizzabili (*photoswitches*) sono molecole capaci di cambiare configurazione E/Z in risposta a fotostimolazione. Il *photoswitch* più applicato alla modulazione delle proprietà di materiali sintetici e naturali è l'azobenzene che opera attraverso l'isomerizzazione della funzione -N=N-. Allo scopo di creare una nuova famiglia di *photoswitches* con proprietà complementari, abbiamo sviluppato gli *N-Alkylated indanylidenepyrroline Schiff bases* (NAIPs),[1] basati sulla fotoisomerizzazione di un doppio legame -C=C- con proprietà simili a quello della base di Schiff protonata del retinale: il cromoforo dei pigmenti visivi. I NAIPs, grazie alla carica positiva della testa pirrolinica, possono modificare le proprietà di sistemi macromolecolari complessi. In questo contributo discutiamo differenti approcci alla sintesi di NAIPs variamente sostituiti al fine di poter controllare le proprietà fotofisiche, fotochimiche di sistemi complessi quali proteine, liposomi, o materiali organo-metallici.



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ORG-O38

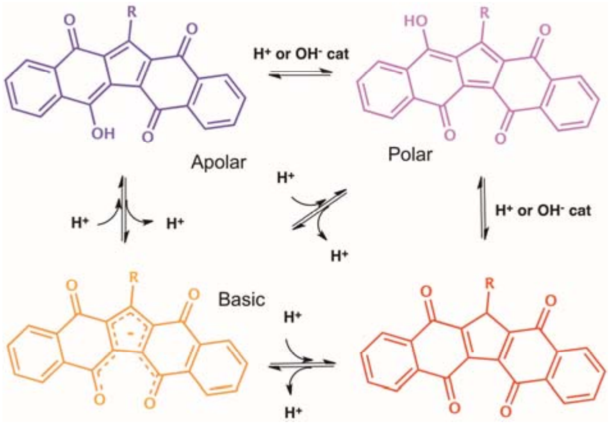
Tautomeric Equilibria in polyquinoid KuQuinones

Pierluca Galloni[a], Sara Lentini[a], Valeria Conte[a], Barbara Floris[a], Gianfranco Bocchinfuso[a], Nelsi Zaccheroni[b], Massimo Sgarzi[b], Luca Prodi[b]

a Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata,
Via ricerca scientifica snc ,00133, Roma ,Italy
b Dipartimento di Chimica "G. Ciamician", Università di Bologna,
Via Selmi 2, 40126 Bologna, Italy

galloni@scienze.uniroma2.it

Keto-enol tautomerization is one of the most widely investigated equilibrium in organic chemistry. Given the solvent polarity influence on tautomeric equilibria, several solvatochromic dyes were designed and employed as polarity-sensitive probes. In fact, the solvatochromic changes induced by the keto-enol interconversion led to important information about micro-environment properties of organic and ionic liquids media.[1-3] The class of KuQuinones[4] is characterized by well distinctive structural features, such as the strong intramolecular hydrogen bonding between the enol and the proximate carbonyl functions, with the enol proton exactly at midway between the oxygen atoms (O···H—O). The interchange between a number of KuQ tautomers leads to substantial spectral variations of the dye depending on the experimental conditions used and it will be discussed and compared with theoretical calculation results.



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ORG-O39

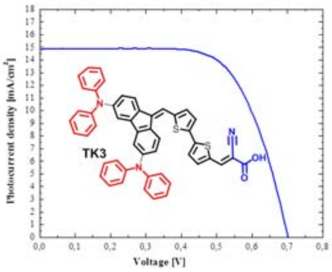
Synthesis and application of new dibenzofulvene-based dyes for DSSCs

A. L. Capodilupo[a], L. De Marco[b], E. Fabiano[a], R. Giannuzzi[b], G. Gigli[a,b] and G. Ciccarella.[a]

a Istituto Nanoscienze – CNR, National Nanotechnology Laboratory (NNL), Via Arnesano, 73100 Lecce, Italy
b Center for Biomolecular Nanotechnologies (CBN) Fondazione Istituto Italiano di Tecnologia (IIT), Via Barsanti 1, Arnesano, 73010, Italy

agostina.capodilupo@nano.cnr.it

Dye sensitized solar cells (DSSCs) represent one of the most promising next-generation photovoltaic devices. These devices have been attracting considerable attention due to high performance and low-cost production. Dyes as photosensitizers are one of the most important components influencing the photovoltaic performances of DSSCs, because they determine the photoresponse range of the device and initiate the primary steps of the photon absorption and the subsequent electron transfer process. In addition to conventional Ru-complex sensitizers, metal-free organic dyes have also been utilized as sensitizers in DSSCs, and the photovoltaic performance of DSSCs based on organic-dye sensitizers has been improved by careful molecular design. [1,2]



η = 7.45%, FF = 0.71, V_{oc} = 0.70 V, J_{sc} = 14.98 mA/cm²

Fig. 1: **TK3** structure and DSSC parameters .

We have designed and synthesized three novel organic dyes containing two donor moieties bonded to the dibenzofulvene core Fig.1, with several thiophene spacer-linker forming a 2D-π-A push-pull system, to improve solar-cell performance of the solar cells. The DSSCs based on the **TK3** dye showed high power conversion efficiency of 7.45%.

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ORG-O40

Aliphatic C-H Oxidation Catalysed by in situ prepared Fe(II) Complexes

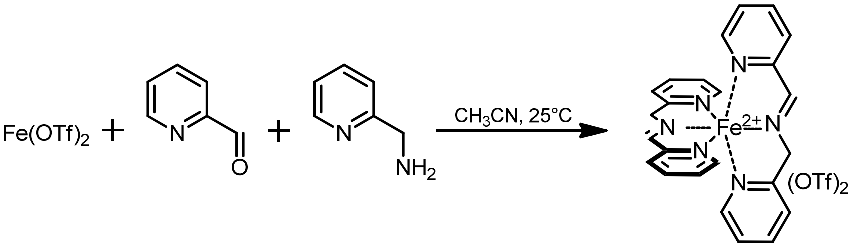
Giorgio Olivo,[a] *Giorgio Arancio,*[a] *Luigi Mandolini,*[a] *Osvaldo Lanzalunga,*[a]
Stefano Di Stefano[a]

a Dipartimento di Chimica, Università di Roma "La Sapienza", Piazzale Aldo Moro 5, Cap, Roma, Italia

giorgio.olivo@uniroma1.it

Nonheme iron complexes are emerging as promising tools in the field of C-H bond activation. During the last decade several ligands have been synthesized and the catalytical activity of the corresponding iron complexes in aliphatic C-H oxidation was tested.[1] It was shown that ligand architecture have a great impact on catalyst's activity and selectivity, with the more elaborated ligands usually performing better than the simple ones. However, this feature often leads to expensive and difficult to obtain ligands, thus hampering the diffusion of this synthetic methodology.[2]

In this context, we prepared a simple nonheme iron complex (3) assembled directly in the reaction vessel from cheap and commercially available reagents (Figure 1). Complex 3 is formed immediately and quantitatively and shows good activity in C-H bond oxidation, at least comparable to those reported in literature for other Fe(II) complexes, albeit with a simpler structure and at catalyst loading as low as 1%.[3]



1 **2** **3**

The results of some hydrocarbon oxidations together with the full characterization of complex 3 will be presented. Some preliminary studies on the catalytic activity displayed by other imine-based nonheme iron complexes will be also disclosed.

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ORG-O41

Cyclocarbonylation approaches to functionalized benzimidazothiazinones

Lucia Veltri[a], *Bartolo Gabriele*[a], *Angela Altomare*[b]

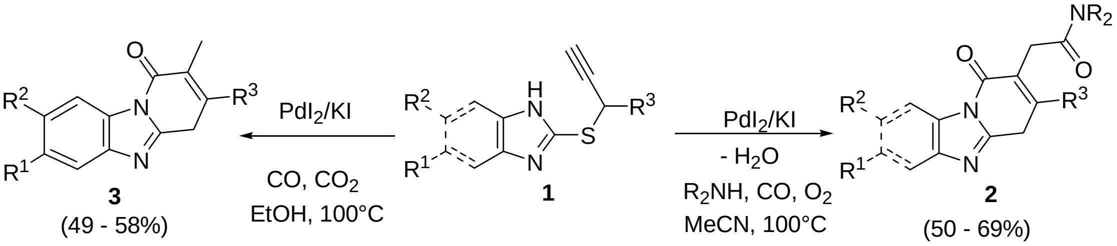
a Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Via P.Bucci, 87036, Rende (CS), Italy
b Istituto di Cristallografia, CNR Via Amendola 122/o, 70126 Bari (BA), Italy

lucia.veltri@unical.it

The imidazo-5-thiazinone core is frequently found in pharmaceutically active molecules, displaying a wide range of activities, such as antiulcer, antifungal and antibacterial activity [1].

Here we report novel approaches to functionalized (benz)imidazo-5-thiazinone derivatives, based on PdI_2-catalyzed cyclocarbonylations of readily available 2-prop-2-ynylthio(benz)imidazole **1**.

Carrying out the reaction of **1** with secondary amines under oxidative carbonylation conditions (under 20 atm of a 4:1 mixture of CO and air, in CH_3CN as the solvent, at 100° C for 6 h), in presence of the PdI_2/KI catalytic system [2], (benz)imidazo-5-thiazinones derivatives **2** were obtained in moderate to good yields, as shown in Scheme 1. The structure of a representative product has been confirmed by X-ray chrystallographic analysis.



Scheme 1

On the other hand, with the same catalytic system, 2-prop-2-ynylthiobenzimidazoles, under additive carbonylation conditions (in the absence of air and under 50 atm of CO and 20 atm of CO_2, in EtOH as the solvent at 100°C for 3h), were selectively converted into imidazo-5-thiazinones **3** (Scheme 1).

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ORG-O42

Mono and double alkynylation to 5- and 4,5-substituted alkynyl imidazoles

Fabio Bellina, Marco Lessi, Alessandro Panattoni

Dipartimento di Chimica e Chimica Industriale, Università di Pisa,
Via Risorgimento 35, 56126, Pisa, Italy

fabio.bellina@unipi.it

Alkynylated heteroarenes represent a recurring structural motif found in bioactive natural products, pharmaceuticals, and organic materials.[1] These compounds are of great importance either as building blocks or synthetic intermediates and have become increasingly attractive for synthetic organic chemists. During our recent studies on the regioselective functionalization of imidazoles,[2] we became interested in developing an effective strategy for the selective alkynylation of the imidazole core. Despite the well-known Sonogashira reaction represents one of the most commonly used methods for installing alkyne moieties onto heteroarene molecules,[3] its application to the synthesis of alkynylimidazoles is scarcely described.[4] In this communication we describe the successful preparation of a variety of 5-alkynylimidazoles **1** by employing a one-pot combination of a C-5 halogenation with a Sonogashira reaction. Through a careful tuning of the catalyst system we were also able to achieve a sequential C-5/C-4 double alkynylation of 4,5-dibromoimidazoles **2** to give unsymmetrically substituted 4,5-dialkynylimidazoles **3**. The optical properties of compounds **1** and **3** will be also showed and discussed.

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ORG-O43

Divergent Syntheses of Isobenzofuranone and Isochromenone Derivatives in Ionic Liquids

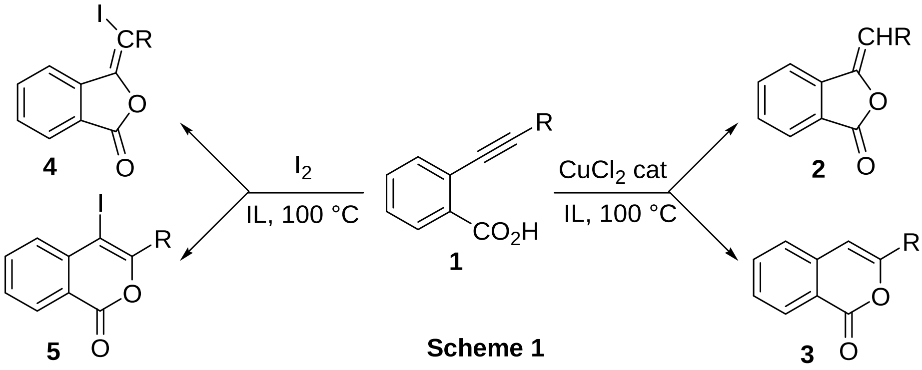
Raffaella Mancuso[a], *Donatella Armentano*[a], *Christian S. Pomelli,*[b]
Cinzia Chiappe[b], *Bartolo Gabriele*[a]

[a] *Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Via P. Bucci, 12/C, 87036, Arcavacata di Rende (CS), Italy*
[b] *Dipartimento di Farmacia, Università di Pisa, Via Bonanno 33, 56126, Pisa, Italy*

raffaella.mancuso@unical.it

In this communication, we report divergent approaches to isobenzofuranone (**2**, **4**) and isochromenone (**3**, **5**) derivatives by either copper-catalyzed heterocyclization or iodocyclization of 2-alkynylbenzoic acids **1** in ionic liquids (ILs) as the solvents.

Very interestingly, we have found that the nature of the IL used directs the regiochemistry in both cyclization processes. In particular, BmimN(CN)$_2$ tends to favor the 5-*exo*-*dig* pathway, with formation of 3-alkylideneisobenzofuranone derivatives **2** and **4**, while EmimEtSO$_4$ tends to promote the 6-*endo*-*dig* mode leading to isochromenones **3** and **5** (Scheme 1). The structure of representative products has been confirmed by X-ray crystallographic analysis.



Scheme 1

Products are formed in good to high yields (75-95%) under relatively mild conditions (100 °C in the presence of 5 mol % of CuCl$_2$ or 100 °C with an equimolar amount of I$_2$). The possibility to recycle the IL-catalyst system (for the copper-catalyzed cyclization) as well as the IL (for the iodocyclization reaction) has been assessed.

ORG-O44

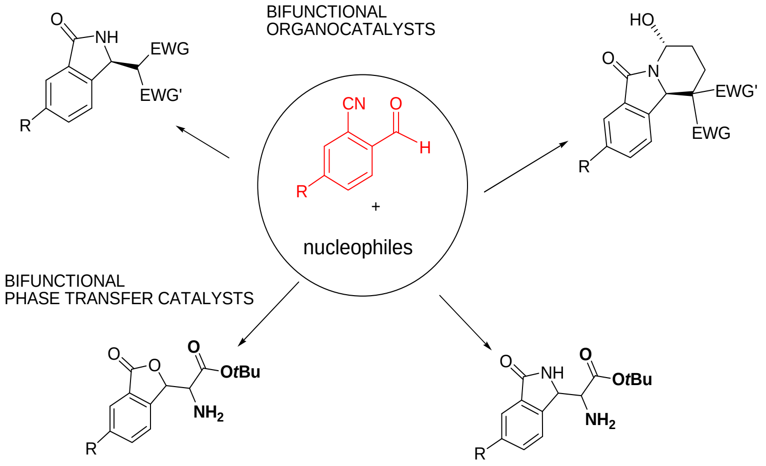
Cascade reactions in the asymmetric synthesis of related heterocyclic compounds

Antonia Di Mola[a] *and Antonio Massa*[a]

[a] *Department of Chemistry and Biology, University of Salerno, Fisciano (SA) Italy*

amassa@unisa.it

Isoindolinone, indolizidine and isobenzofuranone (phthalides) rings are present in a number of molecules with important biological properties and over the past decades a large number of synthetic methods has been developed. However, these methodologies are often complex, non-flexible or require harsh conditions, making the synthetic processes cumbersome. Starting from studies on the aldol addition of active methylene compounds [1] we have developed a series of convenient cascade reactions for the synthesis of the these heterocycles. Different approaches have been applied, using K_2CO_3 [2], electro-initiated [3], asymmetric organocatalytic [4] or chiral phase transfer conditions [5]. In particular, the comparison of different asymmetric conditions gave interesting outcomes, which will be also discussed in the present communication.



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ORG-O45

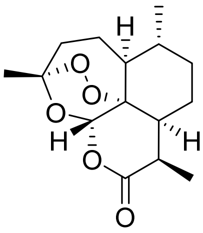
Sintesi di 1,2-diossani come potenziali farmaci antimalarici

Marco Lombardo

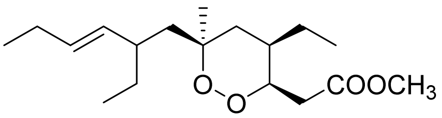
Dipartimento di Chimica "G. Ciamician", Università degli Studi di Bologna,
Via Selmi 2 , 40126, Bologna, Italia

marco.lombardo@unibo.it

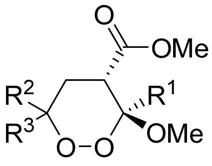
Negli ultimi anni sono stati proposti numerosi farmaci antimalarici a base endoperossidica, prendendo spunto da molecole naturali come l'artemisinina (**1**) o la placortina (**2**), specialmente per il trattamento delle linee clorochino-resistenti del *Plasmodium falciparum*. In questa presentazione saranno discusse la sintesi, la progettazione e le attività biologiche di nuove classi di 1,2-diossani (**3-6**) come potenziali farmaci antimalarici.[1-3]



artemisinina, **1**



2, placortina



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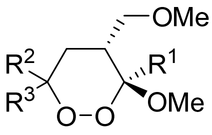

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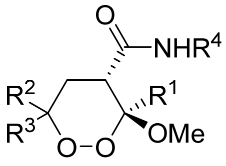

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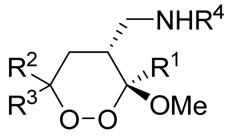

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ORG-O46

Synthesis of new bioactive β-lactam derivatives (from dual activity compounds to integrin inhibitors through differentiating agents)

Roberto Soldati [a], *Paola Galletti* [a], *Matteo Pori* [a], *Daria Giacomini* [a]

a Dipartimento di Chimica "G. Ciamician", Università di Bologna,
Via Selmi 2, 40126, Bologna, Italy

roberto.soldati3@unibo.it

β-Lactam antibiotics are still the main class of antibacterial agents, although the increasing of multidrug-resistant microorganisms requires a continuous development of new compounds. We have contributed to the design and synthesis of new monocyclic β-lactams[1] (azetidinones) as effective scaffolds for antibiotics against resistant bacteria.[2] In an interdisciplinary project focused on the development of new agents against MSSA and MRSA, we tested in vitro a large family of new β-lactam antibiotics.[3] Moreover, we developed a library of dual-active compounds evaluated both as antibacterials and antioxidant agents, in order to treat MRSA pulmonary infections in cystic fibrosis patients.[4] β-Lactam compounds are not only interesting scaffolds for antibiotics against resistant bacteria but also as effective enzymatic inhibitors against a wide number of biological crucial targets.[5] Regarding this aspect, we recently developed the synthesis of new β-lactams, including one with a hybrid retinoid-azetidinone structure, investigating its influence both on the proliferative activity and on the retinoic acid-dependent differentiation of a neuron-like cell line.[6] We are now studying new monocyclic β-lactam peptides with specific interactions with integrins, thus acting like mimetics of the RGD (Arg-Gly-Asp) sequence, key portion in the recognition process of proper integrin ligands.[7]

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ORG-O47

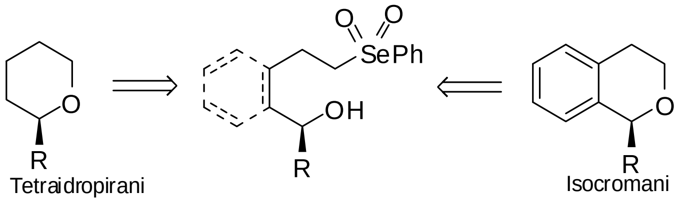
Cicloeterificazione di Fenilselenonil alcooli: Sintesi Stereoselettiva di Isocromani e Tetraidropirani

Andrea Temperini[a], *Lucio Minuti*[b]

a Dipartimento di Scienze Farmaceutiche, Università di Perugia, Via del Liceo 1, 06123, Perugia, Italy
b Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia, Via Elce di Sotto, 06123, Perugia, Italy

andrea.temperini@unipg.it

Gli anelli del tetraidrofurano e del tetraidropirano sono presenti in molti composti naturali come gli antibiotici polieterei e glicosidici, nucleosidi, polichetidi ed O- e C-glicosidi [1]. Recentemente è stata riportata la sintesi stereoselettiva di tetraidrofurani 2-sostituiti a partire da δ-idrossialchil fenil seleniuri chirali non racemici [2] mediante una reazione di ciclizzazione del selenone intermedio. Riportiamo ora la sintesi stereoselettiva di isocromani e tetraidropirani sostituiti ottenuti via anellazione mediante sostituzione nucleofila intramolecolare del gruppo fenilselenonile da parte dell'ossigeno ossidrilico. Questa cicloeterificazione rappresenta il primo esempio di utilizzo dei selenoni per la sintesi di anelli tetraidropiranici.



Gli isocromani e tetraidropirani sostituiti sono stati ottenuti con rese che vanno dal 65 al 75% e con rapporti enantiomerici (determinati tramite HPLC su fase stazionaria chirale) fino a 90:10.

Lavoro eseguito con il contributo della Fondazione Cassa Risparmio Perugia (Progetto 2012.0122.021) e MIUR, PRIN 20109Z2XRJ_010.

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ORG-O48

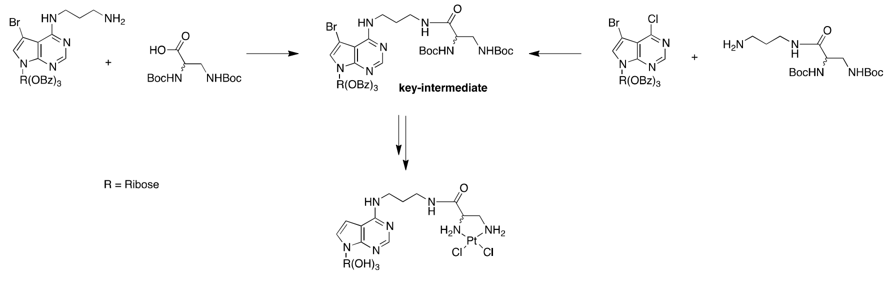
Synthesis and Preliminary Biological Evaluation of Novel Nucleoside-Linked Platinum Complexes

Stefano D'Errico[a], *Giorgia Oliviero*[a], *Nicola Borbone*[a], *Brunella Pinto*[a],
Luciano Mayol[a] *and Gennaro Piccialli*[a]

a Dipartimento di Farmacia, Università degli Studi di Napoli 'Federico II', Via D.
Montesano, 49, 80131, Napoli, Italy

stefano.derrico@unina.it

The metal-based chemotherapy started with the serendipitous discovery of the anti-proliferative properties of cisplatin. However, the poor solubility in biological fluids, the serious side effects, and the intrinsic and acquired resistance of many types of tumors, have limited its use in the clinic. Recently, new platinum complexes have been developed with the aim of increasing cellular uptake and the affinity of the compounds to DNA. To enlarge the toolbox of Pt-based conjugates and to investigate the importance of nucleosides in the construction of platinum complexes [1], here we report a fast and high yielding synthetic plan leading to the obtainment of two novel tubercidin analogues carrying a cisplatin-like unit bonded to the nucleobases through a flexible chiral alkyl chain (Scheme 1). The key intermediate has been efficiently prepared both by a divergent and by a convergent approach. Results from a preliminary anti-proliferative SAR study on two human cancer cell lines are reported as well.



Scheme 1

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ORG-O49

Cyclodextrines: a valuable tool to solubilize uranyl-salophen complexes in water

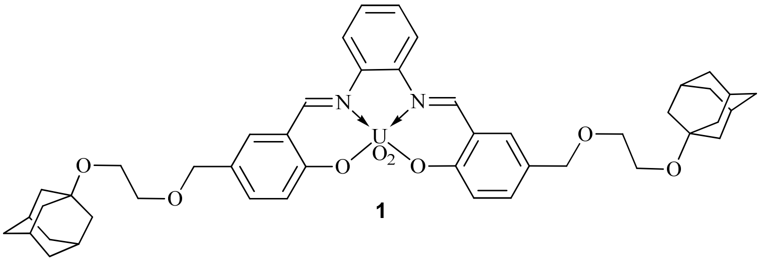
Ilaria Giannicchi[a], *Gianpiero Forte*[a], *Serena Maglione*[a],

Francesco Yafteh Mihan[a], *Antonella Dalla Cort*[a]

a Dipartimento di Chimica, Università di Roma La Sapienza, Piazzale Aldo Moro 5 , 00185, Roma, Italia

ilaria.giannicchi@uniroma1.it

The recognition of anions is a very important target in supramolecular chemistry due to their ubiquitous presence in biochemical processes and as water pollutants.[1]
Still, anion recognition in aqueous solutions is a quite challenging goal to achieve, as receptors must be able to overcome the strong competition of water.
The properties of metal-salophen complexes to bind anions in organic solvents are well established.[2] Over the last years we focused our attention on viable strategies to carry these lipophilic receptors in water.[3] In this communication we report a specific approach based on the introduction of the adamantyl moiety on the salicylaldehyde precursor of the salophen ligand, **1**. In this way water solubilization can be easily achieved through the addition of β-cyclodextrines. Preliminary results on the binding properties of these receptors towards anionic species in water will be also provided.



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**Work carried out in the frame of COST Action 1005 "Supramolecular chemistry in water"*

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ORG-O50

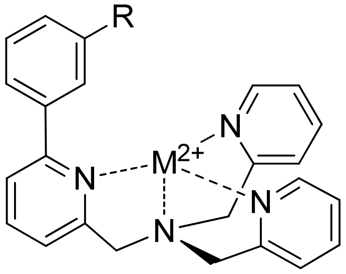
Tris(2-pyridylmethyl)amine metal complexes: Application in catalysis and molecular recognition

E. Badetti[a], F.A. Scaramuzzo[a], G. Licini[a], C. Zonta[a]

a Dipartimento di Scienze Chimiche, Università di Padova, Via Marzolo 1, 35131, Padova, Italia

cristiano.zonta@unipd.it

In the past years, we have been interested in the synthesis of tripodal ligands and their relative metal complexes for their application in catalysis and in supramolecular chemistry.[1] Herein we show our recent applications on modified tris(2-pyridylmethyl)amine ligands, and their complexes in molecular recognition and catalysis.[2]



M = Zn, Co, Fe, ...

R = CHO
Molecular recognition via imine condensation chemistry

R = CHO, CH_2OH, COOH, ...
Effects of remote H-bonds in catalysis

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ORG-O51

Liquidi Ionici: solventi sempre “verdi”?

Alessio Paternò, Giuseppe Musumarra, Salvatore Sciré

Dipartimento di Scienze Chimiche, Università di Catania, Viale A. Doria 6, 95128 Catania, Italy.

paternoalessio@unict.it

I Liquidi Ionici (ILs), hanno suscitato un notevole interesse come solventi “verdi” per le loro proprietà e la loro versatilità, con numerose applicazioni anche su scala industriale. Ciò rende sempre più necessario un attento studio della loro tossicità [1]. Il termine “tossicità” è molto ampio e la sua valutazione dipende fortemente dalla complessità degli organismi scelti come “sensori”. I dati disponibili in letteratura riguardano piante ed organismi acquatici, funghi, batteri, linee cellulari animali e umane, oltre che inibizione di specifici *target* biologici [2]. In un tale contesto questo lavoro di ricerca, intende valutare la possibilità di effettuare uno studio di tossicità degli ILs verso un elevato numero di *target* biologici. Un approccio multivariato ha permesso di riassumere i numerosi dati presenti in letteratura in poche scale di tossicità e di correlare fra loro *scores* di tossicità a differenti livelli di complessità biologica. Da un’analisi di relazioni struttura-attività, è apparso evidente come il maggiore effetto strutturale sull’attività sia principalmente imputabile al catione, e in particolare alla lunghezza delle catene laterali legate al *core* centrale, ed alla presenza di atomi di ossigeno nelle stesse. E’ stato altresì interessante osservare un andamento a “vulcano” per ILs con sostituenti eterei (nella fattispecie dialchilossi eteri), dove un bilancio fra idrofobicità e idrofilicità si rende necessario per una efficace interazione con la membrana cellulare del *target* analizzato.

In conclusione, per quanto i Liquidi Ionici possiedano in molti casi le caratteristiche di solventi “verdi”, a volte possono presentare una notevole tossicità o una bassa eco-sostenibilità, in relazione alla loro struttura.

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ORG-O52

Advanced structural analysis of lignin

Heiko Lange[a], *Marco Sette*[a], *Claudia Crestini*[a,*]

a: Dipartimento di Scienze e Tecnologie Chimiche, Università degli Studi di Roma
'Tor Vergata', Via della Ricerca Scientifica, 00133, Roma (RM), Italia

heiko.lange@uniroma2.it

Lignin is the second most abundant of all the natural polymers that comprise plant biomass. Its challenging structural and chemical properties still present the main obstacle to its widespread use in chemical, pharmaceutical, and medicinal applications. An *rather exact* knowledge about i) its chemical features in terms quantitative data for the intrinsic functional groups, ii) its structural features in terms of quantitative data regarding interunit bonding motifs and non-phenolic end-groups, as well as iii) its key molecular mass data, namely the number average molecular weight Mn, the weight average molecular weight Mw, and the polydispersity PD, are the prerequisites for achieving reasonable tailored chemical functionalisation for targeted high value-added applications.[1]

As part of our on-going efforts to develop reliable and easy-to-adopt protocols and general data analysis schemes for the characterisation of the plant-derived polyphenols lignins and tannins, as preparation of their chemical modification for targeted applications, we systematically evaluated methods widely used for lignin characterisation, focussing on elements that normally give rise to misunderstanding, misinterpreting and false results.[2]
We compared different advanced quantitative NMR techniques (QQ-HSQC, $HSQC_0$, ^{31}P NMR) for the analysis of lignins, and quantified often under-estimated error sources in the chromatographic analyses, such as i) the nature of calibration of the analytical set-up, the influence of the nature of the detector used for recording, and the effect on the molecular masses caused by solubility-enhancing functionalisation methods used in lignin chromatography. By com-bining and correlating the different analyses, we obtain unprecedented levels of accuracy in the structural and chemical characterisation of lignins and tannins.[3,4]

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ORG-O53

Synthesis of polymerisable bicontinuous microemulsion membranes for water treatment application

Francesco Galiano[a], Alberto Figoli[a], Giorgio De Luca[a], Shamim Deowan[b], Jan Hoinkis[b], Lucia Veltri[c], Raffaella Mancuso[c], Bartolo Gabriele[c]

[a] ITM-CNR, University of Calabria, Via Bucci 17/C, 87036 Arcavacata di Rende, Italy
[b] Karlsruhe University of Applied Sciences, 76100 Karlsruhe, Germany
[c] Department of Chemistry and Chemical Technologies, University of Calabria,
Via Bucci 12/C, 87036 Arcavacata di Rende, Italy

galiano.francesco@hotmail.it

Novel polymeric membranes have been obtained by bicontinuous microemulsion polymerisation (PBM), which is an innovative approach to produce nanostructured porous membranes. The purpose of the study was to produce a hydrophilic, antifouling and antimicrobial membrane through the polymerisation of polymerisable bicontinuous microemulsions (PBM), and to provide a technological breakthrough in the field of water treatment.

The bicontinuous microemulsion was prepared by using the polymerisable surfactant acryloyloxyundecyltriethylammonium bromide (AUTEAB), synthesised in our laboratories in the course of the project. The polymerised microemulsion was then applied as coating material on polyether sulfone (PES) commercial membranes.

The newly-developed PBM membranes were applied in Membrane Bioreactor (MBR) technology for textile wastewater treatment, and presented several advantages in comparison to uncoated commercial membranes, such as constant water permeability in time, good quality of the filtrate by rejection of organic compounds, modest oxygen consumption, an increase in the efficiency and durability of the membranes and a significant reduced use of cleaning agents [1].

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ORG-O54

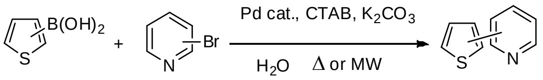
Micellar Synthesis of Thienyl-Pyridines

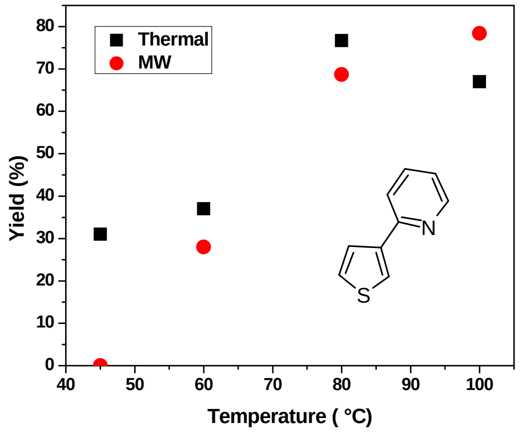
P. Quagliotto, C. Barolo, R. Buscaino, P. Carfora,
S. Prosperini, G. Viscardi

Dipartimento di Chimica, Università di Torino, Via P. Giuria 7 , 10125, Torino, Italia

pierluigi.quagliotto@unito.it

Thienyl-pyridines are small molecules having several potential applications in electron-transfer processes such as artificial photosynthesis [1a], photocatalysis [1b], molecular photovoltaic cells [1c] and optoelectronic devices [1d]. Since their interest, we prepared them as a model for the synthesis of ligands, using simple and clean methodologies as suggested by Green Chemistry. We adapted the micellar protocol developed by Cerichelli et al. [2a] to the Suzuki coupling of both electron-rich and electron-poor heterocycles by using CTAB surfactant, $Pd(PPh_3)_4$, Pd/C or $PdCl_2$ catalysts, in both thermal or MW conditions. While 2-thiopheneboronic acid reacted at RT, the 3-thiopheneboronic acid required temperatures in the range 80-100°C [2b]. Among the catalysts, $Pd(PPh_3)_4$ gave the best yields (75-80%) with respect to $PdCl_2$ (60%) and Pd/C (40%). Reaction conditions were optimized for the 2-bromopyridines (see Figure) and the ligand 4-(thiophen-3-yl)-2,2'-bipiridine, was prepared (yield: 85%).





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ORG-O55

Multibranched organic sensitizers for photovoltaics and solar fuels

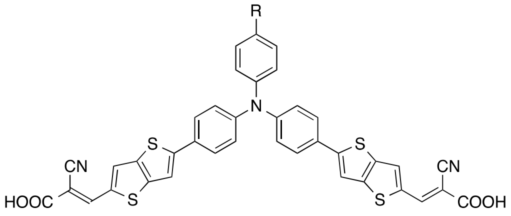
Norberto Manfredi[a], Bianca Cecconi[a], Carmine Coluccini[a], Fabio Melchiorre,[b]
Giorgio Giannotta,[b] Paolo Biagini,[b] Alessandro Abbotto[a]

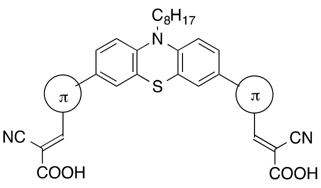
[a] Dipartimento di Scienza dei Materiali, MIB-Solar, Università di Milano-Bicocca, Via R. Cozzi, 55 , 20125, Milano, Italia
[b] Research Center for Non Conventional Energy, Istituto eni-Donegani, eni S.p.A., via Fauser, 4, 28100, Novara, Italia

norberto.manfredi@unimib.it

In recent years, metal free organic sensitizers for solar energy applications, such as dye sensitized solar cell or dye sensitized photo catalysis, have attracted great attention because of some advantages they have respect to the metal based ones. The development of new architectures to improve both optical and photovoltaic properties is, at present, a "hot topic" in chemistry field of research. One of the most promising design for metal free sensitizer in order to achieve broader UV-Vis absorption spectrum and to reduce detrimental effect such as intermolecular charge recombination seems to be the multi-branched multi-anchoring D(-π-A)$_2$ approach. This architecture introduced for the first time in 2009 by some of us and now widely reported in many papers shows better light harvesting properties and higher stability compared to the corresponding linear D-π-A sensitizers.

Here we present two systematic studies upon the influence of the functionalization of two similar D(-π-A)$_2$ structures to better understand the correlation between structure and photovoltaic performance. A new family of dibranched dyes as DSSC sensitizers where the donor triphenylamine conventional core has been functionalized with both linear and branched alkyl chains, alkoxy chains, and aromatic groups in order to affect the electrolyte-TiO$_2$ interaction is described. Moreover, a new family of dibranched dyes were synthesized starting from the well-known phenothiazine donor group, was used in combination with different π-spacer to better investigate the effect of electron-donation in a process of heterogeneous photo-catalyzed solar fuels generation. A various type of thiophene ring were selected as spacers and tested in hydrogen generation reaction.





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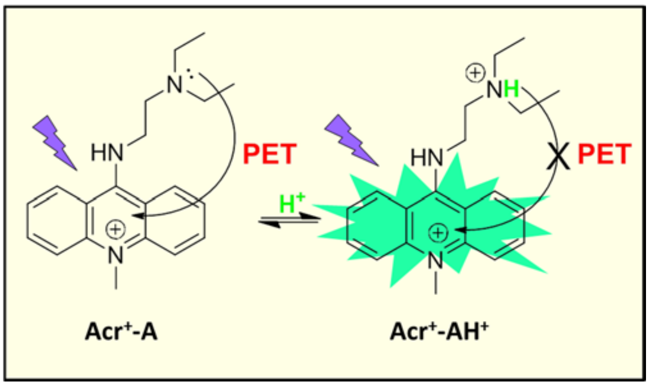
ORG-O56

Acridinium-Based Sensor as Fluorescent Photoinduced Electron Transfer Probe for Proton Detection Modulated by Anionic Micelles

Tiziana Del Giacco, *Stefano Basili, Fausto Elisei, Raimondo Germani*

Dipartimento di Chimica, Biologia e Biotecnologie and Centro di Eccellenza Materiali Innovativi Nanostrutturati (CEMIN), Università di Perugia, Via Elce di Sotto 8, 06123, Perugia, Italy.

tiziana.delgiacco@unipg.it



The design of fluorescent chemosensors is of great interest due to the wide application in analytical chemistry, cell biology, biomedicine and environment survey.[1] Various chemical and biochemical analytes can be detected by these devices with high sensitivity and low detection limits.[2] In this context we have investigated a simple and water-soluble fluorescent pH sensor of 9-amino-10-methylacridinium chromophore with 2-(diethylamine)ethyl chain as receptor (**Acr$^+$-A**). It shows "off-on" response going from basic to acid solution. The action of a photoinduced electron transfer (PET) process as fluorescence quenching mechanism, in few cases directly demonstrated in the literature, is here endorsed by the nature of the transients detected by pulsed techniques. The presence of anionic micelles increases significantly the signaling efficiency of the sensor, due to the particular immobilization of its protonated form on the charged micelle surface, an effect never invoked so far. Moreover, the micelle regulates the working pH interval of the sensor. In particular, it moves the ON window, positioned at the physiological pH range (6.8-7.4) in water, to higher pH. Thus, this approach could be used to visualize if the pH of biological systems is shifting out or returning in the physiological range.

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ORG-O57

Engineering organic materials through serendipity

Davide Bonifazi[a,b]

a) Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Trieste, Via Giorgieri 1, 34127, Trieste, Italia
b) Namur Research College (NARC), University of Namur, Rue de Bruxelles 61 , 5000, Namur, Belgium

dbonifazi@units.it

Organic architectures are considered amongst the most promising candidates for engineering molecular-based devices. It is however necessary to develop systems that can form at interfaces organized molecular assemblies featuring addressable and controllable arrangements. In this respect, the hierarchical self-assembly of organic molecules featuring complementary non-covalent recognition sites allowing the simultaneous assembly of several units and long-range order is one of the most promising approaches.

In this talk, I will describe our approaches to engineer multidimensional structures through the exploitation of weak interactions established by programmed molecules. Quoting a letter (dated 28 January 1754) from Horace Walpole to Horace Mann, he said he formed it from the Persian fairy tale "*The Three Princes of Serendip*", whose heroes "were always making discoveries, by accidents and sagacity, of things they were not in quest of". Therefore, specific serendipitous examples will be discussed with the attempt to answer to the question of whether and how the supramolecular approach can bridge organic chemistry with molecular organization and to which extend we can achieve macroscopic functions solely through molecular engineering.

Chimica Organica

Poster

ORG-P1

Epoxidation of Multi-Walled Carbon Nanotubes by TFDO

Cosimo Annese[a], *Lucia D'Accolti*[b], *Valentina Armuzza*[c], *Tatiana Da Ros*[c], *and Caterina Fusco*[a]

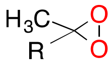
a CNR-ICCOM, Dipartimento Chimica, Università di Bari, Via Orabona, 4, 70126 Bari, Italy
b Dipartimento Chimica, Università di Bari "A. Moro", Via Orabona, 4, 70126 Bari, Italy.
c Dipartimento di Scienze Chimiche e Farmaceutiche, Università degli Studi di Trieste, Piazzale Europa 1, 34127, Trieste, Italy

annese@ba.iccom.cnr.it

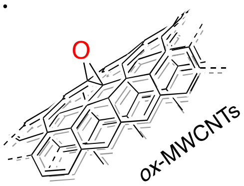
The application in synthesis of the popular dimethyldioxirane (**1a**; DDO) and methyl(trifluoromethyl)dioxirane (**1b**; TFDO) in isolated form have facilitated access to key products that are useful in organic chemistry.[1] TFDO (**1b**) is an efficient, selective and environmentally friendly oxygen-transfer reagent that is capable of operating at 0 °C in the epoxidation of C–C double bonds. In a recent paper, [2] we proposed a simple method to introduce epoxy groups on single-wall carbon nanotubes (SWCNTs) walls via TFDO (**1b**) that may find useful applications in materials science and technology and also in medicinal chemistry, field in which carbon nanotubes are set to play an important role.

In this work, multi-wall carbon nanotubes (MWCNTs) were oxidized either with classic method from **1b**, or with an alternative method involving the use of hydrogen peroxide, a process developed by the Kokotos et al. [3]

These oxidative strategies generate oxygen-containing functional groups, which are primarily epoxides (*ox*-MWCNTs). These can be further modified by ring opening, obtained with various nucleophilic agents.



1a: R = CH_3
1b: R = CF_3



The so obtained modified MWCNTs have been characterized by thermogravimetric analysis (TGA), elemental analysis, and Raman and X-ray photoelectron spectroscopy (XPS). In addition, transmission electron microscopy (TEM) has been used to access the retention of the original morphological aspect.

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ORG-P2

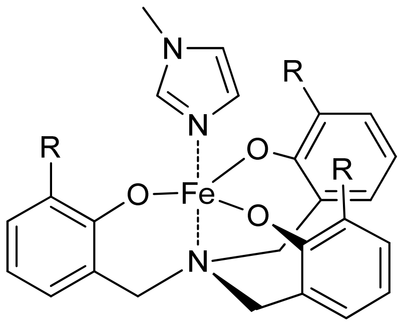
Catalase Activity of Iron(III) *tris*(2-methylaryl)amine Complexes

E. Badetti, E. Benazzi, G. Licini and C. Zonta

Dipartimento Scienze Chimiche, Università di Padova, via Marzolo 1, 35131 Padova, Italy

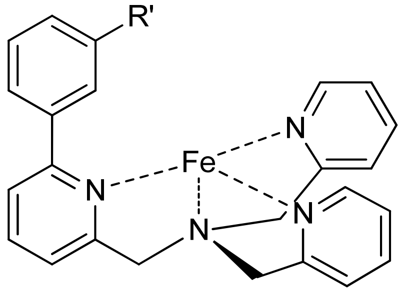
elena.badetti@unipd.it

Catalase-like activity[1] of iron(III) tris(2-methylfenolate)amine[2] TPA and tris(2-methylpyridine)amine[3] TPy complexes are reported. In the case of TPA complexes, functional groups of different steric size are compared. In the case of TPy, functional groups able to interact with the hydrogen peroxide but not with the metal have been introduced in the ligand. These structural variations have furnished kinetic data which can be related to the catalase mechanism.



TPA

R = Me, *t*-Bu, Ph



TPy

R' = H, OH, CH_2OH, NH_2, $CONH_2$, CHO, COOH

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Acknowledgments: Università di Padova. Grant Number: PRAT-CPDA099121, MIUR PRIN-2010-11 2010CX2TLM_002

ORG-P3

Lipophilization of hydroxytyrosol present into natural fractions of *Olea europaea*

Roberta Bernini[a], *Isabella Carastro*[a], *Patrizia Pinelli*[b], *Annalisa Romani*[b]

a Dipartimento di Scienze e Tecnologie per l'Agricoltura, le Foreste, la Natura e l'Energia (DAFNE), Università degli Studi della Tuscia,
Via S. Camillo De Lellis, 01100 Viterbo, Italia
b Dipartimento di Statistica, Informatica, Applicazioni "G. Parenti" (DiSIA),
Viale Morgagni 65, 50134 Firenze, Italia

berninir@unitus.it

Hydroxytyrosol [2-(3,4-dihydroxyphenyl)ethanol, HTyr] is a simple phenol found in olive trees, in particular in leaves and fruits and then in extra-virgin olive oil. Considering the beneficial properties for human health, many synthetic procedures have been optimized to prepare this compound with high purity degree [1,2]. At the same time, several efforts have been focused to extract HTyr from natural sources and agro-industrial waste. In this context, an innovative process based on membrane technologies and chromatographic resins has been developed for producing extracts from tissues and by-products of *Olea europaea* [3].

Due to the limited solubility in lipidic media, the search of procedures to prepare lipophilic hydroxytyrosol derivatives is of great interest both in food industry and in medicine. Among them, the introduction of aliphatic chains into HTyr is a simple strategy useful to increase its lipophilicity and then to modify the physical properties such as the solubility and miscibility in oils and emulsions. In this communication we report an inexpensive and ecofriendly procedure to esterify HTyr present into *Olea europaea* extracts with acyl chlorides in dimethyl carbonate without any catalysts. Work is in progress in our laboratories in order to evaluate the antioxidant and antitumor activities of these extracts.

[1] R. Bernini, G. Fabrizi, L. Pouysegu, D. Deffieux and S. Quideau *Curr. Org. Synth.* 2012, **9**, 650-669

[2] R. Bernini, N. Merendino, A. Romani and F. Velotti *Curr. Med. Chem.* 2013, **20**, 655-670.

[3] D. Pizzichini, C. Russo, M. Vitagliano, M. Pizzichini, A. Romani, F. Ieri, P. Pinelli and P. Vignolini. EP Patent 2,338,500A1.

ORG-P4

Green preparation of wheat starch nanoparticles, promising carriers for controlled release of bioactive compounds

Roberta Bernini[a], *Alessandro Di Michele*[b], *Barbara Albertini*[c], *Ermelinda Botticelli* [a], *Paolo Blasi*[c], *Giorgio Balestra*[a], *Stefano Grego*[a], *Domenico Lafiandra*[a], *Luca Santi*[a]

a Dipartimento di Scienze e Tecnologie per l'Agricoltura, le Foreste, la Natura e l'Energia (DAFNE), Università degli Studi della Tuscia,
Via S. Camillo De Lellis, 01100, Viterbo, Italia
b Dipartimento di Fisica e Geologia, Università di Perugia,
Via A. Pascoli, 06123, Perugia, Italia
c Dipartimento di Scienze Farmaceutiche, Università di Perugia,
Via Fabbretti, 06123, Perugia, Italia

berninir@unitus.it

Starch is a versatile and inexpensive polysaccharide polymer which has received great attention in drug delivery applications being nontoxic, biodegradable and biocompatible. Chemically, it consists of amylose (AM), a linear polymer composed of glucose connected by α-(1,4) linkages and amylopectin (AP), a branched polymer of glucose containing linear stands with α-(1,4) linkages and branches linked by α-(1,6) bonds. In wheat varieties the AM/AP ratio is 1:3. The use of classical and novel breeding approaches has allowed the manipulation of this ratio in durum and bread wheat targeting different genes involved in starch biosynthesis. In particular, by a non transgenic technology, bread wheat lines having high AM content (about 70%) have been produced [1]. We used starch granules of these lines as starting materials for the preparation of NPs by a green procedure based on high-intensity ultrasonication in water without any chemical reagents. Particle size distribution and Scanning Electron Microscopy (SEM) showed the morphology and structure of the resulting NPs. Overall this nano-system bears a great potential to stabilize biologically active compounds and to allow their controlled release.

[1] D. Lafiandra, F. Sestili, E. Botticella and A. Phillips. 2012 In *Plant breeding for future generations, Proc. 19th Eucarpia General Congress*, Bedo Z. and Lang L. (Eds.), Budapest, Hungary pp.180-183.

ORG-P5

A Tentative Authentication of Valle D'Aosta PDO Lard Using Near Infrared Spectroscopy

Sara Panseri[a], *Sonia Bonacci*[b], *Domenico Britti*[b], *Luca Chiesa*[a], *Antonio Procopio*[b],

a Department of Veterinary Science and Public Health-Università degli Studi di Milano, Via Celoria 10, 20133 Milan, Italy;
b Department of Health Science-Università degli Studi "Magna Græcia" di Catanzaro, Viale Europa – Germaneto, 88100 Catanzaro, Italy;

s.bonacci@unicz.it

Food authenticity and food traceability are of great concern to consumer, food processor, retailer and regulatory bodies therefore food characterization represents an important strategic issue for the food industry. Many consumers now seek high quality products with a clear regional and local identity. The determination of authenticity of high-value food, that carry the PDO, plays a crucial role in quality control and safety. Valle D'Aosta Arnad lard is a typical Italian product monitored under the Protected Designation of Origin. Its distinctive properties of aroma and taste are due to the long maturing process (4 months minimum) and to the peculiarity production process in term of aroma, arising to salt and spices mix added to the lard blocks. The aim of the present study was to evaluate the usefulness of Near Infrared Spectroscopy (NIR) to characterize Valle D'Aosta lard samples in order to distinguish it from other typologies of lards without designation of origin. In all cases, LDA analysis was able to discriminate PDO lard samples and correctly classified about 90% of lard samples so NIR spectroscopy appears to be a useful tool to discriminate samples from the rest.

Delgado FJ, Gonz´alez-Crespo J, Cava R, Garc´ıa-Parra J and Ram´ırez R,Characterisation by SPME–GC–MS of the volatile profile of a Spanish soft cheese P.D.O. Torta del Casar during ripening. Food Chem 118:182–189 (2010).
Fernrandez-Garcıa E, Imhof M, Schlichtherle-Cerny H, Bosset JO and Nu˜nez M, Terpenoids and benzenoids in La Serena cheese made at different seasons of the year with a Cynara cardunculus extract as coagulant. Int Dairy J 18:147–157 (2008).
Hickey DK,Kilcawley KN,Beresford TP,Sheehan EMandWilkinson MG, The influence of a seasonal milk supply on the biochemical and sensorypropertiesofCheddarcheese.IntDairyJ 16:679–690(2006).

ORG-P6

Metal-free organic D-π-A dyes for dye-sensitized solar cells

Carmela Bonaccorso[a], *Cosimo G. Fortuna*[a], *Francesca De Rossi*[b], *Monica Panigati*[c], *Gianluca Farinola*[d], *Giuseppe Musumarra*[a].

a Dipartimento di Scienze Chimiche, Università di degli Studi di Catania,
Viale Andrea Doria 6, Cap. 95125, Catania, Italia
b C.H.O.S.E. (Centre for Hybrid and Organic Solar Energy), Dipartimento di Ing. Elettronica, Università di Roma – Tor Vergata, via del Politecnico 1, Roma, Italia
c Dipartimento di Chimica e C.I.Ma.I.NA, Università di Milano, via Golgi 19, 20133, Milano, Italia
d Dipartimento di Chimica, Università degli Studi di Bari Aldo Moro, via Orabona 4, I-70126, Bari, Italia

bonaccorsoc@gmail.com

Dye-sensitized solar cells (DSSCs) have received considerable attention as cost effective alternative to conventional solar cells. One of the main issues for the development of DSSCs is the design and synthesis of dyes that serve as light absorber for energy conversion. Up to now, many pure organic dyes and transition metal complexes have been evaluated as sensitizers. DSSCs sensitized with pure organic dyes have relatively lower power conversion efficiencies than those with metal complexes; however, pure organic dyes have many advantages for their application in DSSCs, such as lower cost, higher adsorption coefficient and easy control of redox potential of LUMO and HOMO levels.

We report on three new bisthiophene-based metal-free organic sensitizers with the aim of improving the dye-sensitized solar cell (DSSC) performance of pure organic sensitizer. The molecular structure of the new dyes were tuned by varying the distance between the donor and anchoring groups or by introducing different donor and electron accepting groups. The photophysical and electrochemical studies of the newly synthesized sensitizers revealed that their absorption and energy levels ensure their suitability for DSSC applications. The DSSC performances of each of sensitizers were investigated with and without coadsorbent and compared with those of standard D35.

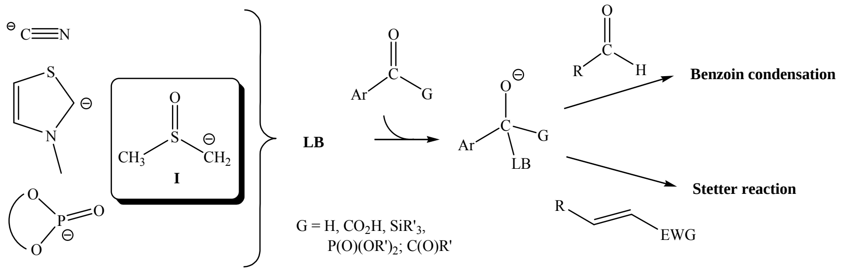
ORG-P7

Methylsulfinyl (Dimsyl) anion as valuable replacement of CN$^-$ in benzoin- and Stetter-like reactions

Olga Bortolini, Alessandro Massi and Daniele Ragno

Department of Chemical and Pharmaceutical Sciences, University of Ferrara, Via Fossato di Mortara 19, 44121 Ferrara Italy;
olga.bortolini@unife.it

The *umpolung* strategy represents nowadays a powerful tool for the development of new, selective, and efficient routes for the synthesis of target molecules. The benzoin condensation and Stetter reactions are classical examples of this concept as they proceed through the generation of an acyl anion equivalent from an aldehyde, pyruvate, acylsilane, acylphosphonate, or α-diketone which can react with various electrophiles, namely aldehydes and polarized C=C double bonds. Three main classes of catalysts (Lewis bases, LBs) are currently employed to enable this reactivity: cyanide anion, *N*-heterocyclic carbenes (NHCs), or metallophosphites, Scheme.



We recently succeeded in the use of the methylsulfinyl (dimsyl) anion **I** as an effective replacement of toxic and hazardous cyanide sources for the polarity reversal chemistry. The dimsyl anion, conveniently obtained by direct deprotonation of DMSO solvent with a base, displays enhanced selectivity toward α-diketones as precursors, thus opening to the possibility of highly chemoselective cross-benzoin reactions with aldehydes [1]. The activity of the couple **I**/α-diketone has been also investigated with activated α,β-unsaturated systems; in this case the expected classical Stetter products have been replaced by densely functionalized 1,4-diketone derivatives formally arising from the sequential addition of an acyl anion and cation on the carbon-carbon double bond of the Michael acceptor. An overview of this research is herein presented.

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ORG-P8

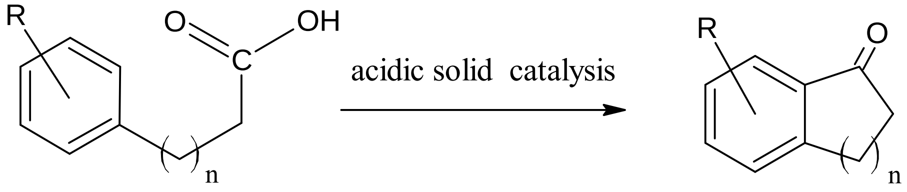
A Green Approach for the Intramolecular Friedel-Crafts Acylation

Giovanna Bosica[a], *Alessandro Palmieri*[b], *Gabriel Galea*[a], *Mark Grech*[a], *Ian Zammit*[a]

a Department of Chemistry, University of Malta, Msida, MSD2080, Malta
b School of Science and Technology - Chemistry Division - University of Camerino - Via S. Agostino 1, 62032 Camerino (MC) Italy.

giovanna.bosica@um.edu.mt

The Friedel-Crafts acylation is one of the most utilised methods for C-C bond formation in aromatic chemistry.[1] The development of an environmentally-benign and economically-feasible pathway of the Friedel-Crafts reaction is of great value and highly desired, particularly in the pharmaceutical industry wherein the acylation reaction is extensively employed.[2] In this study, the intramolecular Friedel-Crafts acylations of different aryl substituted carboxylic acids were investigated under environmentally-friendly heterogeneous solid catalysis[3] in order to obtain the corresponding cyclic aromatic ketones, which are widely recognized as useful synthetic intermediates in various industrial fields, particularly drugs. Preliminary conditions and results will be presented.



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ORG-P9

Tra moda e chimica: una veste da infante del XVII secolo

Simona Casiglia-[a], Maurizio Bruno[a]

[a] STEBICEF, Università di Palermo, Parco d'Orleans Ed. 17, 90128 Palermo

maurizio.bruno@unipa.it

I tessili, a differenza di altre classi di manufatti, sono prevalentemente oggetti aventi una fruizione d'uso e conservano frequentemente tracce e testimonianze della vita di tutti i giorni, che vanno preservate. Il manufatto, oggetto d'indagine, é una veste infantile databile tra la fine del XVII e inizi XVIII secolo. Il verso e il recto dell'abito sono costituiti da un tessuto operato (lampasso) in seta e filati metallici presenti sia nelle rifiniture delle asole che nelle trame broccate del lampasso. L'interno è, invece, costituito da una fodera in tela di lino color ecrù. Per una maggiore comprensione dei materiali [1], sono state eseguite analisi per il riconoscimento del tessuto ed analisi chimiche riguardanti l'identificazione dei coloranti. L'analisi dei coloranti del manufatto è stata effettuata mediante Reverse Phase High-Performance Liquid Chromatography-Photodiode Array Detector (RP-HPLC–DAD). Gli esperimenti cromatografici sono stati eseguiti utilizzando un apparato Agilent 1200 series system e la determinazione dei picchi ha permesso l'identificazione di diversi coloranti naturali.

Per garantire la corretta conservazione nel tempo si è ritenuto opportuno affrontare un intervento di restauro mediante il consolidamento ad ago. Le lacune, le mancanze e le consunzioni, presenti nella veste infantile, hanno comportato la scelta di supporti parziali di tessuto per la fase del consolidamento. Si descrive nella presente comunicazione la sperimentazione sulla tintura di tali supporti, mediante l'utilizzo di coloranti sintetici, con caratteristiche di omogeneità, stabilità nel tempo e durabilità testata scientificamente. Ciò si è reso necessario allo scopo di applicare supporti compatibili con il tessuto del manufatto, sia per tipologia che per colore.

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ORG-P10

Characterization and antimicrobial activity of the volatile components of the flowers of *Magydaris tomentosa* (Desf.) DC. collected in Sicily and Algeria

Guesmia Khaoukha[a], *Mariem Ben Jemia*[b], *Smain Amira*[c], *Hocine Laouer*[d], *Maurizio Bruno*[e]*, *Elia Scandolera*[f], *Felice Senatore*[f]

[a]Department of Microbiology and Biochemistry, University of M'sila, Algeria; [b]Laboratoire des Plantes Extremophiles - Biotechnologic Center Borj-CedriaTechnopark, B.P. 901, 2050 Hammam-Lif, Tunisia; [c]Department of Animal Biology and Physiology, University Setif 1, Setif 19000, Algeria; [d]Department of Biology and Vegetal Ecology, University Setif 1, Setif 19000, Algeria; [e]Dipartimento di Scienze e Tecnologie Biologiche Chimiche e Farmaceutiche (STEBICEF), Università di Palermo, Viale delle Scienze, Parco d'Orleans II - 90128 Palermo, Italy; [f]Department of Pharmacy, University of Naples "Federico II", Via D. Montesano, 49 - 80131 Naples, Italy

maurizio.bruno@unipa.it

The genus *Magydaris* belongs to Apiaceae family. In Europe and in the Mediterranean area it is represented by only two species: *Magydaris tomentosa* (Desf.) DC. and *Magydarids panacifolia* (Vahl.) Lange. *Magydaris tomentosa* (Desf.) DC. [syn. *M. pastinacea* (Lam.) Paol.] it is present in Sicily, Sardinia, Corse, Baleares and North Africa (Tunisia, Algeria, Morocco) [1]. Previous studies on this species allowed the isolation of several glucosides from the fresh rhizomes [2], some known coumarins from the fruit [3] and a new irregular acyclic diterpene magytomol acetate [4]. Furthermore, the antibacterial and anticoagulant activities of the coumaris isolated from the flowers were investigated [5]. We report herein on the chemical composition and the antimicrobial activity of the essential oil of two populations of *Magydaris tomentosa* collected in Sicily and in Algeria, respectively.

The analyses, although showed a very different profile in the composition of the two populations, allowed the identification of the chemotaxonomy markers of the species. A good activity against *Staphylococcus epidermidis* was observed.

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ORG-P11

Antioxidant activity of Tunisian *Ruta chalepensis* leaves extract

Monica Rosa Loizzo[a], *Mariem Ben Jemia*[b], *Francesco Menichini*[a], *Maurizio Bruno*[c], *Rosa Tundis*[a]

[a]*Department of Pharmacy, Health Sciences and Nutrition, University of Calabria, Rende (CS), Italy*
[b]*Laboratoire des Plantes Extremophiles - Biotechnologic Center Borj-Cedria Technopark, B.P. 901, 2050 Hammam-Lif, Tunisia*
[c]*Department STEBICEF, University of Palermo, Viale delle Scienze, Parco d'Orleans II - 90128 Palermo, Italy*

maurizio.bruno@unipa.it

Ruta chalepensis L. is a native herb of the Mediterranean region where it is used in the traditional medicine [1]. Leaves were used in perfumery and as flavouring agents in food. *R. chalepensis* leaves were extracted with methanol in order to obtain a total extract that was submitted to the determination of total phenol content using Folin-Ciocalteu method [2]. Reactive oxygen species (ROS) are closely related to many pathological and physiological phenomenon, such as aging, tumor, inflammation, mutation, atherosclerosis, cardiovascular, cerebral ischemia and diabetes [3]. Several natural products are able to act as antioxidant and inhibit radical production [4]. In this study *R. chalepensis* extract was investigated for its antioxidant potential using DPPH and β-carotene bleaching test. Leaves extract exhibited a moderate DPPH radical scavenging activity. Concerning β-carotene bleaching test, it is well known that β-carotene undergoes rapid discoloration in the absence of an antioxidant. The presence of an antioxidant such as phenol can hinder the extent of β-carotene destruction by "neutralizing" the linoleate free radical [5]. *R. chalepensis* extract showed a promising activity with an IC_{50} of 16.9 μg/mL. The founded antioxidant activity is related to the total phenol content.

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ORG-P12

Chemical composition and cytotoxic activity of *Tetraclinis articulata (Cupressaceae)*

Luana Riccobono[a], *Mariem Ben Jemia*[b], *Sergio Rosselli*[a], *Antonella Maggio*[a],
Maurizio Bruno[a]

a Dipartiment STEBICEF, University of Palermo, Viale delle Scienze , 90128,Palermo, Italy
b Laboratoire des Plantes Extremophiles - Biotechnologic Center Borj-Cedria Technopark,
B.P. 901, 2050 Hammam-Lif, Tunisia

maurizio.bruno@unipa.it

Tetraclinis articulata (Vahl) Mast. (Sandarac tree) belongs to the Cupressaceae family and has two synonyms: *Thuya articulata* Desf. and *Callitris quadrivalvis* Rich. It is widespread in North Africa where is used in traditional and veterinary medicine, to treat diabetes, hypertension, intestinal and respiratory ailments [1,2]. A previous investigation reported the presence of 8 news pimarane diterpenoids, a new aromatic menthane dimer and a new totaratriol from the leaves and wood of *T. articulate* collected in Morocco [3].In the present study, the chemical composition and the cytotoxic activity of the aerial parts of *Tetraclinis articulata*, collected in Tunisia, were investigated. Some new pimarane derivatives were isolated from the hexane extract and their structures were established by extensive spectroscopic techniques, including 2D NMR spectra. Furthermore, a good cytotoxic activity of the hexane and DCM extracts of *T. articulata* against A375 tumor cell line was observed.

Tetraclinis articulata

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ORG-P13

Totally green and scalable MW- assisted protocol for oleuropein peracetilation

Carla Calandruccio[a], *Manuela Oliverio*[b], *Raffele Salerno*[c], *Jessica Maiuolo*[d], *Antonio Procopio*[e]
Università degli Studi Magna Graecia, Campus "C. Venuta", Loc. Germaneto, CZ

calandrucciocarla@gmail.com

Acetylation reaction is among the most common transformation in organic synthesis. In particular, peracetylation of organic compounds bearing catechol groups is recognized as a transient chemical modification which allows to increase the stability and bioavailability of the natural active ingredient. Our research group has developed an environmental friendly method for the acetylationof oleuropein (Fig.1), related to extraction from natural sources and subsequently transformated into its aglycone e HT, all oleuropein hydrolysis products, both peractylated[1].

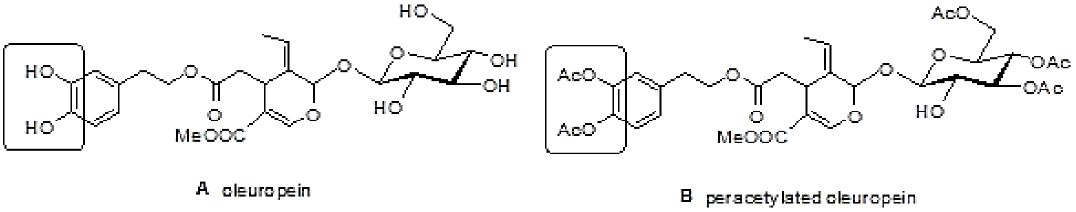

Fig.1.: Chemical structures of oleuropein (A) and peracetylated oleuropein (B). The free catechol moiety responsible for the anti-oxidand activity of compound A, is protected in compound B with the acetyl group.

Optimization peracetylation method starts from the consideration that peracetylated oleuropein, due to its dual purpose as a lipophilic molecule by the action of pro-drug, may find use in industry as a "food additive". The method uses an environment-friendly process typical of the so-called "Green Chemistry. The characterization of the products was made possible by high-performance liquid chromatography coupled to mass spectrometry (LCMS). The key point is that the process allows to obtain a simple derivation of molecules of natural sources having biological and pharmacological effects with the aim of improving their bioavailability through enhanced lipophilicity and solubility in fat matter.

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ORG-P14

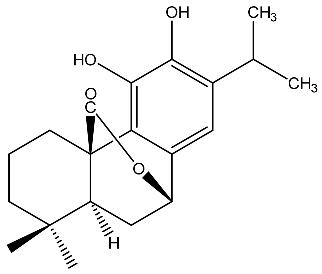
Antinflammatory activity of carnosol on mPGES-1 through inverse virtual screening

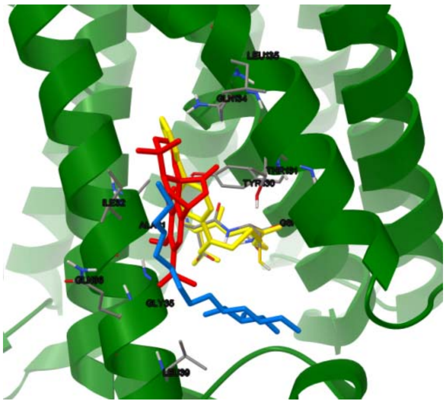
Cantone V.[a], *De Tommasi N.*[a], *Werz O.*[b], *Riccio R.*[a] *and Bifulco G.*[a]

a Department of Pharmacy, University of Salerno, Via Giovanni Paolo II 132, 84084, Fisciano, Italia
b Department of Pharmaceutical/Medicinal Chemistry, Institute of Pharmacy, Friedrich Schiller University, Jena, Philosophenweg 14, D-07743 Jena, Germany

vcantone@unisa.it

The world of plants has always been a rich source of natural compounds, which have taken an important role in drug discovery and drug development for their large pharmacological and biological activities. In this field, carnosol is receiving increasing attention for its anti-inflammatory and anticancer biological activities.[1] A re-evaluation of the specific biological activity of this compound may further clarify its modulatory activity, by means of inverse virtual screening.[2] Starting from a large panel of proteins involved in cancer and inflammation events, it is possible to identify and direct the subsequent biological tests on a focused set of promising interacting targets.[3] We here identified spleen tyrosine kinase (syk) and microsomal prostaglandin E synthase-1 (mPGES-1) as a new putative targets of interaction of carnosol, and confirmed the computational prediction for mPGES-1 through *in vitro* biological tests (50% inhibition at 10 μM).





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ORG-P15

Natural Products Target Discovery by Chemical Proteomics

[1]*Angela Capolupo*, [1]*Raffaele Riccio*, [1]*Angela Cordella*, [1]*Agostino Casapullo and* [1]*Maria Chiara Monti*

[1]*Department of Pharmacy, University of Salerno, via Giovanni Paolo II, 132*
84084, Fisciano, Italy
ancapolupo@unisa.it

Although the therapeutic potential of the most promising natural compounds is usually evaluated in preclinical and clinical trials, very often their intracellular targets and interaction profile remain largely unknown. In recent years, mass spectrometry-based chemical proteomic-approaches have been applied to the macromolecular targets discovery and to the characterization of drug–targets interactions under near physiological conditions[1,2].

Since natural products have acquired a central role in the drug discovery research, we are focusing our attention onto the application of the chemical proteomics based approach for the interactome identification of several bioactive natural compounds, such as oleochantal[3] and, more recently, gymnemic acid I. This molecule belongs to a large family of gymnemic acids, isolated from *Gymnema sylvestre* used in the Ayurvedic medicine for its anti-obesity and anti-diabetic properties[4]. Although its biological profile proves to be interesting, the mechanism of action and molecular target(s) remain still unclear.

The experimental procedure usually requires three steps: 1) preparation of solid support bearing the molecule of interest, 2) isolation of the potential targets, through affinity chromatography on a crude cell extract, 3) analysis of the eluting proteins and identification of the interacting target(s) by nanoLC-MSMS and database search. On this molecule, both a qualitative and a quantitative approach will be performed. The second one will employ the well known strategy of stable isotope dimethyl labeling, a simple, cost-effective and fast procedure of quantization[5]. Finally, a panel of *in vitro* and/or *in vivo* based assays will be required to validate the proteomic data.

Some of our recent results on gymnemic acid I interactome are reported herein to fully clarify how chemical proteomics can help in the discovery of unknown natural drug target(s).

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ORG-P16

Flash oral communication FO1

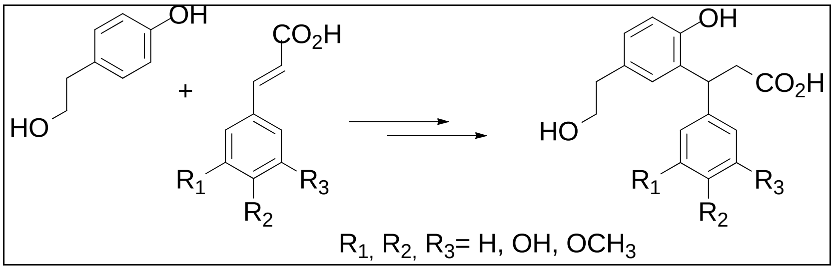
Synthesis and DPPH radical scavenging activity of novel phenolic compounds from tyrosol and cinnamic acids

Isabella Carastro[a], *Roberta Bernini*[a], *Maurizio Barontini*[a], *Patrizia Gentili*[b], *Annalisa Romani*[c]

a Dipartimento di Scienze e Tecnologie per l'Agricoltura, le Foreste e l'Energia (DAFNE),
Università della Tuscia di Viterbo,
Via San Camillo De Lellis, 01100, Viterbo, Italia
b Dipartimento di Chimica, IMC-CNR Sezione Meccanismi di Reazione,
Università degli Studi di Roma La Sapienza, P. le A. Moro 5, 00185 Roma, Italia
c Dipartimento di Statistica, Informatica, Applicazioni ''G. Parenti'' (DiSIA),
Viale Morgagni 65, 50134 Firenze, Italia

i.carastro@unitus.it

Novel phenolic compounds were synthesised by a trifluoroacetic acid-mediated hydroarylation of cinnamic esters with tyrosol to produce 4-aryl-3,4-dihydrocoumarins, followed by a basic hydrolysis.



All compounds were evaluated about the DPPH radical scavenging activity. Experimental results demonstrated that they showed an efficacy significantly higher than tyrosol [1].

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ORG-P17

Glicoconiugati di analoghi del resveratrolo: sintesi, attività antiproliferativa e inibizione di glicosidasi

<u>Nunzio Cardullo</u>[a], *Carmela Spatafora*[a], *Nicolò Musso*[b], *Vincenza Barresi*[b], *Daniele Condorelli*[b], *Corrado Tringali*[a]

a Dipartimento di Scienze Chimiche, Università di Catania, Viale A. Doria 6, 95125, Catania, Italia
b Dipartimento di Scienze Bio-mediche, sezione di Biochimica, Università di Catania, Viale A. Doria 6, 95125, Catania, Italia Nazione

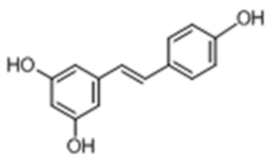
nunzio.cardullo@hotmail.it

Il nostro gruppo di ricerca da diversi anni si interessa di analoghi del resveratrolo (**1**), uno stilbenoide ben noto per le sue molteplici attività biologiche che purtroppo ha una bassa biodisponibilità; per questo motivo sono stati sintetizzati numerosi analoghi con maggiore stabilità metabolica, fra i quali i polimetossistilbeni hanno manifestato interessanti proprietà antitumorali.

Abbiamo quindi ritenuto utile sintetizzare dei glicoconiugati di polimetossistilbeni, in quanto potrebbero essere assorbiti preferenzialmente in quelle cellule tumorali di cui si osserva un alterato metabolismo del glucosio e una maggiore espressione delle proteine trasportatrici di glucidi, *in primis* del glucosio (GLUTs). Composti di questo tipo potrebbero anche agire da pro-farmaci, sfruttando l'azione idrolitica delle β-glicosidasi citosoliche.

In base a questi presupposti abbiamo quindi sintetizzato i composti **2** – **4** e **5** – **7**, rispettivamente glucosil- e galattosilconiugati di polimetossistilbeni .

I composti ottenuti sono stati caratterizzati mediante ESI-MS e metodi 1D e 2D-NMR; successivamente sono stati valutati (insieme ai loro agliconi) per l'attività antiproliferativa nei confronti di linee cellulari tumorali Caco-2 e SH-SY5Y. Su questi composti sono stati inoltre stati effettuati studi *in vitro* di idrolisi enzimatica ad opera di β-glicosidasi e β-galattosidasi e di inibizione di α- e β-glicosidasi.



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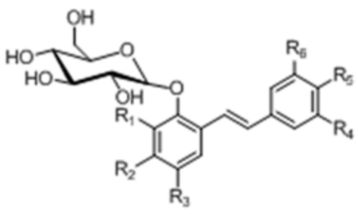
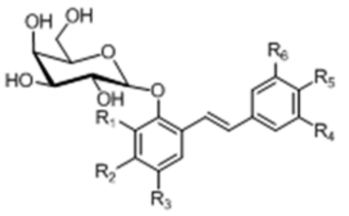


2 $R_1 = R_3 = R_5 = OMe$, $R_2 = R_4 = R_6 = H$
3 $R_1 = R_3 = R_5 = R_6 = OMe$, $R_2 = R_4 = H$
4 $R_1 = R_3 = R_4 = R_6 = OMe$, $R_2 = R_5 = H$



5 $R_1 = R_3 = R_5 = OMe$, $R_2 = R_4 = R_6 = H$
6 $R_1 = R_3 = R_5 = R_6 = OMe$, $R_2 = R_4 = H$
7 $R_1 = R_3 = R_4 = R_6 = OMe$, $R_2 = R_5 = H$

ORG-P18

Sintesi biomimetica di neolignanammidi mediata da laccasi

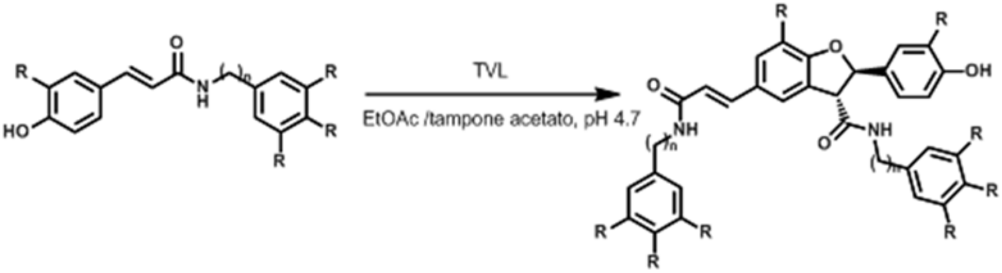
Nunzio Cardullo[a], *Luana Pulvirenti*[a], *Carmela Spatafora*[a], *Corrado Tringali*[a]

a Dipartimento di Scienze Chimiche, Università di Catania, Viale A Doria 6, 95125, Catania, Italia

nunzio.cardullo@hotmail.it

La biosintesi dei lignani ha origine da un *coupling* ossidativo di due unità fenilpropanoidiche (C6C3); l'accoppiamento fra radicali in posizione 8 e 8' genera i lignani veri e propri; tutti i composti che si formano da un accoppiamento differente da 8-8' vengono definiti neolignani. Fra questi, i neolignani diidrobenzofuranici includono esempi noti per attività antitumorale, antiangiogenica, antimalarica o antiossidante. Un certo numero di dimeri diidrobenzofuranici bioattivi è stato ottenuto da acidi o esteri cinnamici; ben pochi sono invece i casi riportati di neolignanammidi, cioè dimeri di ammidi cinnamiche. La funzione ammidica, isosterica rispetto a quella esterea, comporta una maggiore stabilità metabolica e le ammidi dimeriche potrebbero quindi manifestare una maggiore attività biologica.

Su questa base abbiamo progettato la sintesi di nuove neolignanammidi con nucleo diidrobenzofuranico a partire da ammidi degli acidi cumarico, caffeico e ferulico. In questo progetto abbiamo fatto ricorso a una metodologia biomimetica ed '*eco-friendly*' basata su accoppiamento ossidativo mediato da laccasi. In una prima fase sono state messe a punto le condizioni di reazione valutando sia l'effetto di differenti co-solventi che quello di diverse laccasi. La sintesi su scala preparativa è stata poi effettuata utilizzando laccasi da *Trametes versicolor* (TVL) che ha dato i risultati migliori.



I composti sintetizzati sono stati caratterizzati mediante ESI-MS e metodi 1D e 2D-NMR. Il successivo *step* sarà la valutazione dell'attività antiproliferativa delle neolignanammidi verso colture di cellule tumorali.

ORG-P19

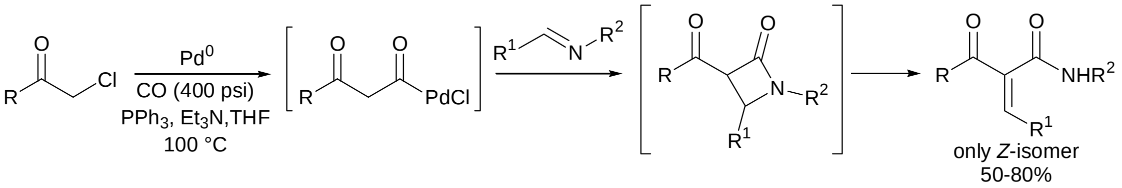
Stereoselective Synthesis of Unsaturated β-Ketoamides by Pd-Catalyzed Carbonylation

Antonio Caroli[a, d], *Serena Perrone*[a], *Antonio Salomone*[c, d], *Giuseppe Cannazza*[b], *Cinzia Citti*[a], *Aurelia Falcicchio*[e] *and Luigino Troisi*[a]

a Dipartimento di Scienze e Tecnologie Biologiche ed Ambientali, Università del Salento,via Prov.le Lecce-Monteroni, Lecce 73100, Italy
b Dipartimento di Scienze della Vita, Università degli Studi di Modena e Reggio Emilia, via Università 4, Modena 41121, Italy
c Dipartimento di Farmacia-Scienze del Farmaco, Università degli Studi di Bari "Aldo Moro", Via E. Orabona 4, Bari 70125, Italy
d Consorzio Interuniversitario Nazionale Metodologie e Processi Innovativi di Sintesi (C.I.N.M.P.I.S.), Via E. Orabona 4, Bari 70125, Italy
e Istituto di Cristallografia IC-CNR, Via Amendola 122/o, I-70125 Bari, Italy

Antonio.caroli@hotmail.com

Palladium-catalyzed carbonylation reaction represents a useful route for the direct incorporation of a carbonyl moiety into a molecule, leading to a wide range of carbonyl compounds starting from simple substrates.[1]
We have recently described as Pd-catalyzed carbonylation of unsaturated halides in the presence of amines, imines and alcohols constitutes a valuable methodology for the synthesis of amides, β-lactams and esters respectively.[2]
In this communication we report a Pd-catalyzed cascade process involving carbonylation-cyclization- ring opening reactions starting from *α*-chloroketones, CO and imines. This methodology allows a simple and highly stereoselective synthesis of *α*-functionalized *β*-ketoamides through the formation of *β*-lactam intermediates.



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ORG-P20

Flash oral communication FO2

Elucidating new structural features of triazole scaffold for the development of mPGES-1 inhibitors

Maria Giovanna Chini[a], *Paolo Dambruoso*[b], *Greta Varchi*[b], *Oliver Werz*[c], *Raffaele Riccio*[a], *Ines Bruno*[a] *and Giuseppe Bifulco*[a]

a Dipartimento di Farmacia, Università degli Studi di Salerno, Via Giovanni Paolo II n°132, 80084, Fisciano (SA), Italia
b SOF - CNR Area della Ricerca di Bologna, Via P. Gobetti 101, 40129, Bologna, Italia
c Department of Pharmaceutical/Medicinal Chemistry, Institute of Pharmacy, Friedrich Schiller University, Jena, Philosophenweg 14, D-07743 Jena, Germany

mchini@unisa.it

Microsomal prostaglandin E_2 synthase-1 (mPGES-1) enzyme has greatly emerged as an attractive target for new efficient anti-inflammatory and anticancer drugs discovery and development. This enzyme is responsible, in the arachidonic acid cascade, of the conversion of COX-derived unstable peroxide PGH_2 in PGE_2,[1] and it is over expressed in several inflammatory disorders as well as in many human tumors. Thanks to the resolution human mPGES-1 X-ray structure,[2] and starting from our previous results,[3] we report the structure based drug design of new simplified version of mPGES-1 triazole inhibitor with IC_{50} of 0.7 ± 0.2 μM. The active compound should be able to interact with the membrane protein occupying the PGH_2 binding site. In particular, the halogen bonding of iodine atom with the backbone of receptor was disclosed as a new key interaction useful for the design of new mPGES-1 inhibitors. Our hypothesis, in fact, was proved by the incomplete suppression of mPGES-1 activity removing the iodine atom at position 5 of triazole ring (20% inhibition at 10 μM, $IC_{50} > 30$ μM).

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ORG-P21

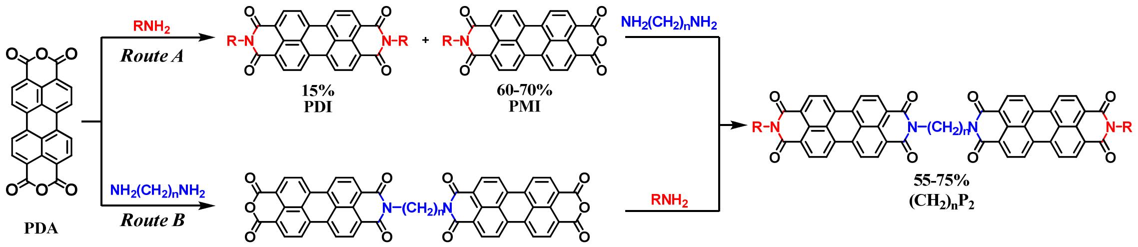
Synthesis of alternative acceptor materials for organic photovoltaics

Cinzia Citti[a], *Luigino Troisi*[a], *Catia Granito*[a], *Serena Perrone*[a], *Ludovico Valli*[a], *Simona Bettini*[a], *Gabriele Giancane*[b], *Alessandro Troisi*[c]

a Dipartimento di Scienze e Tecnologie Biologiche ed Ambientali, Università del Salento, Via Prov.le Lecce-Monteroni, I-73100 Lecce, Italy
b Department of Cultural Heritage, Università del Salento, Via Birago 64, I-73100 Lecce, Italy
c Chemistry Department and Centre for Scientific Computing, University of Warwick, Coventry, United Kingdom

cinzia.citti@unisalento.it

Organic photovoltaics (OPV) is a technology that may be able to provide a clean, sustainable and low-cost source of energy [1]. This work is focused on the synthesis of a class of compounds that may find interesting applications in organic electronics. Specifically, the proposed molecules bind one or more sp^3 carbons to two identical acceptors (P) with a general formula **$(CH_2)_nP_2$**. Perylene (P) has been chosen as the central core of the acceptor due to its electronic and chemical properties as well as its low cost [2]. In this complex architecture the π-π interactions would develop in a 3D plane, unlike most planar conjugated molecules [3]. Two synthetic routes have been developed starting from commercially available perylene dianhydride (**PDA)** that reacts with different aliphatic amines and gives the final products in good yield (55-75%). The procedure can be easily carried out with quinoline or *N*-methylpyrrolidinone as solvent. Furthermore, the very useful but so-far elusive intermediate perylene monoimide (**PMI)** has been synthesised in very good yield and a 4:1 ratio with perylene diimide (**PDI)**.



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ORG-P22

Sintesi di *hosts* calix[6]arenici chirali via p-*bromodienone route*

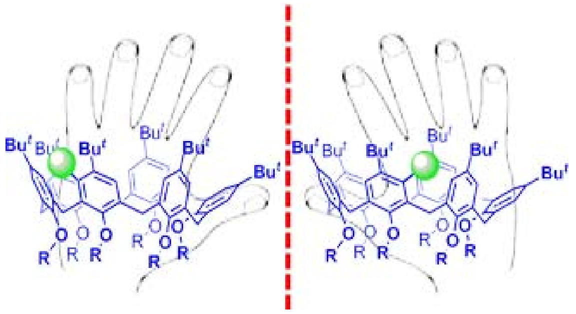
Gerardo Concilio, Carmen Talotta, Yuri Norcino, Carmine Gaeta e Placido Neri

Dipartimento di Chimica e Biologia e NANO_MATES Research Center, Università di Salerno, Via Giovanni Paolo II 132, I-84084 Fisciano (Salerno)

gconcilio@unisa.it

Negli ultimi anni è stato messo a punto un metodo estremamente efficiente per ottenere *endo*-complessazione e *through-the-annulus threading* di calix[6-7]areni sfruttando l'approccio del "*superweak anion*" TFPB.[1] Tale strategia è stata efficacemente adoperata per l'ottenimento di diversi sistemi interpenetrati e/o interbloccati.[2]

Proseguendo in questa direzione, ci si propone di realizzare nuovi *hosts* calix[6]arenici chirali da utilizzare nell'ambito di un riconoscimento supramolecolare chirale. La sintesi di tali *hosts* sarà possibile estendendo, per la prima volta, la "*p*-bromodienone route"[3] ai calix[6]areni. Si potranno utilizzare nucleofili chirali o la *meta*-trasposizione dienone-fenolo che genera chiralità inerente.[4]



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ORG-P23

Symmetry as an Unexplored Tool for Tailoring Optoelectronic Properties in Melanin-Inspired Triazatruxenes

Criscuolo V.[a], *Manini P.*[a], *Pezzella A.*[a], *Crescenzi O.*[a], *Maglione M. G.*[b], *Tassini P.*[b] *and Marco d'Ischia*[a]

a Dept. Chemical Sciences, Univ. Naples Federico II, I-80126 Naples, Italy
b Lab. Nanomaterials and Devices, ENEA C. R. Portici, p.le E. Fermi 1, 80055, Portici (NA), Italy

valeria.criscuolo@hotmail.it

The development of flat π-conjugated platforms with tailored semiconducting and photoluminescence properties is an increasingly active issue in the field of organic electronics. Considerable interest in this connection is attracted by triazatruxenes (TATs), which exhibit good charge mobility,[1] redox behavior, intense electroluminescence and a C_3 symmetry which makes them suitable building blocks for star-shaped structures. Some TATs can generate electroactive discotic liquid crystals and have been tested in organic field-effect transistors (OFETs), bulk heterojunction solar cells,[2] organic light emitting diodes (OLEDs)[3] and sensing devices.[8] In this work we capitalize on the reactivity of 5,6-dialkoxyindoles, stable derivatives of the key eumelanin building block 5,6-dihydroxyindole, to gain access for the first time to unexplored representative members of the asymmetric TAT series (aTATs) 1a and 2a along with their corresponding C3 symmetrical isomers 1b and 2b.[4] Reported herein is a survey of the optoelectronic properties of ATATs revealing for the first time a higher fluorescence quantum efficiency, a lower HOMO-LUMO gap and superior film quality properties, which may expand the range of organic electronics applications of traditional C_3-symmetric TATs. In this connection we tested also the potentiality of TATs and ATATs as a novel organic emitting layer in OLED devices. Preliminary results are presented.

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ORG-P24

Controlling The Vinylogous Reactivity of Oxindoles Bearing non Symmetric 3-Alkylidene Groups

Nicola Di Iorio, Riccardo G. Margutta, Paolo Righi, Giorgio Bencivenni

Dipartimento di Chimica Industriale "Toso Montanari" Alma Mater Studiorum – Università di BolognaViale del Risorgimento 4 – 40136 Bologna, Italia

nicola.diiorio2@unibo.it

In this work we present the organocatalytic asymmetric vinylogous Michael addition of non symmetric 3-alkylideneoxindole to nitrostyrene derivatives[1]. The peculiarity of our reaction is that a bifunctional catalyst bearing thiourea and tertiary amine moieties is able to control the regiochemistry of the nucleophilic attack and the diastereo- and enantioselection of the reaction, affording mainly one pure stereochemically complex product in good yield and excellent optical purity. Central key of the mechanism that we propose is the control exerted by the catalyst over the geometry of the active intermediate (figure_1) independently from the configuration of the double bond of the starting oxindole. This way we were able to obtain products of high biological interest[2,3] with stereocenters far away from the active site and a double bond that, by virtue of its particular structure, introduced a high degree of complexity and at the same time, unveiled the regiochemistry of the reaction.

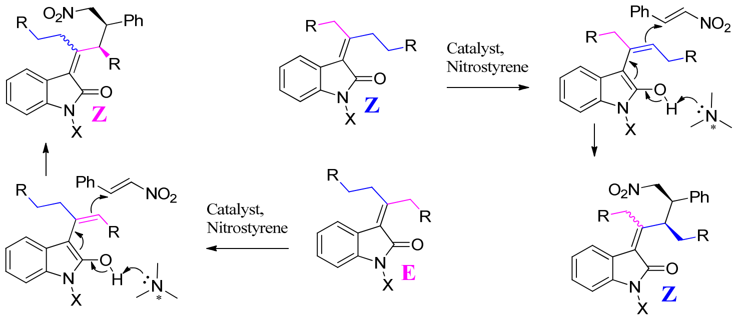

Figure 1: **Scheme of the reaction**

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ORG-P25

Identification of lead compounds as inhibitors of STAT3 SH2 domain, by design, synthesis and biological evaluation

Simone Di Micco[a], *Antonio Botta*[a], *Esther Sirignano*[a], *Ada Popolo*[a], *Carmela Saturnino*[a], *Maria Stefania Sinicropi*[b], *Pasquale Longo*[c], *Giuseppe Bifulco*[a]

a Dipartimento di Farmacia, Università di Salerno, Via Giovanni Paolo II n°132 , 80084, Fisciano (SA), Italia
b Dipartimento di Farmacia e Scienze della Salute e della Nutrizione, Università della Calabria, 87036 Arcavacata di Rende, Cosenza, Italy
c Dipartimento di Chimica e Biologia, Università degli Studi di Salerno, Via Giovanni Paolo II, 84084 Fisciano, Salerno, Italy

sdimicco@unisa.it

STAT3 belongs to the signal transducers and activators of transcription (STAT) family [1]. It has been demonstrated that STAT3 is involved in carcinogenesis and tumor progression, and for this reason has being considered a potential target for cancer therapy [2].

In this context, we have designed, synthesized and experimentally tested 1,4-dimethyl-carbazoles derivatives, targeting the SH2 domain of STAT3. Moreover, MTT assay performed on A375 and HeLa, showed significant antiproliferative activity of some of synthesized compounds (**3**-**5**). The same compounds (**3**-**5**) significantly reduced STAT3 expression, as demonstrated by Western blot analysis. Our multidisciplinary approach shows that some of these 1,4-dimethyl-carbazoles compounds are potential scaffolds to develop more affinity ligands of STAT3

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ORG-P26

Marine and semi-synthetic hydroxysteroids as new scaffolds for pregnane X receptor modulation

Carmen Festa,[a] Valentina Sepe,[a] Francesco Saverio Di Leva,[a] Claudio D'Amore,[b] Simona De Marino,[a] Barbara Renga,[b] Maria Valeria D'Auria,[a] Ettore Novellino,[a] Vittorio Limongelli,[a] Lisette D'Souza,[c] Mahesh Majik,[c] Angela Zampella,[a] Stefano Fiorucci[b]

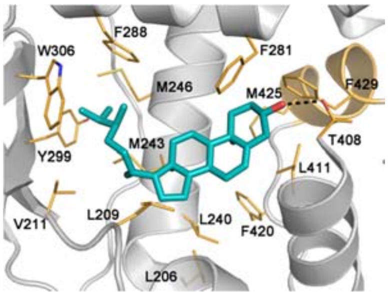
a Department of Pharmacy, University of Naples "Federico II", Via D. Montesano, 49, I-80131 Napoli, Italy;
b Department Experimental and Clinical Medicine, University of Perugia, Via Gambuli 1, S. Andrea delle Fratte, 06132 Perugia, Italy;
c CSIR-National Institute of Oceanography, Dona Paula, Goa 403004, India.

carmen.festa@unina.it

The pregnane X receptor (PXR) belongs to the nuclear receptor (NR) family and is well recognized for its pivotal role as a "xenobiotic sensor" that transcriptionally regulates the expression of Phase I and Phase II drug/xenobiotic metabolizing enzymes and transporters. PXR can be activated by various ligands that can bind to the ligand binding domain (LBD), such as antibiotics, antineoplastic, anti-inflammatory and antihypertensive drugs [1] and several natural products [2,3] or herbal remedies. Activators of the PXR play a therapeutic role in the treatment of intestinal inflammation and of other immune-mediated dysfunctions in humans [4].

In this poster we will report the isolation of a series of 24-alkylated-hydroxysteroids from the soft coral *Sinularia kavarattiensis*, acting as PXR modulators. Starting from this scaffold a number of derivatives have been prepared and evaluated for their ability to activate the PXR by assessing transactivation and quantifying gene expression.

Our study reveals that ergost-5-en-3β-ol induces PXR transactivation in HepG2 cells and stimulates the expression of the PXR target gene CYP3A4. The bioactivity of the most potent compound of the series on nuclear receptor PXR was rationalized by docking experiments, to shed light on the molecular basis of the binding mechanism to LBD of PXR. Our findings provide useful functional and structural information to guide further investigations and drug design.



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ORG-P27

Discovery of UDCA derivatives as new modulators of bile acid receptors

Claudia Finamore,[a] *Valentina Sepe,*[a] *Claudio D'Amore,*[b] *Carmen Festa,*[a] *Barbara Renga,*[b] *Francesco Saverio Di Leva,*[a] *Vittorio Limongelli,*[a] *Ettore Novellino,*[a] *Angela Zampella,*[a] *Stefano Fiorucci*[b]

a Department of Pharmacy, University of Naples "Federico II", Via D. Montesano, 49, I-80131 Napoli, Italy;
b Department Experimental and Clinical Medicine, University of Perugia, Via Gambuli 1, S. Andrea delle Fratte, 06132 Perugia, Italy.

claudia.finamore@unina.it

Bile acids exert genomic and non-genomic effects by interacting with membrane G-protein coupled receptors, including the bile acid receptor GP-BAR1, and nuclear receptors, such as the farnesoid X receptor (FXR) [1,2]. These receptors regulate overlapping metabolic functions, thus GP-BAR1/FXR agonists, by enhancing the biological response, represent an innovative strategy for the treatment of entero-endocrine disorders[3,4].

UDCA (ursodeoxycholic acid), present in human bile at low concentrations, has been shown effective in biliary and liver diseases and is now considered as the first-line treatment for primary biliary cirrhosis (PBC), primary sclerosing cholangitis (PSC), and intrahepatic cholestasis of pregnancy (ICP) [5]. UDCA is the 7β–hydroxy epimer of CDCA and, despite its pharmacological profile, UDCA is not a FXR agonist and its mechanism of action remains unclear and still subjected to intense scientific debates. Indeed UDCA is considered a safety molecule with a clinical history with minimal side effects, also when used in large doses. In this context we decided to manipulate UDCA chemical scaffold obtaining a large library of derivatives. This research work resulted in the identification, for the first time, of several UDCA analogues endowed with bile acid receptors agonistic profile.

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ORG-P28

Studio della reazione di Grignard su derivati dell'acido ursolico

Giuseppe Mattia Lo Piccolo, Francesco Ferrante[a], Maurizio Bruno[b],
Gianfranco Fontana[b], Antonella Maggio[b], Sergio Rosselli[b]

a Dipartimento di Fisica e Chimica, Università degli Studi di Palermo, Viale delle Scienze ed. 17, 90128, Palermo, Italia
b Dipartimento di Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche (STEBICEF), Università di degli Studi di Palermo, Viale delle Scienze ed. 17, 90128, Palermo, Italia

gianfranco.fontana@unipa.it

Lo studio presentato in questa comunicazione è stato incentrato sulla sintesi di alcuni derivati triterpenici e sullo studio computazionale del decorso stereochimico della reazione di addizione nucleofila al carbonio carbonilico del *metil ursonato* con MeMgCl e PhMgCl. I derivati dell'acido ursolico, come il *metil ursonato*, mostrano numerose interessanti attività biologiche[1,2].

Oltre alla determinazione teorica della distribuzione dei prodotti epimerici, sono stati anche simulati gli spettri ^{1}H e ^{13}C NMR per tutti i prodotti teoricamente ottenibili in modo da poter confrontare dati sperimentali e previsioni teoriche. I tensori di schermaggio risultanti del calcolo, condotto usando il metodo DFT-GIAO a livello B3LYP/cc-pVTZ, sono stati trasformati in *chemical shift* usando un approccio differenziale per il composto di riferimento.

Da un'analisi conformazionale (B3LYP/cc-pVDZ, con inclusione degli effetti del solvente tramite PCM) è risultato che la molecola in esame è coinvolta in un equilibrio tra due strutture che si differenziano solo per la conformazione dell'anello A.

Confrontando gli spettri NMR sperimentali con quelli calcolati è stato possibile identificare due prodotti di metilazione e un unico prodotto di arilazione. Dai risultati ottenuti sul decorso di reazione si può affermare che entrambe le addizioni di MeMgCl e PhMgCl avvengono sotto controllo cinetico.

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ORG-P29

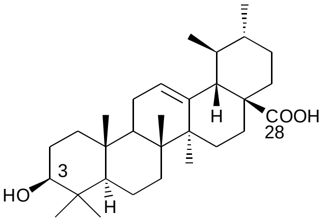
Sintesi e attività antitumorale di derivati dell'acido ursolico

Gianfranco Fontana[a], *Simona Buccheri*[b], *Maurizio Bruno*[a], *Antonella Maggio*[a], *Sergio Rosselli*[a]

a Dipartimento di Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche (STEBICEF).
Università degli Studi di Palermo. Viale delle Scienze, ed. 17, 90128 Palermo, Italia
b Dipartimento di Biopatologia e Biotecnologie Mediche e Forensi (DIBIMEF), Università
degli Studi di Palermo, Corso Tukory, 90128 Palermo, Italia

gianfranco.fontana@unipa.it

Due acidi triterpenici ubiquitari, l'acido oleanoico e l'acido ursolico (**1**), mostrano una significativa attività citotossica in vitro verso alcune linee cellulari tumorali[1]; ciò è vero anche per numerosi loro derivati semisintetici[1,2] per mezzo dei quali sono state ottenute utili relazioni struttura-attività[3]. Sebbene non via sia un andamento assolutamente generale, in una buona parte della casistica disponibile è emersa l'importanza di un'opportuna funzionalizzazione delle posizioni C-3 e C-28 di entrambi i composti naturali. In questo quadro generale si inserisce l'argomento di questa comunicazione poster, che verte sulla semisintesi di un gruppo di derivati dell'acido ursolico, funzionalizzati alle posizioni prima citate. Sono stati ottenuti composti con un grado variabile di ossidazione degli atomi di carbonio e con sostituenti che permettono una variazione della lipofilia della molecola. Tutti i derivati ottenuti sono stati valutati come agenti citotossici verso la linea cellulare di carcinoma del colon HCT116. Sebbene in numero non elevatissimo, le prove effettuate hanno permesso di razionalizzare i dati ottenuti in modo tale da rilevare alcune importanti informazioni sulla relazione tra struttura molecolare ed attività antitumorale verso questo tipo cellulare. Ulteriori studi sono ovviamente necessari per completare il quadro.



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[1] M K. K. Bai, Z. Yu, et al. *Bioorg. & Med. Chem. Lett.*, 2012, **22**, 2488-2493.
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[3] Y. Q: Meng, D. Liu et al. *Bioorg. Med. Chem.*, 2009, **17**, 848-854.

ORG-P30

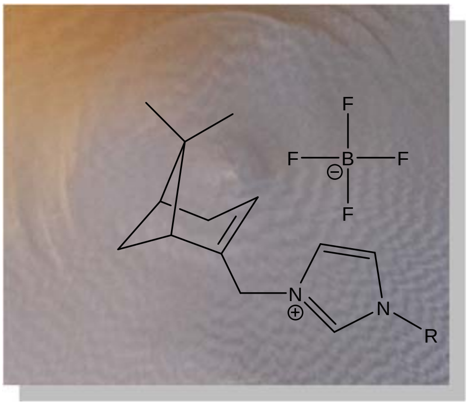
Flash oral communication FO3

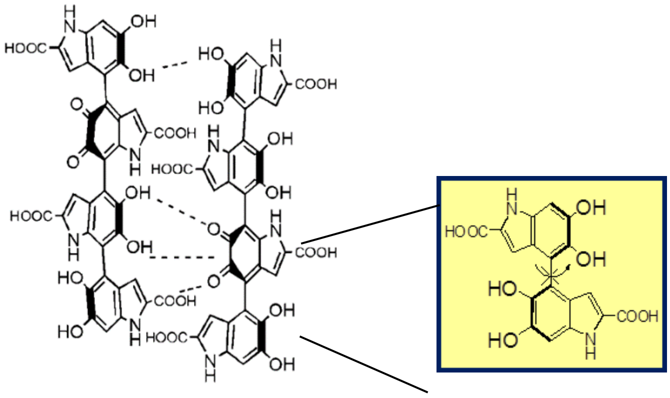
New Chiral Ionic Liquids for surface polymerization processes

C. Chiappe[a], *T. Ghilardi*[a],*C.P. Pomelli*[a], *F .Bellina*[b], *A. Iuliano*[b], *P. Manini*[c], *M. d'Ischia*[c]

[a] *Dipartimento di Farmacia, Università di Pisa, Via Bonanno 33 , 56126, Pisa, Italia*
[b] *Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, 56126, Pisa, Italia.* [c] *Dipartimento di Scienze Chimiche, Università di Napoli, Via Cintia 4, 80126, Napoli, Italia*
tiz.ghilardi@gmail.com

Chiral ionic liquids (CILs) have received considerable attention as enantioselective catalysts and as media for asymmetric syntheses or extraction processes. The aim of this work was to design and synthesize novel chiral ionic liquids starting from natural or synthetic chiral alcohols, and to investigate their ability to form orderly liquid surfaces for specific technological processes. 1*R*-Nopol, (*S*)-(-)-β-citronellol, (1*R*,2*S*,5*R*)-(-)-menthol and (*S*)-1-(naphthalen-2-yl)ethan-1-ol were selected among the natural chiral alcohols, while synthetic enantiopure alcohols were prepared through simple procedures starting from (*R*)-propylene oxide. In order to minimize the interactions between the chiral moiety and the positively charged imidazolium ring, an appropriate spacer was inserted between the nitrogen atom and the stereogenic centre. When anions such as bistriflimide, tetrafluoroborate and mesylate were employed, the resulting chiral salts melt at or near room temperature (always below 100 °C) allowing their use in oxidative coupling reactions involving thermolabile substrates. The main physico-chemical properties of these new CILs, generally obtained in high yields, and preliminary data about their possible application as functional media for the synthesis of melanin-based coatings via surface polymerization of 5,6-dihydroxyindoles and catecholamine precursors will be reported. In particular, the potential of CILs as templates for the synthesis of axially chiral melanin-related polymers from 5,6-dihydroxyindole-2-carboxylic acid (DHICA) will also be discussed.





ORG-P31

Flash oral communication FO7

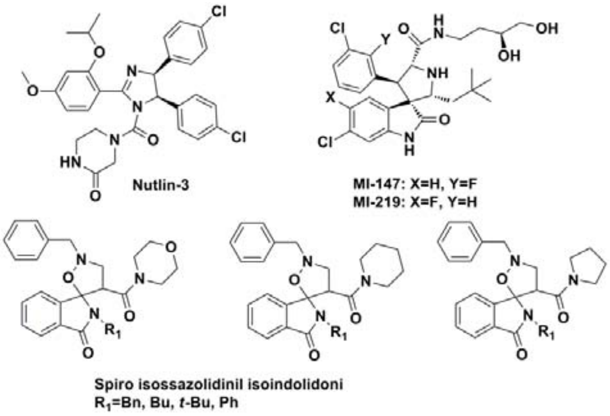
Spiro-Isoindolin Isossazolidine: potenziali agenti antitumorali

Salvatore V. Giofrè [a], *Raffaella Mancuso* [b], *Roberto Romeo* [a], *Ida Ziccarelli*[b],
Santa Cirmi [a], *Bartolo Gabriele* [b]

a Dipartimento di Scienze del Farmaco e Prodotti per la Salute, Università di Messina, Via S.S. Annunziata, 98168-Messina, Italia
b Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Via P. Bucci, 12/C, 87036 Arcavacata di Rende (CS), Italia

sgiofre@unime.it

Nella ricerca di nuove molecole a potenziale attività antitumorale, lo scaffold indolinonico e isoindolinonico riveste un ruolo importante nelle interazioni con diversi target cellulari. In particolare, negli ultimi anni la ricerca si è focalizzata sulla inibizione dell'interazione MDM2-p53, che produce un effetto antitumorale, soprattutto in tumori che presentano una sovraespressione di MDM2. Il trattamento dell'interazione MDM2-p53 come "drug target" può essere effettuato con numerose classi di inibitori; i migliori risultati sono stati ottenuti con la **Nutlin-3** e con una classe di spiroossindoli, **MI-147** e **MI-219**.



In questo contesto, è stata sviluppata la sintesi di una classe di isoindolinoni,[1] che per reazione di cicloaddizione 1,3-dipolare con *N*-benzil nitrone, hanno fornito una nuova serie di spiro-isoindolin isossazolidine che hanno mostrato attività, in un range µM, nei confronti di tre diverse linee cellulari tumorali, SH-SY5Y (neuroblastoma), HT-29 (colorectal adenocarcinoma) e HepG2 (hepatocellular carcinoma). Studi di Molecular Modelling suggeriscono che i composti sintetizzati fittano con il sito di binding di MDM2-p53, in particolare, sovrapponendosi con i residui aminoacidici della p53 interessati nell'interazione, Phe19, Trp23 e Leu26. Sono in corso studi biologici per valutare l'attivazione della p53 attraverso Western blotting.

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ORG-P32

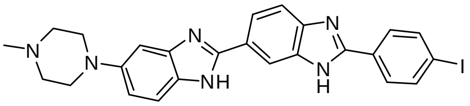
Benzimidazole derivatives by Lewis acid catalyzed heterocyclocondensations in DNA-binders

Matteo Di Nicola, Simone Giorgi, Marco Glucini, Pamela Piermattei, Mara Tomassetti, Enrico Marcantoni

School of Science and Technology, Chemistry Division, University of Camerino,
Via S. Agostino n.1, 62032 Camerino (MC)

simone.giorgi@studenti.unicam.it

Numerous small molecules have been developed that can bind DNA or RNA with nanomolar affinity and high specificity. Researchers of Scripps Florida have recently identified benzimidazole derivatives that can target microRNAs, which are important cellular targets for cancer and other diseases.[1] They can act as agents with a selective type of anticancer activity. In this an important role is played by organic chemistry in developing new strategies for the preparation of such small molecules. In these last decades the $CeCl_3$ is interesting compound for organic chemistry applications.[2] We observed that different inorganic iodides (MI_n) increase the Lewis acid activity of $CeCl_3 \cdot 7H_2O$ in carbon-heteroatom bond formation reactions, and the nature of the metal M promotes this Lewis acid activity. In the course of our program aimed to develop general methods for the synthesis of nitrogen-containing heterocycles,[3] we explored the potential of $CeCl_3 \cdot 7H_2O$-CuI system in Lewis acid catalyzed heterocyclocondensation reactions. The method represents a new, selective and more eco-sustainable synthetic path to Hoechst molecules with benzimidazole moieties such as **1**.[4]



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[2] G. Bartoli, E. Marcantoni, M. Marcolini and L. Sambri *Chem. Rev.* 2010, **110**, 6140-6142.
[3] R. Properzi and E. Marcantoni *Chem Soc. Rev.* 2014, **43**, 779-791.
[4] M. Dasari, S. Lee, J. Sy, D. Kim, S. Lee, M. Brown, M. Davis and N. Murthy *Org. Lett.* 2010, **12**, 3300-3303.

ORG-P33

Fragment Virtual Screening for the identification of new potential microsomal prostaglandin E_2 synthase-1 (mPGES-1) inhibitors

Gianluigi Lauro[a], Ines Bruno[a], Oliver Werz[b], Raffaele Riccio[a], Giuseppe Bifulco[a]

a Dipartimento di Farmacia, Università degli Studi di Salerno, Via Giovanni Paolo II 132, 84084, Fisciano (SA), Italy
b Department of Pharmaceutical/Medicinal Chemistry, Institute of Pharmacy, Friedrich Schiller University, Jena, Philosophenweg 14, D-07743 Jena, Germany

glauro@unisa.it

Fragment virtual screening computational approach[1] has emerged as a significant tool in the field of medicinal chemistry for discovery of new hit compounds. It focuses on low-molecular-weight compounds (<300 Da), which once identified, can be linked or optimized to design high affinity ligands. Here we show the application of a structure-based fragment virtual screening campaign (~440000 compounds) on microsomal prostaglandin E_2 synthase-1 (mPGES-1)[2,3] by means of molecular docking experiments. The use of different filters (predicted binding affinity, ligand efficiency, key interactions with receptor counterpart) led us to the selection of a restricted number of compounds for the subsequent biological tests.[4] The promising biological activities found suggest the optimization of the fragments for the design of potent mPGES-1 inhibitors featuring new chemical cores.

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[2] B. Samuelsson, R. Morgenstern and P. J. Jakobsson *Pharmacol.Rev.* 2007, **59**, 207-224.
[3] T. Sjögren, J. Nord, M. Ek, P. Johansson, G. Liu and S. Geschwindner *Proc.Natl.Acad.Sci. U.S.A.* 2013, **110**, 3806-3811.
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ORG-P34

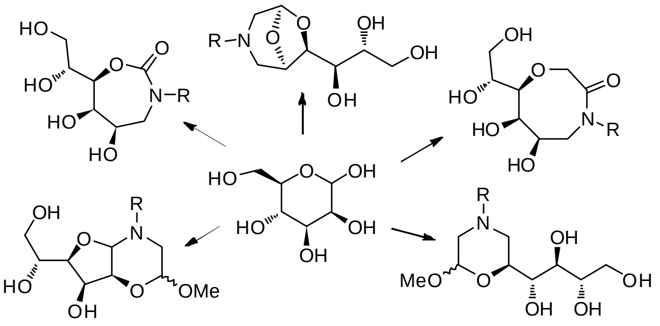
Diversity-Oriented Synthesis of glycopeptidomimetic scaffolds derived from mannose and glycine

Elena Lenci[a], *Andrea Trabocchi*[a], *Antonio Guarna*[a]

a Dipartimento di Chimica "Ugo Schiff", Università di Firenze, Via della Lastruccia 13,
50019 Sesto Fiorentino, FI, Italy

elena.lenci@unifi.it

Diversity-Oriented Synthesis (DOS) is a new approach to drug discovery which has proven to be very effective for the synthesis of large compound libraries.[1] It combines the generation of a functionalized precursor with further synthetic elaborations, in order to generate the maximum diversity and complexity from simple starting material.



With this strategy, Guarna's research group have made a significant contribution in the field of peptidomimetics, synthesizing dipeptide isosteres, integrin ligands and *C. albicans* aspartyl protease inhibitors.[2] Using D-mannose as the starting material, new glycopeptidomimetic scaffolds were obtained, as showed in the figure, following the DOS strategy named "build/couple/pair". Mannose and glycine were assembled in polyfunctionalized intermediates exploiting different types of coupling reactions. Then, in the pairing phase, intramolecular cyclizations (mostly by *trans*-acetalization) lead to skeletally different scaffolds containing glyco and peptidomimetic moieties, opening the way to novel hit chemical entities, with potential therapeutic applications as protein-protein interactions inhibitors.

[1] *Diversity-Oriented Synthesis,* ed. A. Trabocchi, Wiley, **2013**
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ORG-P35

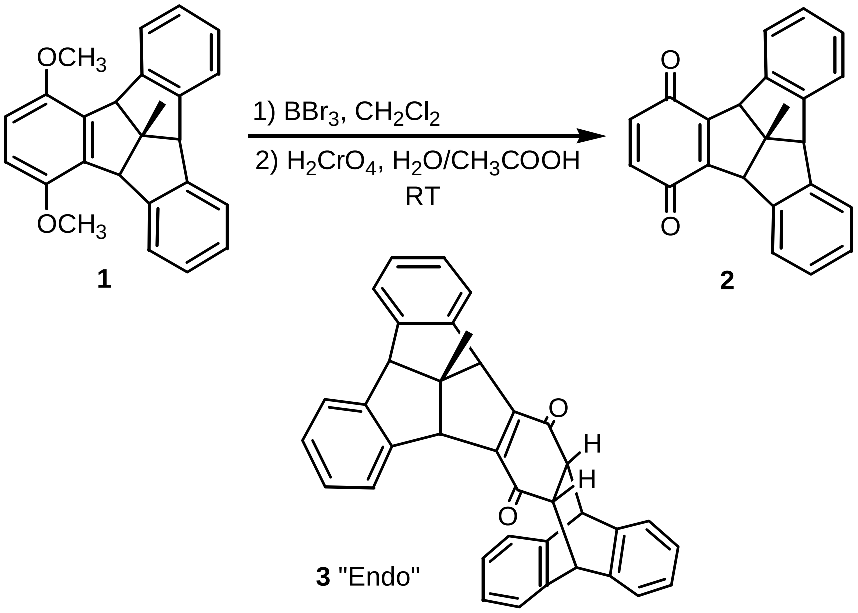
Quinone Derivatives of Tribenzotriquinacene: Possible Building Blocks for New Hydrocarbon Structures

Francesco Lucchesini[a], *Dietmar Kuck*[b]

a Dipartimento di Farmacia, Università di Genova, Viale Cembrano 14 , 16147, Genova
b Department of Chemistry, Bielefeld University, Universitätsstrasse 25, 33615 Bielefeld (Germany)

lucchesini@difar.unige.it

The dimethoxymethyltribenzotriquinacene **1** has been prepared by applying a general synthetic procedure [1] and easily transformed in 76% yield into the quinone **2**, which reacts with anthracene in a Diels-Alder reaction to afford the “endo” adduct **3** as the main product. Aromatization of the cyclohexenedione ring in **3** can be performed in different ways and affords molecules which join a triptycene and a tribenzotriquinacene structure.



1

2

3 "Endo"

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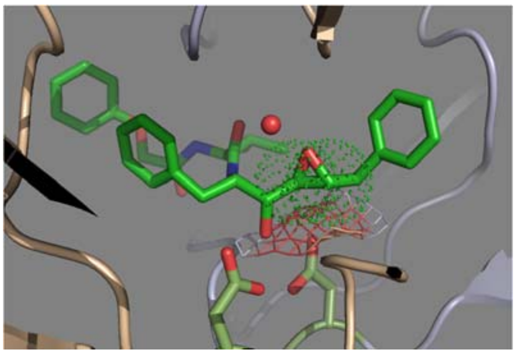
ORG-P36

Synthesis, Activity and Structural Characterisation of Epoxide-Based HIV-PR Inhibitors

Fabio Benedetti,[a] Federico Berti,[a] Pietro Campaner,[a] Matteo De March,[a,b]
Nicola Demitri,[a,b] Lidia Fanfoni,[a] Silvano Geremia,[a,b] Folasade M. Olajuyigbe.[b,c]

a Department of Chemical and Pharmaceutical Sciences, and
b Centre of Excellence in Biocrystallography, University of Trieste, Via Giorgeri 1, 34127 Trieste, Italy
c Department of Biochemistry, Federal University of Technology, P.M.B. 704, Akure 340001, Ondo State, Nigeria

benedett@units.it



Current treatment of AIDS is based primarily on cocktails of inhibitors of two viral enzymes: reverse transcriptase and protease [1]. However, drug resistance is a common drawback of treatments based on reversible inhibitors [2]. Irreversible inhibition is a possible way to escape resistance and alkylation of the protease's catalytic aspartates by epoxides has been proposed as a strategy thereof [3].

A series of HIV-protease inhibitors in which an epoxyalcohol is inserted into a peptidomimetic structure has been synthesized in several steps, starting from phenylalanine. The epoxides have good affinities for the target enzyme, with IC_{50} in the μM range, but behave as reversible inhibitors, rather than irreversible ones. The X-ray crystal structure of a member of the series, with $IC_{50} < 0.6$ μM, complexed with HIV-PR (figure) shows the intact epoxide ring in the enzyme's active site, in spite of a nearly optimal alignment with the carboxylate nucleophile, and the presence of a water molecule hydrogen-bonded to the epoxide oxygen that should favour ring opening.

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ORG-P37

Biological Evaluation of Benzofuran-2-acetic Esters as Antiproliferative Agents in Breast Cancer Cells

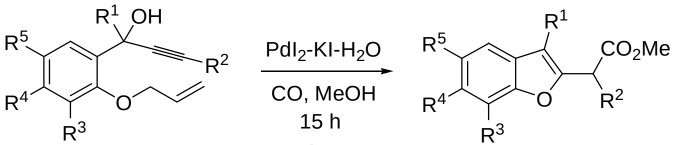
Cinzia Giordano[a], *Raffaella Mancuso*[b], *Francesca Chemi*[c], *Stefania Catalano*[a,c], *Sebastiano Andò*,[a,c] *Bartolo Gabriele*[b]

[a] *Centro Sanitario, Università della Calabria, Via P. Bucci 34/B, 87036 Rende, Italy*
[b] *Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Via P. Bucci 12/C, 87036 Arcavacata di Rende, Italy*
[c] *Dipartimento di Farmacia e Scienza della Salute e della Nutrizione, Università della Calabria, 87036 Arcavacata di Rende, Italy*

raffaella.mancuso@unical.it

The benzofuran moiety constitutes the core of several interesting biologically active natural products. Benzofuran derivatives are, in fact, potent active inhibitors against many diseases, viruses, microbes, fungus and enzymes [1].

In this study, we have evaluated the effects of some synthetic benzofuran-2-acetic esters, prepared by a carbonylation approach (Scheme 1) [2, 3], on the growth of several breast cancer cell lines. Using MTT assay we found that some of the different compound tested displayed excellent antiproliferative activity against breast cancer cells with an IC_{50} ranging from 40 to 80μM. Further, western blot analysis revealed that treatment with these compounds reduced expression of many regulators of cell cycle such as cyclin D1 and cyclin E.



Scheme 1

These data demonstrate that the molecules tested exert antiproliferative effects on breast cancer cells highlighting their potential use as a new breast cancer therapeutic agents.

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ORG-P38

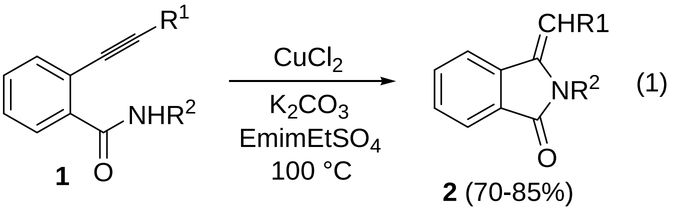
Copper-Catalyzed Cycloisomerization of 2-Alkynylbenzamides in Ionic Liquids

Raffaella Mancuso[a], *Cinzia Chiappe*[b], *Tiziana Ghilardi*[b],
Bartolo Gabriele[a]

[a] *Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Via P. Bucci, 12/C, 87036, Arcavacata di Rende (CS), Italy*
[b] *Dipartimento di Farmacia, Università di Pisa, Via Bonanno 33, 56126, Pisa, Italy*

raffaella.mancuso@unical.it

Isoindolinones are very important heterocyclic derivatives with many important applications. Many molecules containing the isoindolinone nucleus have shown important biological activities, including antimicrobial and antiproliferative effect.[1]
We have found that 3-alkylideneisoindolinones **2** can be conveniently synthesized in good yields (70-85%) by copper-catalyzed cycloisomerization of readily available 2-alkynylbenzamides **1** in an ionic liquid as the solvent (EmimEtSO$_4$) under basic conditions, according to Equation 1.



Reactions are carried out at 100 °C in the presence of catalytic amounts (5 %) of CuCl$_2$ and 2 equiv of K$_2$CO$_3$. The solvent-catalyst-base system can be conveniently recycled several times without appreciable loss of activity.

[1] See, for example: (a)C. Yu, T. Wang, K. Xu, J. Zhao, M. Li, S. Weng; J. Zhang, *Dyes and Pigments*, **2013**, 96, 38-44; (b) A. Bhardwaj, J. Kaur, S. K. Sharma, Z. Huang, E. E. Knaus, F. Wuest, *Bioorg. Med. Chem. Lett.* **2013**, 23, 163-168; (c) C. Kar, G. Das, M. D. Adhikari, A. Ramesh, *Inorg. Chem.* **2013**, 52, 743-752.

ORG-P39

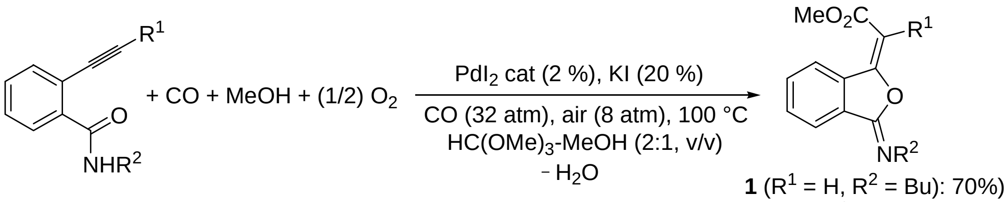
3-(Methoxycarbonylmethylene)-isobenzofuran-1-imines: a New Class of Synthetic Herbicides

Raffaella Mancuso[a], *Fabrizio Araniti*[b], *Ida Ziccarelli*[a], *Francesco Sunseri*[b], *Maria Rosa Abenavoli*[b], *Bartolo Gabriele*[a]

[a] *Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria,*
Via Pietro Bucci, 12/C, 87036 Arcavacata di Rende (CS), Italy
[b] *Dipartimento di AGRARIA, Università Mediterranea di Reggio Calabria, 89124 Reggio Calabria, Italy*

raffaella.mancuso@unical.it

The protection of crops from weeds is a constantly recurring problem in agriculture. To face this problem, many synthetic chemicals have been produced, often characterized by a relatively small number of target sites in plants. This narrow spectrum of activity has resulted in the development of herbicide-resistant weed. To fight evolution of resistance in weeds, multi-mechanism of action for herbicides are highly desirable. We have discovered a novel class of synthetic herbicides, consisting of 3-(methoxycarbonylmethylene)isobenzofuran-1-imines, prepared by palladium-catalyzed oxidative carbonylation of 2-alkynylbenzamides (Equation 1) [1].



(1)

1 (R^1 = H, R^2 = Bu): 70%)
2 (R^1 = R^2 = Ph): 55%

The herbicidal activity has been tested on two particular molecules, that are, (*E*)-methyl 2-[3-(butylimino)isobenzofuran-1(3*H*)-ylidene]acetate (**1**) and (*E*)-methyl 2-phenyl-2-[3-(phenylimino)isobenzofuran-1(3H)-ylidene]acetate (**2**), Both compounds **1** and **2** showed a strong phytotoxicity effect on both the hypogean and epigean parts, while had different effects on root growth. The effects observed on the aerial part were similar for both molecules, and they were probably due to an indirect effect of the alterations observed on root morphology.

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ORG-P40

Orthogonal reactions for the synthesis of new fluorescent bile acid-bisphosphonate conjugates

Chiara Massarenti[a], *Alessandro Massi*[a], *Daniela Perrone*[a], *Anna Zaghi*[a], *Olga Bortolini*[a]

a Dipartimento di Chimica, Università di Ferrara, Via L. Borsari 46 , 44121, Ferrara, Italy

msschr@unife.it

Bisphosphonates (BPs) are widely used to inhibit osteoclastic activity in diseases associated with increased bone resorption, such as osteoporosis, and tumor bone diseases. (1) In a recent work has been reported that chenodeoxycholic-containing hydroxyl-bisphosphonate salt demonstrated a higher activity than neridronate in inhibition of osteoclastogenesis and a higher affinity to HAP. (2) Other works underlined that fluorescent analogues of bisphosphonates are of increasing interest as biological probes exploiting the high bone affinity of these compounds. (3) Following up these considerations, we envisaged the synthesis of new fluorescent bile acid-bisphosphonate conjugates by using a "click chemistry" approach. CA, UDCA, CDCA and LCA scaffolds were functionalized at C-3 with an azide moiety and C-24 with a thiol group. Bisphosphonates, bearing a double or triple bond, were synthetized starting from commercially available tetraethyl methylenediphosphonate and dansyl chloride was functionalized with an alkyne moiety. Finally, modified bile acids, bisphosphonates and fluorescent tag were linked together using “click chemistry” orthogonal reactions such as copper-catalyzed Huisgen cycloaddition, thiol-ene coupling (TEC) and thiol-yne coupling (TYC). Further details about the new fluorescent bile acid-bisphosphonate conjugates will be discussed during presentation.

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ORG-P41

Modification on bile acid scaffold in the identification of FXR and GP-BAR1 modulation

Dario Masullo,[a] *Valentina Sepe,*[a] *Claudio D'Amore,*[b] *Carmen Festa,*[a] *Barbara Renga,*[b] *Simona De Marino*[a] *Angela Zampella,*[a] *Stefano Fiorucci*[b]

a Department of Pharmacy, University of Naples "Federico II", Via D. Montesano, 49, I-80131 Napoli, Italy;
b Department Experimental and Clinical Medicine, University of Perugia, Via Gambuli 1, S. Andrea delle Fratte, 06132 Perugia, Italy;

dario.masullo@unina.it

Bile acids (BAs) are cholesterol metabolites that have been extensively studied in the last ten years. Beside their role in the fat digestion, they acts as signal molecules involved in a lot of physiological functions, through modulation of nuclear and G-protein coupled receptors like FXR and GP-BAR1, respectively.[1] FXR is expressed in liver, intestine, kidney and it's involved in the regulation of BAs biosynthesis by a negative feedback mechanism.[2] FXR is also involved in controlling lipid and glucose homeostasis, via the limitation of triglyceride synthesis and acting on phosphoenolpyruvate carboxykinase and glucose-6-phosphatase levels, respectively.[3,4] GP-BAR1 is a G-protein coupled receptor expressed mostly in the liver, intestine and brown adipose tissue; GP-BAR1 promotes energy expenditure by increasing β-oxidation of fatty acids in brown adipose tissue and skeletal muscle and is also involved in the release of insulin from pancreas.[5] In this research work we decided to manipulate some BAs scaffolds in order to obtain new synthetic derivatives useful in the modulation of FXR and GP-BAR1 functions and therefore in the pharmacotherapy of several human deseases.

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ORG-P42

Sintesi di perilen-diimmidi con catene peptidiche come nuovi ligandi del DNA G-quadruplex

Carmela Miele [a], Alessandro Altieri [a], Armandodoriano Bianco [a], Marco Franceschin[a], Pasqualina Punzi [a], Anita Scipioni [a]

a Dipartimento di Chimica, Sapienza Università di Roma, Piazzale Aldo Moro n°5, 00185, Roma, Italia

carmela-miele@libero.it

Nella progettazione di nuovi farmaci antitumorali, concepiti come inibitori della telomerasi, una strategia largamente seguita consiste nell'indurre il suo substrato, il DNA telomerico, ad assumere una conformazione che non permetta il legame con l'enzima. I risultati migliori si sono ottenuti con molecole in grado di indurre e stabilizzare strutture G-quadruplex. A questa classe di inibitori appartengono composti aventi come caratteristica comune un esteso nucleo aromatico da cui si dipartono catene laterali basiche, cosicché tali molecole interagiscono col DNA sia mediante interazioni di stacking, che per via elettrostatica.[1]

In quest'ottica, sono stati sintetizzati derivati a scheletro perilenico e coronenico,[2] ideali per favorire le interazione di *stacking* con il G-quartet.

In questo lavoro si è provveduto a funzionalizzare l'anidride perilenica con degli amminoacidi in quanto essendo carichi in ambiente fisiologico apportando così una maggiore polarità al *core* perilenico e migliorando la sua solubilità in acqua.

Le catene laterlali scelte sono state progettate mediante *molecoular modelling*, con il quale è stato possibile predire le caratteristiche che i ligandi ipotizzati dovessero avere per interagire al meglio col DNA.

A completamento dello studio condotto in questo lavoro di tesi si prevede sia di verificare la capacità del target ottenuto di interagire con il DNA G-quadruplex, sia di valutarne la selettività nei confronti della quadrupla elica rispetto alle strutture duplex.

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ORG-P43

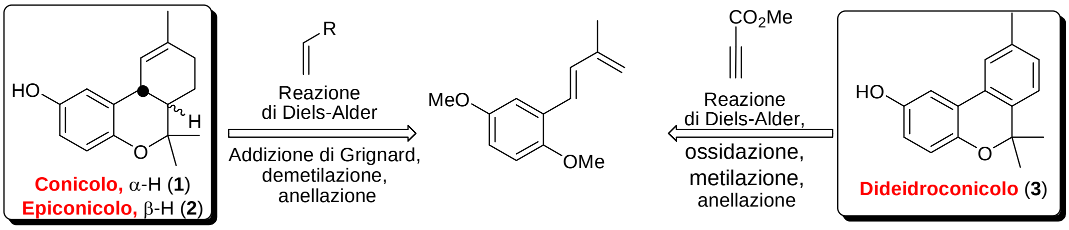
Nuovo Approccio alla Sintesi di Conicoli

Lucio Minuti[a], *Andrea Temperini*[b]

[a]Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia,
Via Elce di Sotto 8, 06123, Perugia, Italia
[b] Dipartimento di Scienze Farmaceutiche, Università di Perugia,
Via del Liceo 1, 06123, Perugia, Italy

lucio.minuti@unipg.it

Recentemente, sono stati isolati da organismi marini il (+)-conicolo (**1**), il (+)-epiconocolo (**2**) e il dideidroconicolo (**3**), i quali hanno mostrato possedere interessanti proprietà biologiche.



Riportiamo qui un approccio efficiente alla sintesi di conicolo (**1**), epiconicolo (**2**) and dideidroconicolo (**3**) basato sulla reazione di Diels-Alder di 1',4'-dimetossi-2'-((E)-3-metilbuta-1,3-dienil)benzene, con metil vinil chetone, metil acrilato o metil propiolato. L'attivazione di queste reazioni con l'alta pressione (9 kbar) o con acidi di Lewis, rende le reazioni altamente efficienti e totalmente regioselettive e *endo*-diastereoselettive. La sintesi del conicolo, epiconicolo and dideidroconicolo è stata quindi realizzata con alte rese a partire dagli appropriati addotti di Diels-Alder. Quanto riportato qui, insieme a quanto da noi prodotto precedentemente sulla sintesi dei Δ^8-*cis*- e Δ^8-*trans*-THCi, Δ^9-*cis*- e Δ^9-*trans*-THCi, e cannabinoli [1-3] rende il nostro approccio sintetico una strategia sintetica efficiente per accedere ad un ampio spettro di molecole farmacologicamente importanti in modo regio- e stereoselettivo.

Si ringrazia la Fondazione Cassa Risparmio Perugia (Progetto 2012.0122.021) e il Ministero dell'Istruzione dell'Università e della Ricerca (MIUR), PRIN 20109Z2XRJ_010.

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ORG-P44

Low Impact Ethereal Solvents in the Synthesis of Acetals

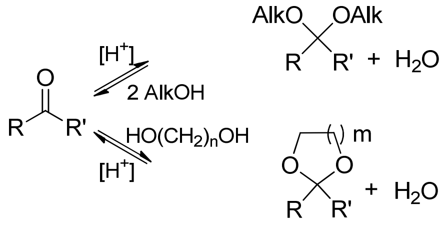
Ugo Azzena, Massimo Carraro, Ashenafi Damtew Mamuye, Ilaria Martinez, Irene Murgia, Luisa Pisano

Department of Chemistry and Pharmacy, University of Sassari, Via Vienna 2 , 07100, Sassari, Italy

irmurgia@uniss.it

Acetals, tipically employed as protecting group[1] for aldehydes and ketones, find employment as intermediates for diols monoprotection[2] as well as substrates in reductive metalation reactions and as fragrances for cosmetics and cleaning agents.

Cyclopentyl methyl ether (CPME)[3,4] and 2-methyltetrahydrofuran (2-MeTHF)[4,5] are benign alternatives to hazardous solvents. Taking into consideration their low miscibility and formation of azeotropes with water, we investigated their employment as solvents in the synthesis of acetals, in the presence of safe acid catalysts,[6] under Dean-Stark reaction conditions.[7]



R = Alkyl, Aryl, H; n = 2,3; m = n-1.

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[7] With the financial support of Regione Autonoma della Sardegna (L. 07/09/2007, CRP-59740).

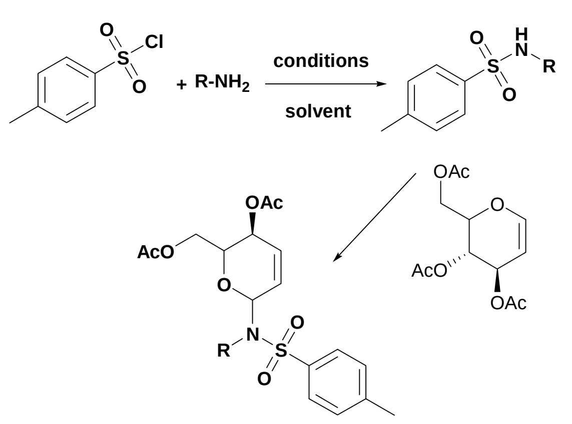
ORG-P45

Eco-friendly protocol for synthesis of sulfonamides and Ferrier azaglycosylation

M. Nardi,[a] *N. Herrera Cano,*[b] *A. De Nino,*[a] *M. Oliverio,*[c] *A. Procopio,*[c] *A. N. Santiago,*[b] *G. Sindona*[a]

a Dipartimento di Chimica, Università della Calabria Cubo 12C, 87036-Arcavacata di Rende (CS), Italia.
b INFIQC, Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria, Córdoba 5000, Argentina.
c Dipartimento di Scienze della Salute, Università Magna Graecia, Viale Europa, 88100-Germaneto (CZ), Italia.

monica.nardi@unical.it



Synthesis one-pot of 2,3-unsaturated-N-pseudoglycals

Sulfonamides continue to play an important role in chemotherapy, despite the abandonment of their use as antibiotics.[1]

An eco-friendly and improved method for the Ferrier sulfonamidoglycosylation of tri-O-acetyl-D-glucal with different N-nucleophiles has been developed using Er(OTf)$_3$ in 2-MeTHF.[2] The conversion of 3,4,6-tri-O-acetyl-D-glucal into 2,3-unsaturated-N-pseudoglycals with sulphonamides previously prepared using the same method as environmentally friendly[2] and the subsequent addition of glucale can be realized in a few minutes with good yields and preferential α-anomeric selectivity.

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ORG-P46

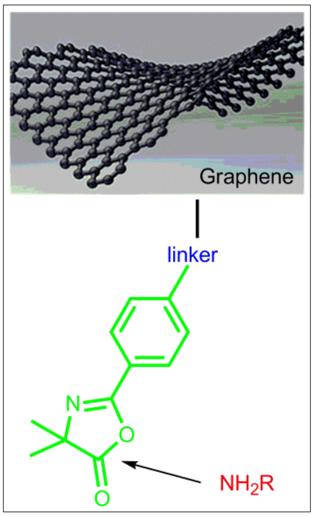
Functionalized Graphene-based materials as nanoplatform for drug delivery

Giulia Neri[a], *Angela Scala*[a], *Anna Piperno*[a], *Giovanni Grassi*[a],

Enza Fazio[b], *Francesco Barreca*[b]

[a] *Dipartimento di Scienze Chimiche, Università di Messina, V.le F. Stagno d'Alcontres 31, 98166, Messina, Italia*
[b] *Dipartimento di Fisica e di Scienze della Terra, Università di Messina, V.le F. Stagno d'Alcontres 31, 98166, Messina, Italia*

nerig@unime.it



The rich reactivity of oxazol-5-(4*H*)-ones enables a wide variety of transformations, which make them useful precursors of amino acids and heterocycles [1]. Recently, we have exploited the oxazolone reactivity to functionalize multiwalled carbon nanotubes by dipolar cycloadditions [2]. As a result of their unique structure and fascinating properties, in recent years graphene and its derivatives have found extensive applications in the biomedical area [3]. Here, we describe an efficient and versatile approach to introduce pendant oxazolone functionalities on graphene surfaces. The functionalized nanomaterials can be exploited as convenient reactive platforms to introduce biological active molecules for biomedical applications. The products have been fully characterized by XPS, UV-vis, FT-IR, Raman, TGA, SEM and AFM measurements.

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ORG-P47

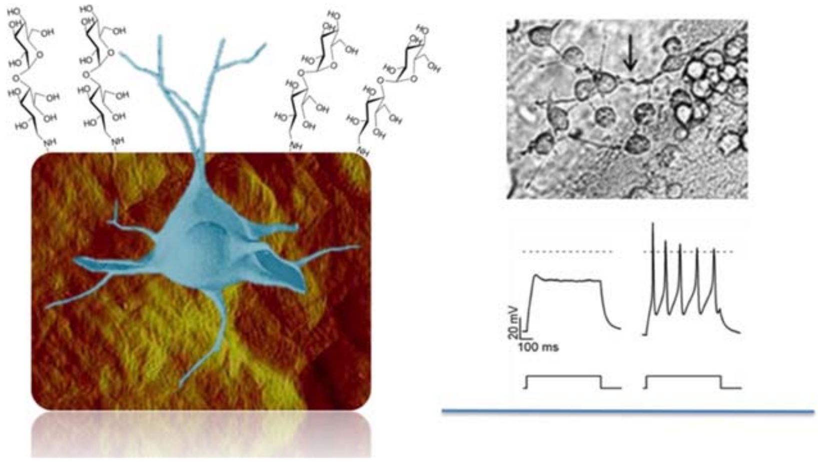
Neoglicosilazione del collagene, sintesi e proprietà biologiche

F. Nicotra[a], *L. Cipolla*[a], *L. Russo*[a], *A. Sgambato*[a], *D. Bini*[a], *C. Battocchio*[b], *G. Polzonetti*[c], *B. Costa*[a], *M. Lecchi*[a]

a Dipartimento di Biotecnologie e Bioscienze, Università degli Studi di Milano-Bicocca, Piazza della Scienza 2 , 20126, Milano, Italia
b Departimento di Scienze, INSTM, CNISM e CISDiC, Università Roma Tre, Via della Vasca Navale 84, 00146 Roma, Italia

francesco.nicotra@unimib.it

In considerazione del ruolo fondamentale esercitato dai carboidrati nei processi di riconoscimento cellulare, abbiamo voluto studiarne l'impatto nello sviluppo di nuovi biomateriali per l'ingegneria tissutale. Il collagene, uno dei materiali più utilizzati in medicina rigenerativa, è stato funzionalizzato in superficie con differenti carboidrati, utilizzando processi chemoselettivi, che non modificassero le sue caratteristiche morfologiche [1]. Test *in vitro e in vivo* hanno mostrato il ruolo dei differenti zuccheri nei processi rigenerativi.



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ORG-P48

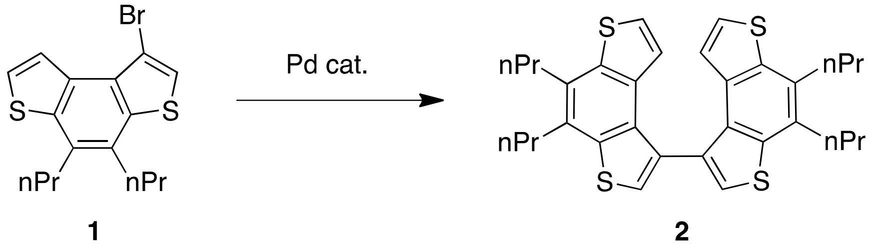
Chiral thiophene-based biaryl systems: synthesis and characterization

Silvia Cauteruccio, Davide Dova, Emanuela Licandro

Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, I-20133, Milano, Italia

silvia.cauteruccio@unimi.it

The biaryl motif occupies an iconic role in chemistry, being a key structural feature of natural products, biologically active molecules, drugs, agrochemicals, and other novel optical and mechanical materials. Furthermore, the stereogenic axes provide rigid molecular frameworks for highly efficient tools in asymmetric synthesis.[1] Exploiting the experience acquired in our laboratories on the synthesis of compounds based on alternating thiophene and benzene rings[2], we have started the study of a simple and efficient synthetic route to prepare bis(benzoditiophenes) system **2**, through Pd-catalysed cross coupling reactions, starting from bromide **1**.



This strategy provides a convenient approach to an interesting class of chiral atropisomeric biaryl derivatives with C_2-symmetry, which are expected to have broad applications in asymmetric reactions, including the enantioselective synthesis of tetrathiahelicene derivatives.

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ORG-P49

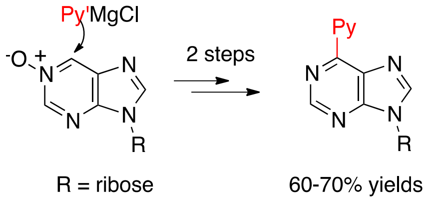
Exploiting the Reactivity of Nebularine N1-Oxide toward Pyridinyl Grignard Reagents

<u>Giorgia Oliviero</u>[a], Stefano D'Errico[a], Nicola Borbone[a], Brunella Pinto[a], Vincenzo Piccialli[b], Fabrizia Nici[a], Luciano Mayol[a] and Gennaro Piccialli[a]

a Dipartimento di Farmacia, Università degli Studi di Napoli 'Federico II', Via D. Montesano, 49, 80131, Napoli, Italy
b Dipartimento di Scienze Chimiche, Università degli Studi di Napoli 'Federico II', Via Cinthia, 21, 80126, Napoli, Italy

golivier@unina.it

The functionalization of the base moiety of nucleosides and nucleotides has always been an important synthetic goal to afford novel tools to be evaluated not only as novel antiviral and anticancer agents but also as probes in synthetic nucleic acids by virtue of their altered base-pairing properties. Recently, we have focused our attention in developing new and more general methods to introduce C-substituents on the C2 and C6 positions of purine nucleosides. On this ground we have reported studies on the reactivity of nebularine N1-oxide demonstrating that its C6(C2)-N1-O$^-$ nitrone moiety can react with Grignard reagents leading to their addition on the C6 or C2 carbons of the purine base [1-3]. Intrigued by the lack of a general synthetic procedure to obtain C6-pyridinyl purine nucleosides, herein we report the first examples of addition to nebularine N1-oxide of pyridinyl Grignard reagents, the last obtained *via* bromine-magnesium exchange between bromopyridines and ^{i}PrMgCl.



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ORG-P50

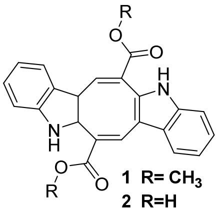
Metaboliti di *Caulerpa racemosa* (Forsk.) J. Agarth, alga invasiva dell'Arcipleago di La Maddalena

A.Bianco[a], M. Ballero[b], Y. Donno[c], L.Ornano[a,b], C. Sanna[b]

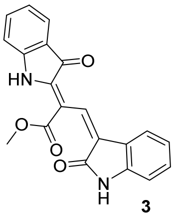
[a] Dipartimento di Chimica, "Sapienza" Università di Roma
[b] Consorzio CoSMeSe, Università di Cagliari
[c] Parco Nazionale, Arcipelago di La Maddalena, La Maddalena (OT).

luigi.ornano@uniroma1.it

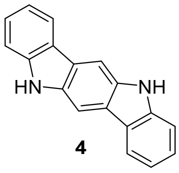
La *Caulerpa racemosa* (Forsk.) J. Agarth, è un'alga alloctona del mar Mediterraneo, la quale insieme con la *Caulerpa taxifolia* (Vahl) C. Agarth sta minacciando le prateria di *Posidonia oceanica* L. Delile. Il presente lavoro riguarda l'analisi fitochimica di un campione di *C. racemosa* raccolta nell'Arcipelago di La Maddalena. Nel presente lavoro sono stati isolati la caulerpina (**1**), l'acido caulerpico (**2**), la racemosina A (**3**) e l'ancorinazolo (**4**) che presentano il nucleo bis indolico. Sono stati isolati due caulerpreniloli: caulerpale A e B (**5**,**6**); i quali contengono un nucleo indanico e presentano attività antiproliferativa [1-2]. Inoltre è stato isolato il derivato sesquiterpenoide (**7**) in cui è presente la funzione enol-acetica [3] tale metabolita non è mai stato riportato per il genere C. racemosa, ed è fino ad ora, il composto **7** è stato isolato solo in un campione di *C. ashmeadii* raccolta nell'Oceano Indiano.



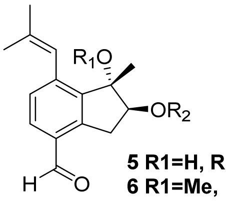
1 R= CH_3
2 R=H



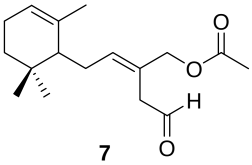
3



4



5 R1=H, R2=Ac
6 R1=Me, R2= H



7

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ORG-P51

Frazione triterpenoide di *Olea europea* var. *oleaster* (Hoffmanns. & Link) dell'aerale Sardo

A. Bianco[a], M. Ballero[b], F. Bonina[c], L. Ornano[a,b]

[a] Università di Roma "La Sapienza", Dipartimento di Chimica
[b] Consorzio CoSMeSe, Università di Cagliari.
c Dipartimento di Scienze Farmaceutiche, Università di Catania

luigi.ornano@uniroma1.it

Olea europaea var. *oleaster* è un albero sempreverde, originario dell'area mediterranea. In Sardegna *O. europaea* è particolarmente diffuso, la sua particolare densità ha dato il nome all'Ogliastra, una regione a sud-est dell'isola. Dal punto di vista fitochimico, *O. eur*opaea è una fonte di molti importanti composti naturali. La frazione non polare contiene una grande quantità di triterpenoidi, fra cui il principale è l'acido oleanolico[1]. Recentemente, particolare attenzione è stata rivolta a questa classe di composti, specialmente da un punto di vista farmacologico, dato che a tali metaboliti sono riconosciute attualmente attività anti-HIV, anti-infiammatoria, anti-tumorale[2-4].

L'obbiettivo del lavoro svolto è stato l'analisi fitochimica preliminare di due campioni wild type di *Olea europaea* var. *oleaster* provenienti dall'Arcipelago di La Maddalena (costa nord) e da Galtellì (centro-est). Tale analisi è stata eseguita mediante un approccio metabolomico ottenuto mediante analisi dei fingerprints ^{1}D-^{1}H-NMR ed ESI-MS. Il fingerprint del campione di *O. europaea* proveniente dall'isola di La Maddalena mostra l'idrossitirosolo-1'β–glucoside, cornoside, e l'oloeuropeina. Inoltre è presente una miscela di flavonoidi glicosilati in 3, 5 e in 7 dell'anello A del nucleo flavonoidico assieme a triterpenoidi quali acido oleanolico e acido botulinico in miscela con i loro derivati ossigenati in C-12 e C-19. Il fingerprint del campione di *O. europaea* proveniente da Galtellì, risulta invece nettamente differente presentando solo il fingerprint dei triterpenoidi pentaciciclici.

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ORG-P52

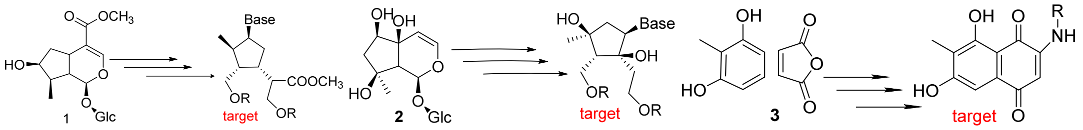
Iridoidi e Rifamicine come substrati per la sintesi di nuovi antivirali

A.Bianco[a,b], *M. Ballero*[b], *L.Ornano*[a,b], *C. Sanna*[b]

[a)]*Chimica, "Sapienza" Università di Roma, P.le A.Moro, 5, 00185 Roma*
[b)]*Co.S.Me.Se. Università di Cagliari.*

luigi.ornano@uniroma1.it

Il presente lavoro riguarda la progettazione e la sintesi di inibitori della trascrittasi inversa del virus HIV. I target di sintesi sono analoghi nucleosidici carbocicliclici e analoghi del nucleo cromoforico della rifamicina, quali inibitori competitivi e non competitivi per la RT del virus dell' HIV [1-3]. Gli iridoidi sono caratterizzati dalla presenza di un nucleo ciclopentanico variamente funzionalizzato ed enantiomericamente puro; in particolare la loganina (**1**) e l'harpagide (**2**) e costituiscono i chiral template in quanto presentano la funzione ossidrilica nella idonea posizione per l'accoppiamento con la base azotata. In tale lavoro, si è eseguita la modificazione chimica di tali iridoidi glucosidici al fine di ottenere due nuovi analoghi nucleosidici carbociclici, i quali saranno oggetto di studi di correlazione-attività con l'enzima (RT).



La rifamicina SV è un antibiotico costituito da un'ansa alifatica e da un nucleo aromatico al quale è attribuita l'attività antivirale. Il nucleo cromoforico della rifamicina agisce come inibitore non competitivo contro l'enzima RT, in quanto produce una modulazione allosterica secondaria in siti specifici. L'obbiettivo di tale lavoro è effettuare la sintesi parziale di analoghi strutturali delnucleo naftochinonico e di valutare la modulazione di tale attività antivirale.

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ORG-P53

β-Nitroacrylates: key starting materials for the synthesis of polysubstituted pyrroles

Alessandro Palmieri[a], *Roberto Ballini*[a], *Giovanna Bosica*[b], *Serena Gabrielli*[a]

a School of Science and Technology, Chemistry Divisioni
University of Camerino, Via S. Agostino n.1, 62032 Camerino (MC), Italy.
b Department of Chemistry, University of Malta, Msida, MSD2080, Malta.

alessandro.palmieri@unicam.it

β-Nitroacrylates are an emerging class of electron-poor alkenes having two electron-withdrawing groups in α- and β-positions (Figure 1).[1] The simultaneous presence of both functionalities makes these compounds extremely interesting from reactivity point of view. In this context, β-nitroacrylates have been used as key starting materials for the preparation of important fine chemicals and in particular for the heterocyclic ones.[2] Following these studies, we developed an alternative one-pot way to obtain 2,5-disubstituited pyrroles starting from β-nitroacrylates and aliphatic or aromatic primary amines under heterogeneous conditions (Scheme 1).

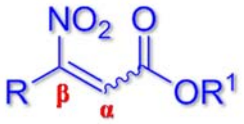
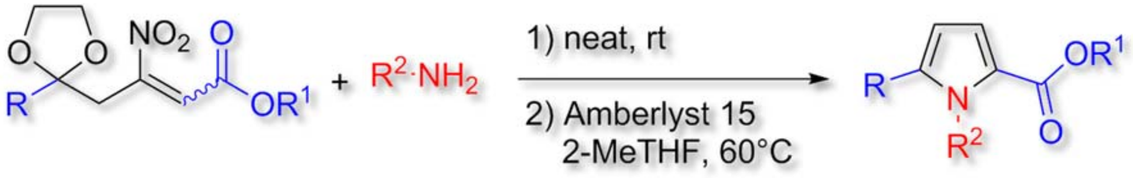


Figure 1.



Scheme 1.

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ORG-P54

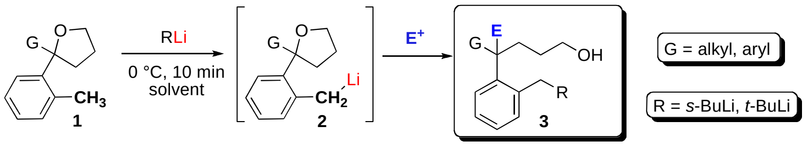
Base-promoted Tetrahydrofuran Ring Opening: Synthesis of Chiral Alcohols

Francesca C. Sassone, Filippo Maria Perna, Antonio Salomone, Saverio Florio, Vito Capriati

Dipartimento di Farmacia-Scienze del Farmaco, Università di Bari "Aldo Moro",
Consorzio C.I.N.M.P.I.S., Via E. Orabona,4 I-70125, Bari, Italy

sassonefrancesca@gmail.com

Among saturated oxygen heterocycles, substituted tetrahydrofuran (THF) derivatives are important scaffold encountered in many synthetic and natural products with wide-ranging biological activity.[1] Their lack of reactivity, however, has discouraged their use as starting material in organic synthesis.[2] We have recently observed that the THF moiety can act as an effective direct metalation group, thereby efficiently promoting an *ortho*-lithiation reaction in the presence of *t*-BuLi.[3] In the course of such an investigation we noticed that the *ortho*-tolyl THF derivative **1** undergoes a lateral lithiation, instead, upon treatment with *t*-BuLi. The putative intermediate **2**, in turn, triggers an unprecedented cascade ring opening reaction ending up with the formation of a chiral functionalized alcohol (**3**) with a quaternary stereogenic center upon the reaction with an electrophile.



In the present communication, the scope of such a reaction will be discussed in terms of both the nature of the base and the electrophile, and a possible mechanism proposed for potential application in organic synthesis.

Acknowledgments: Programma Operativo Nazionale Ricerca e Competitività 2007-2013 (PON01_00862).

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ORG-P55

Two-step synthesis of 2,5-disubstituted pyrroles from α-amidosulfones

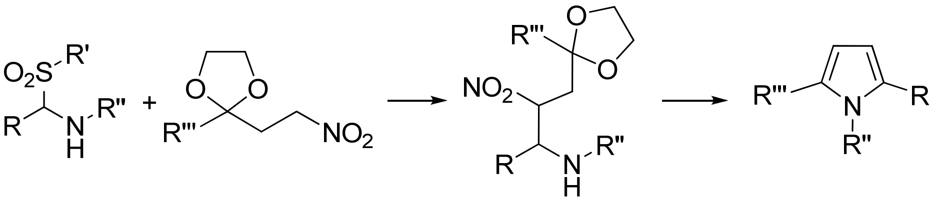
Alessandro Palmieri[a], Roberto Ballini[a], Serena Gabrielli[a], Marino Petrini[a]

a School of Science and Technology, Chemistry Divisioni
University of Camerino, Via S. Agostino n.1, 62032 Camerino (MC), Italy.

alessandro.palmieri@unicam.it

The pyrrole moiety is found in a large number of naturally occurring molecules that are of biological importance such as haem, vitamin B122 and chlorophyll as well as in melanin pigments. In addition, many important pharmaceutical compounds, such as atorvastatin (Lipitor, anti-cholesterol), sunitinib (anti-tumour), etorolac (analgesic) and tolmetin (arthritis) include pyrrole units. The electronic properties of pyrrole are important in the context of conducting polymers, where poly pyrroles have found many useful applications.[1]

In this context, we developed an alternative way to obtain 2,5-disubstituited pyrroles exploiting the reaction between α-amido sulfones, valuable precursors of *N*-acylimines,[2] and γ-protected nitro ketones,[3] which have already been demonstrated to be important building blocks in organic synthesis (Scheme 1).



Scheme 1.

[1] (a) I.S. Young, P.D. Thornton, A. Thompson *Nat. Prod, Rep.* 2010, **27**, 1801-1839. (b) H. Fan, J. Peng, M. T. Hamann, J.-F. Hu *Chem. Rev.* 2008, **108**, 264-287.
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ORG-P56

Synthesis of Enantiopure Sugar-Decorated Triptycene Derivatives

Teresa Papalia[a], Paola Bonaccorsi[b], Anna Barattucci[b], Lucio Minuti[c], Andrea Temperini[d], Carlo Siciliano[e], Maria Luisa Di Gioia[e] and Antonella Leggio[e] .

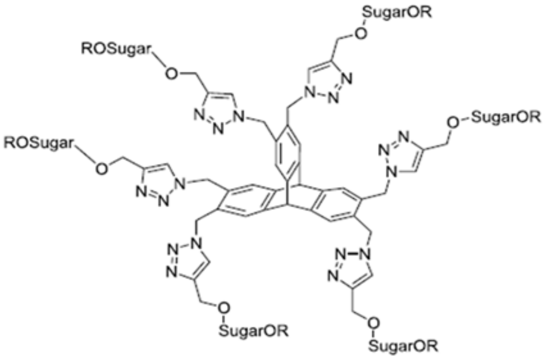
a Dipartimento di Scienze del Farmaco e dei Prodotti per la Salute, Univ. di Messina, Villaggio SS. Annunziata, 98166, Messina, Italy
b Dipartimento di Scienze Chimiche, Univ. di Messina, Viale F. Stagno D'Alcontres 31, 98166, Messina, Italy
c Dipartimento di Chimica, Univ. di Perugia, Via Elce di Sotto 8, 06123, Perugia, Italy
d Dipartimento di Chimica e Tecnologia del Farmaco, Univ. di Perugia, via del Liceo 1, 06123, Perugia, Italy
e Dipartimento di Farmacia e Scienze della Salute e della Nutrizione, Univ. della Calabria, Edificio Polifunzionale, 87030, Arcavacata di Rende, Italy

tpapalia@unime.it

The efficient construction of molecular systems bearing multiple carbohydrate appendages has become a necessary tool in glycobiology and glycomic fields.[1]

The general prototype of a glycoconjugate comprises a core molecule serving as an oligovalent scaffold, a number of sugar moieties and suitable spacers to link the sugar moieties to the central core. In particular, the geometric features of triptycene with a D_{3h} symmetry proved to be very interesting and its derivatives have been used as building blocks for the synthesis of new host molecules in host-guest chemistry and investigated for potential applications in molecular recognition and assemblies, showing powerful complexation abilities toward different kinds of organic guest.[2]

In this communication, our attention will be focused on the accomplishment of a synthetic pathway based on the efficient azide/alkyne 1,3-dipolar cycloaddition for obtaining molecules showing a rigid lipophilic core represented by the triptycene skeleton that is linked, by the arene rings, to six sugar moieties, through six triazole units as spacers (shown in figure).[3]



The preliminary biological results obtained for the six-armed sugar-decorated triptycene derivatives will be discussed.

[1] J. J. Lundquist and E. J. Toone *Chem. Rev.*, 2002, **102**, 555-578.
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ORG-P57

Solvent-free additions of acetacetates to fluorinated imines

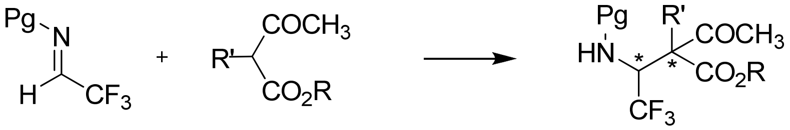
Lucio Pellacani, Stefania Fioravanti, Laura Trulli

Dipartimento di Chimica, Università "La Sapienza", P.le Aldo Moro 5, 00185, Roma

lucio.pellacani@uniroma1.it

Although the reactivity of methylene active compounds is well known, very few examples of addition reaction of these compounds to imines, to form highly functionalized compounds, are known [1].

We report here our results aimed at obtaining fluorinated dicarbonyl nitrogenated compounds, characterized by the presence of two adjacent stereocenters. Suitable reaction conditions were chosen to increase the yields as well as to approach green chemistry (solvent-free), according to our recent findings in the field [2].



These highly functionalized molecules can be considered new building blocks in the synthesis of different fluorinated organic compounds whose importance in the field of bio-organic, pharmaceutical, and medicinal chemistry, is well demonstrated especially for the influence of fluorine atoms [3], whose presence often causes profound changes in the physical and chemical properties of organic molecules giving them a special biological interest [4].

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ORG-P58

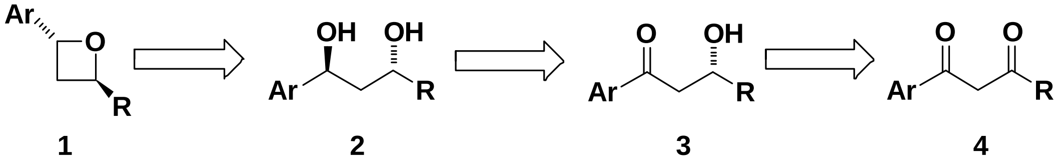
A Chemo-Enzymatic Approach to the Synthesis of Optically Active 2,4-Disubstituted Aryloxetanes

Paola Vitale, Filippo Maria Perna, Vito Capriati

Dipartimento di Farmacia-Scienze del Farmaco, Università di Bari "Aldo Moro",
Consorzio C.I.N.M.P.I.S., Via E. Orabona,4 I-70125, Bari, Italy

filippo.perna@uniba.it

Functionalized oxetanes have been recently highlighted as desirable low molecular weight motifs for drug discovery and also as useful building blocks in preparative chemistry for the synthesis of drugs, materials, and agrochemicals [1]. The synthesis of oxetanes, however, still remains a challenging task. In this communication we report preliminary results of the first chemo-enzymatic synthesis of optically active 2,4-disubstituted oxetanes **1**, prepared by cyclization of optically active 1,3-diols **2** [2], in turn obtained by stereoselective reduction of the corresponding 1,3-diketones **4** with yeasts.



The stereoselective reduction of both symmetrically and non-symmetrically-disubstituted 1,3-diketones was investigated in detail in the presence of conventional and non-conventional yeast strains (e.g., *Saccharomyces cerevisiae*, *Kluyveromyces marxianus*, *Baker's yeast*). Optically active aldols **3** were obtained with high stereopreference employing the baker's yeast reduction as a key step, and were then converted into diols **2** (dr >95%, ee up to 80%), and finally cyclized into the corresponding 2,4-disubstituted oxetanes **1** in good yields.

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ORG-P59

A Simple Synthesis of Imides Promoted by Acyl Palladium Species

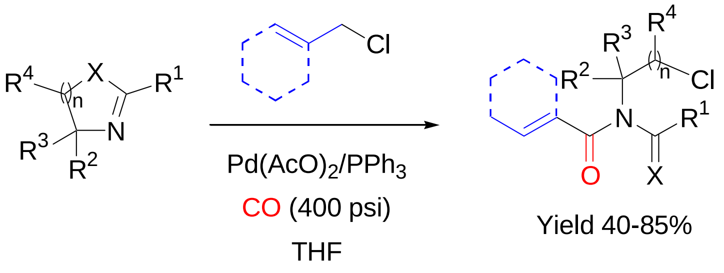
Serena Perrone[a], *Giuseppe Cannazza*[b], *Antonio Caroli*[a, d], *Antonio Salomone*[c, d] *and Luigino Troisi*[a]

a Dipartimento di Scienze e Tecnologie Biologiche ed Ambientali, Università del Salento,via Prov.le Lecce-Monteroni, Lecce 73100, Italy
b Dipartimento di Scienze della Vita, Università degli Studi di Modena e Reggio Emilia, via Università 4, Modena 41121, Italy
c Dipartimento di Farmacia-Scienze del Farmaco, Università degli Studi di Bari "Aldo Moro", Via E. Orabona 4, Bari 70125, Italy
d Consorzio Interuniversitario Nazionale Metodologie e Processi Innovativi di Sintesi (C.I.N.M.P.I.S.), Via E. Orabona 4, Bari 70125, Italy

serena.perrone@unisalento.it

In this work the reactivity of various heterocycles containing a C–N double bond, towards acyl palladium species, generated *in situ* from allyl or benzyl halides and CO, was investigated. Cycles featuring a C–N double bond conjugated to an additional heteroatom (O or N), showed a ring opening reaction leading to functionalized imides with high structural diversity (Figure).[1] On the contrary, cyclic imines such as 2-methyl-2-pyrroline reacted with acyl-palladium intermediates to give bicyclic *β*-lactams.[2]
Such methodology represents a simple and direct way to prepare structurally complex imides. Moreover, a reaction mechanism, involving cationic intermediates, was proposed.

n = 1,2
X = O, NMe
R^1-R^4 = H, Alkyl, Ph



Figure

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ORG-P60

Composti curcumin-like come agenti neuro-protettori. Interazione con HSP60[†]

V. Giacalone[a], *A. Marino Gammazza[a, b], C. Campanella[b, c], S. Buscemi[a], C. Caruso Bavisotto[c], F. Cappello[b c], A. Palumbo Piccionello[a,b]*

a Dipartimento STEBICEF, Università di Palermo, Viale delle Scienze Ed.17, 90128, Palermo, Italia.
b Istituto Euro-mediterraneo di Scienza e Tecnologia IEMEST, Via E. Amari 123, 90139, Palermo, Italia.
c Dipartimento BIONEC, Università di Palermo, Via del Vespro, 90128, Palermo Italia.

valentina.giacalone03@unipa.it

La Malattia di Alzheimer rappresenta una sfida fondamentale del XXI secolo per la salute pubblica. Le terapie attualmente utilizzate per la cura dell'Alzheimer si basano sugli aspetti sintomatici della patologia [1]. Un importante ruolo nella malattia è rivestito dalle Heat shock proteins (HSPs), proteine che presiedono al controllo del ripiegamento proteico [2]. Recentemente, è stato dimostrato che HSP60 media la traslocazione del Precursore della Proteina Amiloide (APP) e del Peptide Beta Amiloide (Aβ) nei mitocondri, portando alla perdita della funzionalità dell'organulo [3]. Nel campo degli approcci delle terapie potenziali, la curcumina sta emergendo come lead compound per lo sviluppo di farmaci neuro-protettivi [4]. Qui presenteremo i nostri recenti studi sull'effetto della curcumina e di composti curcumin-like su un modello *in vitro* di cellule neuronali. In particolare, verranno presentati i risultati relativi alla sintesi di alcuni composti curcumin-like e all'abilità di interferire sull'espressione di HSP60.

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†"FIRB-Futuro in Ricerca 2012" Program- project RBFR12SIPT. Financial support from the Italian MIUR.

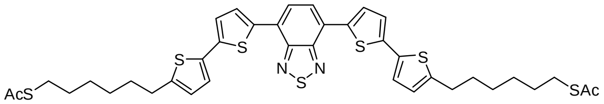
ORG-P61

Influence of chemical functionalization on additives performances in ternary blend P3HT:PCBM polymer solar cells

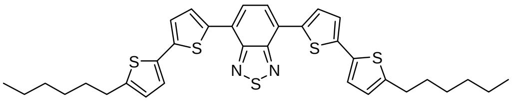
Angela Punzi[a], Alessandra Operamolla[a], Cristina Romita[a], Aurora Rizzo[b], Anna Loiudice[b], Omar Hassan Omar[c], Giuseppe Gigli[b,d], Gianluca M. Farinola[a]

a Dipartimento di Chimica, Università di Bari, Via Orabona 4, 70126, Bari, Italy
b CNR Istituto di Nanoscienze, NNL-Nano, ViaArnesano 16 , 73100, Lecce, Italy
c CNR-ICCOM Istituto di Chimica dei Composti Organometallici, Via Orabona 4, 70126, Bari, Italy
d Dipartimento di Ingegneria dell'Innovazione, Università del Salento, Via per Monteroni , 73100, Lecce, Italy

angela.punzi@uniba.it



4T1BSAc



4T1B

A novel thiophene-benzothiadiazole-based small molecule with peripheral thioacetyl groups (**4T1BSAc**) and its *n*-hexyl-terminated analogue (**4T1B**) were easily synthesized by palladium-catalyzed Suzuki-Miyaura coupling reaction. Both molecules are able to generate cascaded energy levels in P3HT/PCBM blends and to increase order within the P3HT domains resulting in a remarkable improvement in the short circuit current density (J_{sc}) and, in turn, in a higher power conversion efficiency with respect to the pristine P3TH:PCBM device. The devices incorporating 10wt% of **4T1BSAc** or 5wt% of **4T1B** exhibited 3.7% and 3.6% as highest efficiencies, respectively, representing more than a 20% increase compared to the reference P3HT:PCBM cell without additive (η = 2.9%). The difference in optimal loading can be attributed to a better solution processability of **4T1BSAc** conferred by peripheral thioacetyl groups.

ORG-P62

PdI_2-Catalyzed Double Carbonylation of Amines in Ionic Liquids: A Recyclable Synthesis of Oxamides

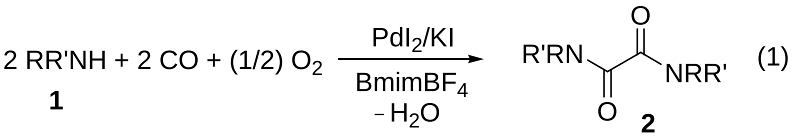
Raffaella Mancuso, Dnyaneshwar Raut, Bartolo Gabriele

Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria,
via Pietro Bucci 12/C, 87036 Rende, Italy

dsraut47@gmail.com

Oxamides are important carbonylated derivatives, used as intermediates in organic synthesis and in coordination chemistry as bidentate ligands. Moreover, their biological significance as anticancer agent and HIV protease inhibitors has been demonstrated [1].

A particularly attractive approach to oxamides is represented by the direct oxidative double carbonylation of amines [2]. Here We report a recyclable version of this kind of approach, based on the use of the PdI_2-KI catalytic system [3] in an ionic liquid as the reaction medium (eq. 1). Working at 100 °C and under 20 atm of a 4:1 mixture of CO-air for 24 h, in the presence of 1 mol% of PdI_2 in conjunction with 10 mol % of KI, oxamides **2** were obtained in excellent yields (90-95%). The catalyst and the ionic liquid medium could be recycled up to six times without appreciable loss of activity and selectivity.



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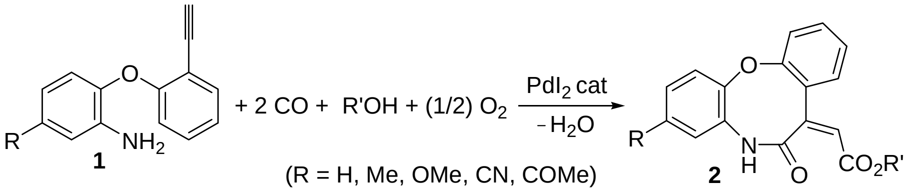
ORG-P63

A Novel Carbonylative Approach to 12-Oxa-5-azadibenzo[*a*,*d*]cycloocten-6-one Derivatives

Raffaella Mancuso, Dnyaneshwar Raut, Donatella Armentano, Bartolo Gabriele
Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, via Pietro Bucci 12/C, 87036 Rende, Italy

dsraut47@gmail.com

The PdI_2-catalyzed carbonylative synthesis of 12-oxa-5-azadibenzo[*a*,*d*]cycloocten-6-one derivatives **2** starting from substituted 2-(2-ethynylphenoxy)anilines **1** is reported. Under suitable oxidative carbonylation conditions, in the presence of the PdI_2/KI catalytic system [1], substrates **1** undergo a cyclocarbonylation process, with closure of an 8-member ring, followed by alkoxycarbonylation to give the final product (Eq. 1). The structure of products **2** has been confirmed by X-ray crystallographic analysis.



(1)

Reactions are carried out in alcoholic solvents (R'OH, R = Me, Et) under relatively mild conditions (at 100°C and 40 atm of a 4:1 mixture of CO-air for 24 h), using 2 mol% of PdI_2, in conjunction with 20 mol % of KI, to give **2** in moderately good yields (50-55%).

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ORG-P64

Flash oral communication FO5

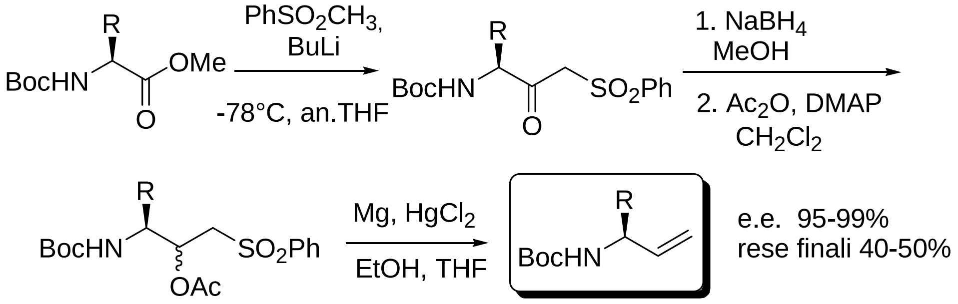
Sintesi di allilammine chirali da α-aminoacidi naturali

Giorgia Regini, Fabio Benedetti, Fulvia Felluga, Lidia Fanfoni,

Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Trieste,
Via L.Giorgieri,1 34127, Trieste, Italia

ffelluga@units.it

Le allilammine α-chirali sono importanti building blocks per la sintesi di composti otticamente attivi. Attraverso reazioni di metatesi si possono ad esempio ottenere 1,4 diamminoalcheni, utilizzati come precursori di isosteri dipeptidici. Questi costituiscono il "core" di inibitori della HIV-proteasi, una proteasi aspartica implicata nella replicazione e maturazione del virus HIV, e pertanto bersaglio di molte terapie anti-AIDS. Nell'ambito di un lavoro di ricerca mirato alla sintesi di isosteri dipeptidici, abbiamo messo a punto una nuova sintesi di allilammine chirali a partire da L-aminoacidi. Questa sintesi, basata su una rivisitazione della reazione di Julia, consente di conservare la purezza ottica originale dell'amminoacido grazie all'utilizzo di L-amminoesteri N-Boc protetti come substrati, configurazionalmente più stabili rispetto alle amminoaldeidi normalmente utilizzate in questo tipo di olefinazione.
A partire da Ala, Phe, Tyr, Pro, Leu, Ileu, Val, si ottengono i prodotti finali con eccessi enantiomerici eccellenti e buone rese.



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ORG-P65

Sintesi di derivati ortogonalmente protetti dell'acido 2,3-diamminopropionico

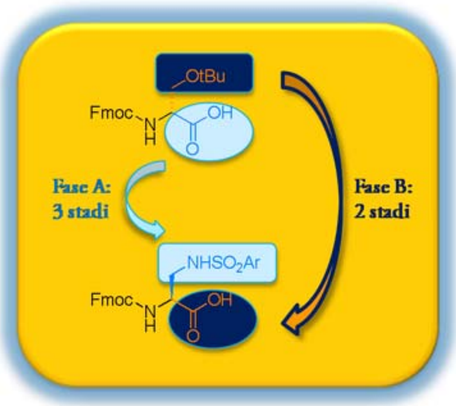
Maria Luisa Di Gioia, Antonella Leggio, Angelo Liguori,

Emanuela Romio, Carlo Siciliano, Marta Tomaselli

Dipartimento di Farmacia e Scienze della Salute e della Nutrizione,
Università della Calabria
Edificio Polifunzionale, 87030 Arcavacata di Rende (CS), Italia

romio.emanuela@yahoo.it

L'acido 2,3-diamminopropionico (DAP) è presente in un numero elevato di sostanze naturali caratterizzate da strutture molecolari di natura peptidica o peptidomimetica e da potenti attività antibiotiche ed inibitorie di metalloproteasi [1]. Molte procedure sintetiche del DAP già apparse in letteratura presentano evidenti limitazioni quali la frequente inaccessibilità dei materiali di partenza, la difficoltà di elaborazione del carbonio chirale e la sua tendenza alla racemizzazione, la purificazione degli intermedi e del prodotto finale [2].



Si presenta qui una strategia multistadio per la preparazione di derivati protetti del DAP basata sull'impiego di precursori serinici commercialmente disponibili ed ortogonalmente protetti (Figura). I passaggi chiave per la costruzione dello scheletro del DAP sono la trasformazione del gruppo carbossilico del precursore serinico via amminazione riduttiva del corrispondente serinale, assistita da specie di Ti(IV), con ammine contenenti gruppi protettori di natura solfonica (Fase A: 3 stadi) e l'ossidazione mediata da TEMPO del residuo alcolico primario serinico (Fase B: 2 stadi). Il recupero e la purificazione degli intermedi sono agevoli, mentre rese totali elevate in prodotto finale accompagnano la completa preservazione della configurazione del carbonio chirale.

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ORG-P66

N-metilazione di esteri metilici di α-amminoacidi protetti sulla funzione amminica con il gruppo 9-fluorenilmetansolfonile (Fms)

Emanuela Romio, Danila Alò, Emilia Lucia Belsito, Maria Luisa Di Gioia, Antonella Leggio, Angelo Liguori e Carlo Siciliano.

Dipartimento di Farmacia e Scienze della Salute e della Nutrizione, Università della Calabria, Edificio Polifunzionale, 87036 Arcavacata di Rende (CS), Italia

romio.emanuela@yahoo.it

Negli ultimi anni l'interesse verso la sintesi di peptidi modificati è notevolmente aumentato in quanto essi trovano larga applicazione come farmaci nei confronti di diversi tipi di patologie. In particolare la *N*-metilazione di amminoacidi e peptidi è stata molto utilizzata al fine di ottenere peptidi modificati con una maggiore potenza e selettività di azione.[1]

Di recente è stato proposto l'utilizzo del diazometano quale agente metilante della funzione amminica di *N*-nosil-α-amminoacidi per l'ottenimento di *N*-metil-α-amminoacidi e *N*-metilpeptidi.[2]

Esteri metilici di α-amminoacidi otticamente attivi protetti sulla funzione amminica con il gruppo 9-fluorenilmetansolfonile (Fms)[3] sono stati metilati utilizzando come agente metilante una soluzione di diazometano in presenza di tricloruro di alluminio. La protezione della funzione amminica con il gruppo 9-fluorenilmetansolfonile ha consentito non solo di metilare facilmente l'atomo di azoto solfonammidico ma anche di ottenere agevolmente, mediante reazione di deprotezione con ammine secondarie, gli esteri metilici di *N*-metil-α-amminoacidi. Questi ultimi costituiscono utili "building blocks" per l'ottenimento di peptidi *N*-metilati nella sintesi peptidica basata sulla strategia Fmoc. Sono stati inoltre sintetizzati idonei sistemi dipeptidici modello per escludere processi di racemizzazione durante l'intero processo sintetico.

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ORG-P67

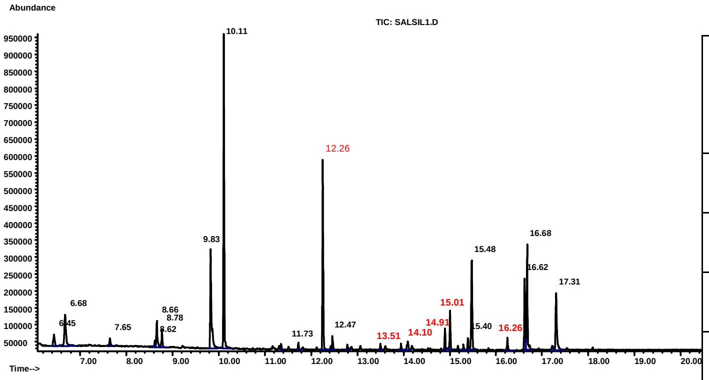
I polifenoli del vino rosso nei salumi calabresi

<u>Emanuela Romio</u>, Emilia Belsito, Maria Luisa Di Gioia, Antonella Leggio, Angelo Liguori, Carlo Siciliano

Dipartimento di Farmacia e Scienze della Salute e della Nutrizione, Università della Calabria, Edificio Polifunzionale, 87036 Arcavacata di Rende (CS), Italia

romio.emanuela@yahoo.it

Nella tradizione calabrese il vino veniva spesso aggiunto alla carne nella preparazione dei salumi al fine di ottenere un prodotto con aumentate valenze organolettiche ed un aroma ben definito. L'aggiunta di vino costituiva per la matrice carne un arricchimento nelle componenti caratteristiche del vino e in particolar modo di sostanze polifenoliche di cui il vino è ricco. Il presente lavoro elabora questa idea e la approfondisce andando a verificare la possibilità di creare nuovi alimenti funzionali quali i salumi addizionati di polifenoli, componenti utili per i loro effetti positivi sulla salute, cioè nel ruolo preventivo verso una serie di patologie legate allo stress ossidativo quali quelle cardiovascolari e neurodegenerative.[1] I salumi addizionati di polifenoli sono stati, in una prima fase, testati per la determinazione dei polifenoli totali con il saggio di Folin-Ciocalteu. In un secondo momento sono stati identificati e misurati i singoli polifenoli utilizzando una tecnica di estrazione SPE abbinata alla analisi mediante GC/MS.



Polifenolo	**T.r.(min.)**	**Concentrazione (mg/g)**
Tirosolo	**12.25**	**0.00194**
Idrossitirosolo	**13.51**	**0.00023**
Acido protocatecuico	**14.10**	**0.00051**
Acido gallico	**14.90**	**0.00095**
Etilgallato	**15.01**	**0.00142**
Acido caffeico	**16.25**	**0.00072**

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ORG-P68

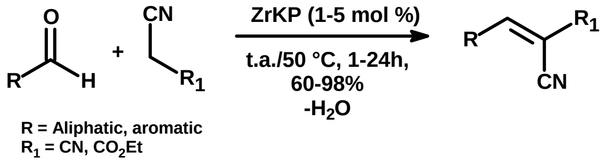
Potassium Exchanged Zirconium Phosphonates as Heterogeneous Catalyst in Knoevenagel Condensation

Ornelio Rosati[a], *Oriana Piermatti*[b], *Raffaella Scavo*[a], *Ferdinando Pizzo*[b], *Massimo Curini*[a]

a Dipartimento di Scienze Farmaceutiche, Università di Perugia, Via del Liceo 1, 06123, Perugia, Italy
b Dipartimento di Chimica, Università di Perugia, Via , 06123, Perugia, Italy

ornelio.rosati@unipg.it

Acid zirconium phosphates and phosphonates [$Zr(HPO_4)_x(RPO_3)_{2-x}$] are solid compounds with important catalytic activity.[1] When exchanged with potassium, zirconium phosphates and phosphonates with weak basic property can be obtained. $Zr(KPO_4)_2$ is the first of this class of compounds and resulted a good catalyst in Knoevenagel condensation.[2] In order to verify the effect of organic substituents on the catalytic efficiency, three different basic zirconium phosphonates [$Zr(KPO_4)_{0.85}(MePO_3)_{1.15}$, $Zr(KPO_4)_{0.76}(PhPO_3)_{1.24}$ and $Zr(KPO_4)_{0.45}(MePO_3)_{0.75}(PhPO_3)_{0.80}$], named ZrKPs for short, were prepared and compared to the catalytic activity of $Zr(KPO_4)_2$ in the Knoevenagel condensation (Scheme 1) in neat and at room temperature.



Scheme 1

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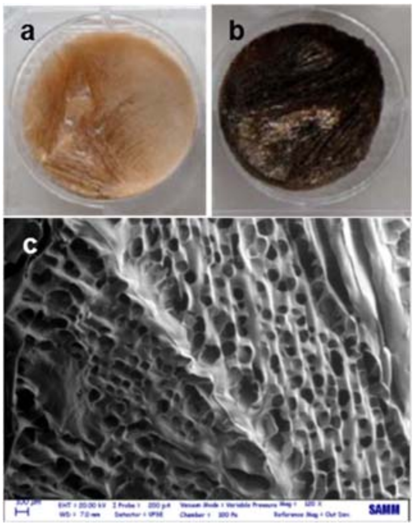
ORG-P69

Melanin-coating as a versatile entry to functionalized cellulose aerogels: synthesis, structure, properties

Bianca Rossi[a], *Lucio Melone*[a], *Carlo Punta*[a], *Lucia Panzella,*[b] *Alessandro Pezzella*[b], *Marco d'Ischia*[b],

a Dipartimento di Chimica, Materiali, Ingegneria Chimica "Giulio Natta", Politecnico di Milano, P.zza Leonardo da Vinci, 20133, Milano, Italy
b Dipartimento di Scienze Chimiche, Università di Napoli Federico II, Via Cintia 4, 80126, Napoli, Italy

bianca.rossi@polimi.it



A two-step approach consisting of the NaClO/TEMPO mediated oxidation of cellulose, followed by a freeze-drying procedure, led to the production of white carboxylated cellulose nanofibre (CNF) aerogels (a) [1]. By means of an ad hoc protocol, involving alkali-induced oxidative polymerization of 5,6-dihydroxyindole (DHI) [2] on the CNF aerogel, the efficient deposition of melanin polymer onto the aerogel leading to a black coating (b) could be achieved. Preliminary characterization of the melanized aerogels (Mel-CNF) by SEM microscopy confirmed the high degree of porosity of the original aerogel with no apparent bulk polymerization (c). Possible applications of the newly developed Mel-CNF material will be discussed based on a systematic characterization of its adsorption, paramagnetic and free-radical scavenging properties.

[1] L. Melone, L. Altomare, I. Alfieri, A. Lorenzi, L. De Nardo, C. Punta *J.Photochem.Photobiol.A:Chem.*, 2013, **261**, 53-60.

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ORG-P70

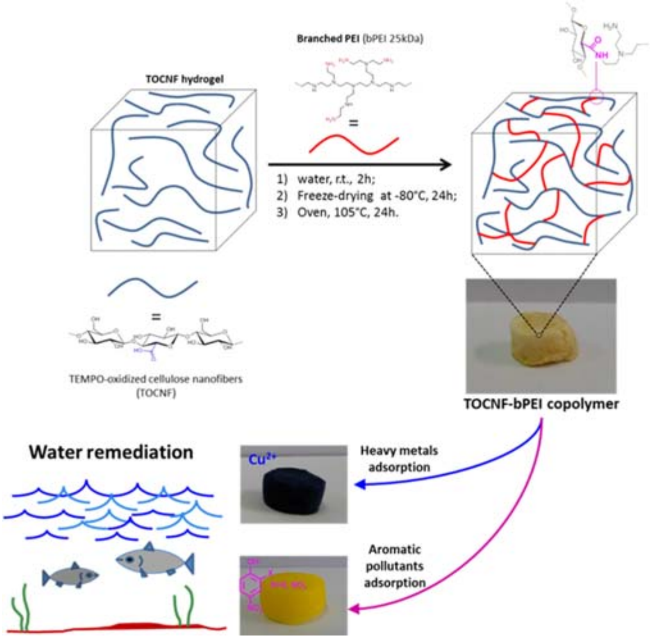
Adsorbent sponges from TEMPO-oxidized cellulose cross-linked with branched-PEI for water remediation

Bianca Rossi[a], *Lucio Melone*[a], *Nadia Pastori*[a], *Andrea Mele*[a], *Carlo Punta*[a]

a Dipartimento di Chimica, Materiali, Ingegneria Chimica "Giulio Natta", Politecnico di Milano, P.zza Leonardo da Vinci, 20133, Milano, Italy

bianca.rossi@polimi.it

A new class of cellular solids with macro and micro porosity have been synthesized by the combination of cellulose nanofibers from TEMPO-NaClO mediated oxidation (TOCNF) [1] and branched polyethyleneimine, via formation of amide-bonds (TOCNF-bPEI copolymer). The sponge-like materials obtained in this way have chelating amino groups as basic sites in the nano-porous structure, showing high performances in removing heavy metal ions and phenolic pollutants from contaminated water.



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ORG-P71

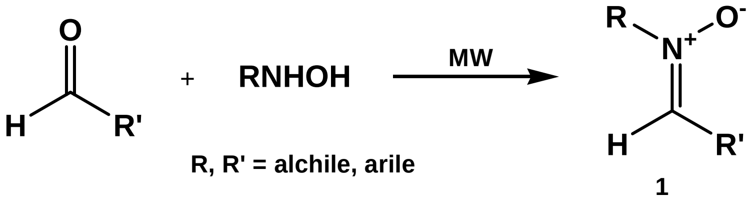
Sintesi di *C*-alchil e *C*-aril nitroni mediate da microonde e in assenza di solvente

Beatrice Russo[a], *Antonio De Nino*[a], *Loredana Maiuolo*[a], *Gaetano Stabile* [a]

a Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Ponte P. Bucci Cubo 12C, 87036, Arcavacata di Rende, Italia

beatrice.russo@unical.it

I nitroni (**1**) sono intermedi versatili impiegati nella sintesi organica. Essi reagiscono come elettrofili con composti organometallici e fungono da 1,3-dipoli in reazioni di cicloaddizione 1,3-dipolare[1]. Inoltre, alcuni nitroni esibiscono potenziale attività biologica[2].
Viene qui riportato, un metodo valido ed alternativo per la sintesi di nitroni, che prevede l'impiego esclusivo di radiazioni di microonde in completa assenza di solvente e di catalizzatore. Tale metodologia porta alla formazione del prodotto desiderato con alte rese, brevi tempi di reazione e completa assenza di sottoprodotti evitando perciò purificazioni successive (Schema 1).



Schema 1

[1] L. Maiuolo, O. Bortolini, A. De Nino, B. Russo, R. Gavioli, F. Sforza *Australian Journal Chemistry*, 2014, **67**, 670-674.
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ORG-P72

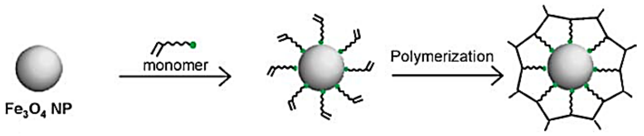
Sintesi di nanoparticelle magnetiche impiegate in organocatalisi

Beatrice Russo[a], *Antonio De Nino*[a], *Loredana Maiuolo*[a], *Maria Francesca Policicchio*[a], *Gaetano Stabile* [a]

a Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Ponte P. Bucci Cubo 12C, 87036, Arcavacata di Rende, Italia

beatrice.russo@unical.it

Nell'ultimo decennio la ricerca nel campo della catalisi si è orientata verso lo sviluppo di nuovi catalizzatori organici a basso impatto ambientale e in questo contesto le nanoparticelle magnetiche si candidano come supporti solidi catalitici altamente attivi e riciclabili. Viene qui riportata la sintesi di un organocatalizzatore[1] magnetico in catalisi eterogenea. Per creare il supporto catalitico si utilizzano delle nanoparticelle di magnetite superparamagnetiche facilmente disperdibili in solvente mediante agitazione meccanica o ultrasuoni. La funzionalizzazione[2] di tali particelle si ottiene mediante l'utilizzo di silicati facilmente polimerizzabili. La presenza sulla superficie del supporto solido magnetico di gruppi silanoli permette così la derivatizzazione con una vasta gamma di gruppi funzionali organici. L'ancoraggio della porzione organica si effettua attraverso un linker, anch'esso a base di silicio, che funge da ponte tra l'ausiliario chirale ed il supporto magnetico. L'ausiliario chirale[3] è, generalmente, una molecola che svolge attività catalitica ed enantioselettiva nelle più comuni e moderne reazioni di sintesi organica ed asimmetrica. L'organocatalizzatore magnetico presenta il vantaggio di potere essere recuperato dall'ambiente di reazione sfruttando le sue proprietà magnetiche ed essere successivamente riutilizzato.



[1] D. W. C. MacMillan *Nature*, 2008, **455**, 304.
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ORG-P73

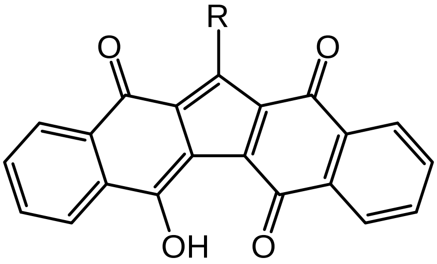
KuQuinones as sensitizers in photoelectrochemical devices.

Federica Sabuzi, Sara Lentini, Emanuela Gatto, Valeria Conte, Barbara Floris, Mariano Venanzi and Pierluca Galloni

Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Via della Ricerca Scientifica, 00133, Roma, Italia

federica.sabuzi@uniroma2.it

Recently, in our research group, we discovered a new class of pentacyclic diquinoid compounds, KuQuinones[1], that have shown a significant antitumor activity against Cisplatin-Resistant SKOV3 and colon carcinoma SW480 cell lines[2].



Concerning their potential applications in different fields, we are now testing their ability to act as sensitive material in photoelectrochemical devices. In fact, among their properties, KuQuinones show a broad absorption spectra in the visible region and a very low reduction potential[1], so they may act as electron acceptor molecules in organic solar cells.

KuQuinones mono- and multilayers have been prepared and the efficiency of each film has been evaluated through the determination of IPCE values (incident photon to current conversion efficiency) and quantum yields (Φ). Photocurrent generation mechanisms will be proposed.

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[2] S. Lentini, F. Sforza, V. Conte, O. Bortolini, B. Floris and P. Galloni *submitted.*

ORG-P74

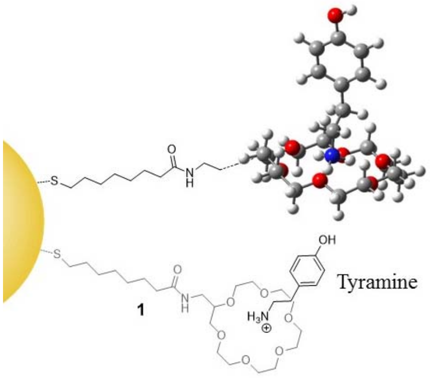
Flash oral communication FO6

Turning supramolecular receptors into NMR chemosensors

Giovanni Salassa, Marie-Virginie Salvia, Federico Rastrelli, Fabrizio Mancin.

Dipartimento di Scienze Chimiche, Università di Padova, Via Marzolo 1, 35131, Padova, Italy

giovanni.salassa@unipd.it



Gold nanoparticles (AuNPs) have shown to be excellent scaffold for the fabrication of novel chemical and biological chemosensors due to their distinct physical and chemical properties.[1] One intrinsic limitation of the currently used approaches is the fact that analyte identification is strictly dependent by chemosensor selectivity. Indeed, the signal produced arises from a modification of a property (absorbance, luminescence, electric potential, etc.) of the sensing system itself and therefore does not provide any direct information on the analyte detected. From the NMR spectroscopy expertise of our group a novel sensing protocol based on AuNPs has been developed which allows the simultaneous identification and quantification of the analyte in a complex mixture.[2] This method relies on the ability of monolayer-protected nanoparticles to bind substrates exploiting non-covalent interactions. After target recognition, the nanoparticle labels it by magnetization transfer (NOE) while the signals of the other present species are cancelled by a diffusion filter. In this way, only the interacting molecule appears in the NMR spectrum allowing its detection and identification.

In principle, any supramolecolar receptor can be converted into a chemosensors simply by grafting it to nanoparticles. To demonstrate this principle, we synthesized a new class of gold nanoparticles) covered with the crown ether-bearing thiol **1** (figure) and successfully applied them in the sensing of protonated primary amines. Remarkable selectivity and switchable behaviour will be discussed in this communication.

[1] K. Saha, S. S. Agasti, C. Kim, X. Li and Vincent M. Rotello *Chem. Rev.*, 2012, **112**, 2739–2779.

[2] B. Perrone, S. Springhetti, F. Ramadori, F. Rastrelli and F. Mancin *J. Am. Chem. Soc.*, 2013, **135**, 11768-11771.

ORG-P75

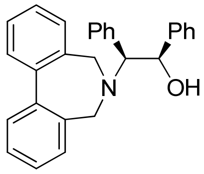
Asymmetric arylation of aldehydes mediated by *tropos* aminoalcohols

Patrizia Scafato, *Stefano Superchi*, *Laura Pisani*

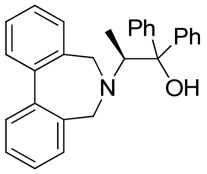
Dipartimento di Scienze, Università della Basilicata, Via Ateneo Lucano 10, 85100, Potenza, Italy.

patrizia.scafato@unibas.it

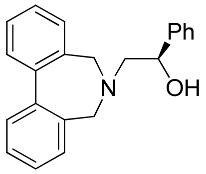
An application of new chiral aminoalcohols **1-3** (shown in figure), which possess a flexible biphenylazepine moiety and can work as *tropos* catalysts, is presented. In these compounds the stereogenic center close to the flexible biphenyl fragment induces a preferred axial chirality in the biphenyl and affects the stereochemical outcome in asymmetric reactions mediated by them. The efficiency of these new ligands has been explored in the asymmetric addition of *in situ* prepared arylzinc compounds to aromatic aldehydes.[1] Among them, aminoalcohol (*1R,2S*)-**1** gave the best results and afforded optically active diarylmethanols,[2] which are precursors of well-known chiral drugs, in high yields and ee's up to 96%.



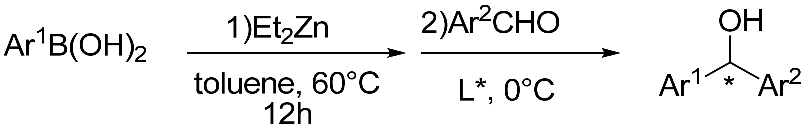
(1*R*,2*S*)-**1**



(*S*)-**2**



(*R*)-**3**



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ORG-P76

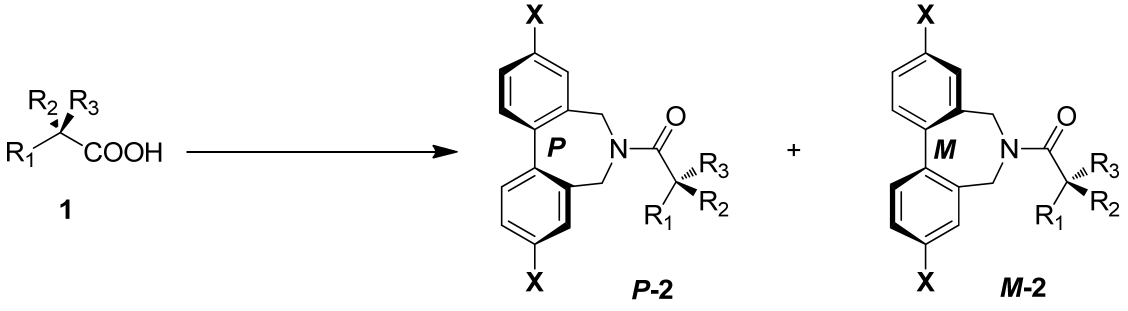
Absolute Configuration of 2-Arylpropionic Acids by Biphenyl Chiroptical Probes

Patrizia Scafato, Stefano Superchi, Stefania Vergura

Dipartimento di Scienze, Università della Basilicata, Via Ateneo Lucano 10, 85100, Potenza, Italy

patrizia.scafato@unibas.it

Flexible biphenyls are efficient and practical chiroptical probes for absolute configuration (AC) assignment of transparent and conformationally mobile molecules.[1] This approach was employed for the AC determination of aliphatic diols[1a] and 2-substituted carboxylic acids (**1**).[1b] The latter are transformed in biphenyl amides **3** in which the preferred *M* or *P* biphenyl twist depends on the acid AC. The biphenyl torsion in **3**, and then the acid AC, can be revealed simply looking at the sign the biphenyl ECD band at ca. 250 nm (A band). Such method can be troublesome with 2-arylpropionic acids, which bears aryl moieties absorbing in the 220-350 nm range and display electronic transitions giving rise to ECD Cotton effects masking the biphenyl A band. To treat these compounds we investigated the use of novel biphenyl probes 4,4'-disubstituted with groups (X = OMe, NH_2, NHAc, NO_2) able to shift the A band at wavelengths not overlapping with aryl absorptions, thus removing any spectral interference. The effect of 4,4'-substitution on UV and ECD spectra and application to 2-arylpropionic acids AC assignment is reported.



[1] (a) S. Superchi, D. Casarini, A. Laurita, A. Bavoso and C. Rosini *Angew. Chem. Int. Ed. Engl.*, 2001, **40**, 451-454. (b) S. Superchi, R. Bisaccia, D. Casarini, A. Laurita and C. Rosini *J. Am. Chem. Soc.*, 2006, **128**, 6893-6902.

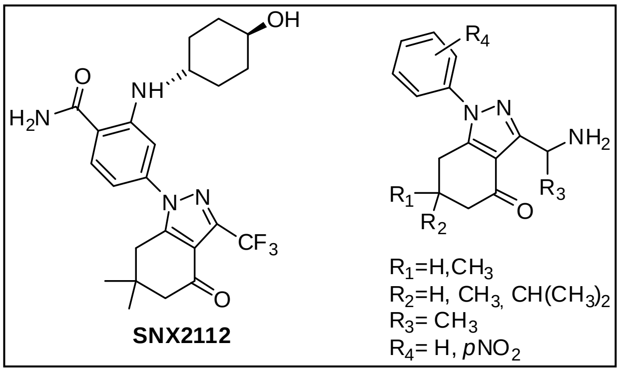
ORG-P77

Synthesis and antiproliferative evaluation of new tetrahydroindazolone derivatives

Angela Scala[a], *Anna Piperno*[a], *Santa Cirmi*[b],
Michele Navarra[b], *Giovanni Grassi*[a]

[a] *Dipartimento di Scienze Chimiche, Università di Messina, V.le F. Stagno d'Alcontres 31, 98166, Messina, Italia*
[b] *Dipartimento di Scienze del Farmaco e dei Prodotti per la Salute, Università di Messina, V.le Annunziata, 98166, Messina, Italia*

ascala@unime.it



SNX2112

R_1=H,CH_3
R_2=H, CH_3, $CH(CH_3)_2$
R_3= CH_3
R_4= H, *p*NO_2

Indazole- and indazolone-based compounds have recently attracted special attention in virtue of their biological properties, such as analgesic, antiinflammatory, anticancer, antimicrobial, and cytotoxic activities. In particular, tetrahydroindazolone derivatives such as SNX-2112 have been identified as potent Hsp90 inhibitors, exhibiting low nanomolar antiproliferative activities against multiple cancer cell lines.[1] In the framework of our studies dealing with the design of polyfunctionalized heterocycles,[2-4] we report the synthesis of novel indazolone derivatives including requirements necessary for Hsp90 inhibition. Their biological relevance has been assessed *in vitro* against HT-29 colorectal adenocarcinoma and HepG2 hepatocellular carcinoma cells, evaluating both the antiproliferative and the cytotoxic effects.

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ORG-P78

Flash oral communication FO8

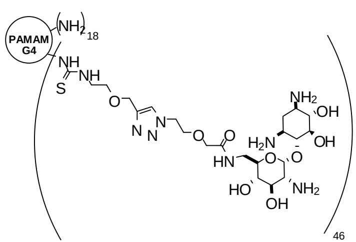
Synthesis of Multifunctional PAMAM-Aminoglycoside Conjugates for Gene Delivery

<u>Aurora Sganappa</u> [a], A. Volonterio [a], G. Candiani[a], D. Pezzoli[a]

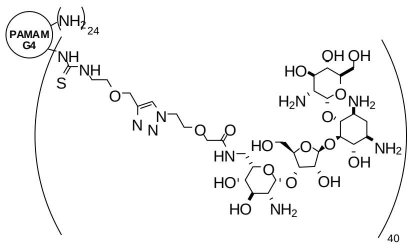
[a] Department of Chemistry, Materials, and Chemical Engineering "G. Natta", Politecnico di Milano, via Mancinelli 7, 20131 Milano, Italy

aurora.sganappa@polimi.it

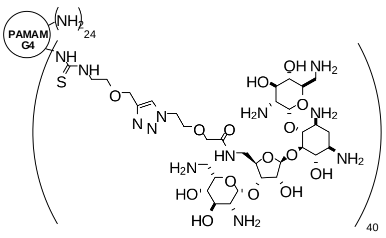
Gene delivery is a fundamental step on gene therapy being the process of introducing foreign DNA or RNA in host cells. In order to achieve this goal, it is necessary to have a carrier, called vectors, that should bind tightly the transgene, bring it selectively into the target cells avoiding degradation in the extracellular matrix, and then release it into the cell nucleus. Recently the researchers have focused their attention on the development of non-viral vectors such as cationic polymers and lipids. Among the cationic polymers, PAMAM dendrimers are very interesting because 1) they have a well-defined geometry and chemistry, 2) they are commercial available, and 3) they possess negligible toxicity. However, PAMAM itself is not very efficient. Thus in order to increase the efficiency of the dendrimer while maintaining the low cytotoxicity, we have chosen to functionalize the surface primary amines with aminoglycoside antibiotics (such as neamine, paromomycin and neomycin). The synthesis of such conjugates, as well as their transfection efficiency, citotoxycity[1] and antibacterial ativity[2] will be reported.



G4-PAMAM-neamine **1**



G4-PAMAM-paromomycin **2**



G4-PAMAM-neomycin **3**

[1] A. Sganappa et al., "Synthesis of Multifunctional PAMAM-Aminoglycoside Conjugates with Enhanced Transfection Efficiency". *Bioconj. Chem.* 2013, *24*, 1928-1936.
[2] A. Sganappa et al. Manuscript in preparation.

ORG-P79

Anion effect on the thermodynamics of tautomerization reaction in ionic liquids

Gabriella Siani, Romina Zappacosta, Antonello Di Crescenzo,Pietro Di Profio, Antonella Fontana

Dipartimento di Farmacia, Università "G. d'Annunzio", Via dei Vestini, 31 , 66100, Chieti, Italia

siani@unich.it

Organic reactions are commonly carried out in solution so that the choice of the "best" solvent is crucial for a reaction to occur successfully. Ionic liquids (ILs) have attracted considerable interest as alternative reaction media to conventional organic solvents for many organic reactions.[1] The most important feature of ILs is that their physico-chemical properties can be fine-tuned simply by combining different cations and/or anions so that the best IL for a specific application can be "designed". In order to choose the best cation/anion combination it is necessary to understand how the structure of ILs can affect their solvent strength and the organic reactivity of dissolved substrates. Recently, the keto-enol interconversion of 2-nitrocyclohexanone (2-NCH) has been used as a probe reaction to obtain information on the solvent properties of ILs.[2] In the present work, the values of the thermodynamic parameters, ΔG^0, ΔH^0 and ΔS^0, for the keto-enol interconversion reaction of 2-NCH have been derived from the tautomeric equilibrium constant values, determined at different temperatures in some ILs and organic molecular solvents. As expected, in conventional solvents the tautomeric equilibrium is enthalpically disfavored and entropically favored by the increase of solvent polarity. In ILs the nature of the anion seems to play a primary role on the thermodynamics of the reaction as positive ΔH values have been obtained in PF_6^-- and TF_2N^--based ILs and negative ΔH values in BF_4^--based ILs. A good correlation between ΔH and ε has been found in PF_6^-- and TF_2N^--based ILs while in BF_4^--based ILs other solvent parameters, such as hydrogen bond basicity, β, and cohesive pressure, δ^2, have to be taken into account. Moreover, the effect of the solvent on ΔG^0 is mainly entropic in origin when BF_4 is used as the anion.

[1] C. Chiappe and D. Pieraccini *J.Phys.Org.Chem.*, 2005, **18**, 275-297.
[2] G. Angelini, C. Chiappe, P. De Maria, A. Fontana, F. Gasparrini, D. Pieraccini, M. Pierini and G. Siani *J. Org.Chem.*, 2005, **70**, 8193-8196.

ORG-P80

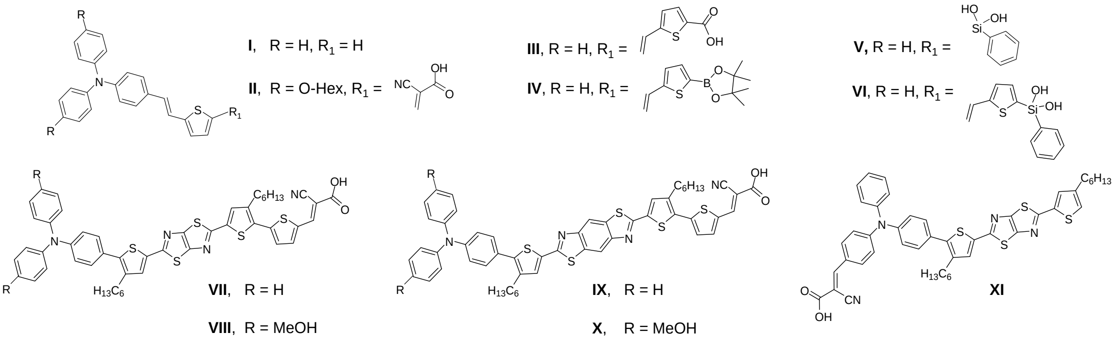
In silico prediction of excited state properties of organic sensitizers for DSSC

C. Bernini[a], L. Zani[b], M. Calamante[b], G. Reginato[b], A. Mordini[b], M. Taddei[a], R. Basosi[a], A. Sinicropi[a]

a Dipartimento di Biotecnologie, Chimica e Farmacia, Università di Siena, Via A. Moro, 2, 53100, Siena, Italia
b CNR – Istituto di Chimica dei Composti Organometallici (CNR-ICCOM),Via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy

adalgisa.sinicropi@unisi.it

Excited state geometries and emission maxima of 11 organic dyes used as sensitizers in Dye-Sensitized Solar Cells (DSSC) have been computed using a PCM/TD-DFT strategy. The investigated dyes can be divided into few groups: triarylamine-thiophene derivatives characterized by different conjugation lengths and anchoring groups (**I-VI**), thiazolothiazole- (**VII-VIII**, **XI**) and benzobisthiazole-containing (**IX-X**) sensitizers.



The results showed that the computed emission energies are in good agreement with the experimental values [1-3] (mean absolute error ~ 0.10 eV). The obtained accuracy opens the way to the design of compounds with improved excited state stability, to be used as photosensitizers in DSSC.

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[2] G. Barozzino Consiglio, R. Basosi, A. Mordini, G. Reginato, M. Taddei, L. Zani et al., *J. Organomet. Chem.* 2013, **723**, 198-206.
[3] L. Zani, G. Reginato, A. Mordini, M. Calamante, M. Taddei, A. Sinicropi, R. Basosi, M. Bruzzi et al., *Tetrahedron Lett.* 2013, **54**, 3944-3948.

ORG-P81

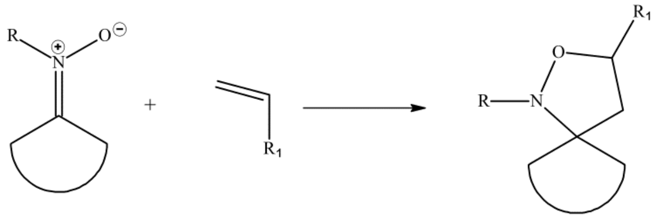
Cicloaddizioni 1,3-dipolari per la formazione di nuove spiroisossazolidine a potenziale attività biologica

Gaetano Stabile[a], *Vincenzo Algieri,*[a] *Antonio De Nino*[a], *Loredana Maiuolo*[a], *Beatrice Russo*[a]

a Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Ponte P. Bucci Cubo 12, 87036, Arcavacata di Rende, Italia

gaetanostabile75@libero.it

I composti spiro rappresentano un'importante classe di sostanze presenti in natura contraddistinti da pronunciate proprietà biologiche[1] dovute alla presenza di un atomo di carbonio ibridato *sp*^{3} noto come "spiro atomo".
In questo lavoro si riportano i risultati ottenuti relativi alla sintesi di nitroni (**1**) e di spiroisossazolidine (**2**) mediante reazioni di cicloaddizione 1,3-dipolare. Un primo approccio di rezione ha visto impiegati come dipolarofili substrati commercialmente disponibili; inoltre, considerato il conclamato incremento dell'attività farmacologica di isossazolidine grazie alla presenza di una nucleobase sulla loro struttura,[2,3] la stessa procedura sintetica è stata estesa usando un set di vinilnucleobasi come dipolarofili secondo lo schema riportato di seguito.



1 **2**

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ORG-P82

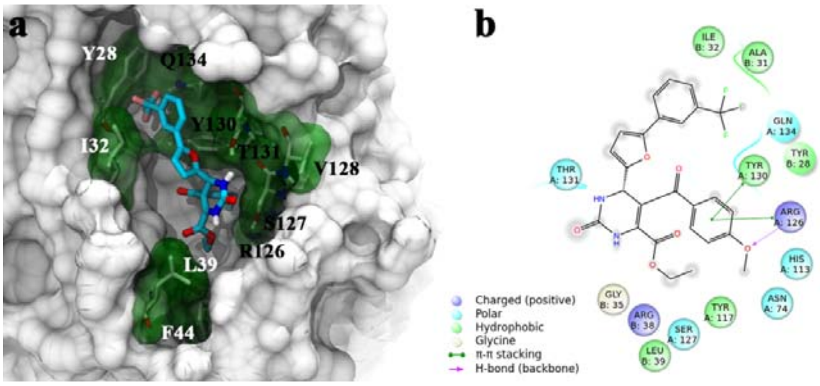
Identification of dihydropyrimidine derivatives as new mPGES-1inhibitors

Maria Strocchia[a], *Stefania Terracciano*[a], *Gianluigi Lauro*[a], *Oliver Werz*[b],
Raffaele Riccio[a], *Ines Bruno*[a] *and Giuseppe Bifulco*[a]

a Department of Pharmacy, University of Salerno, via Giovanni Paolo II, 132, 84084 Fisciano, Italy
b Department of Pharmaceutical/Medicinal Chemistry, Institute of Pharmacy, Friedrich Schiller University, Jena, Philosophenweg 14, D-07743 Jena, Germany

mstrocchia@unisa.it

Microsomal prostaglandin E_2 synthase 1 (mPGES-1) is an inducible GSH-dependent membrane protein, responsible for conversion of PGH_2 into PGE_2 [1]. Since this enzyme is widely involved in several human inflammatory and neoplastic diseases, it may be considered as an attractive target for therapeutic application. Here we report the results of a focused collection of dyhidropyrimidin-2(1H)-one based molecules selected through virtual screening approaches. The synthesis of our compounds has been performed by a one-pot microwave-assisted multicomponent Biginelli reaction [2]. The biological evaluation revealed a new hit with a promising in vitro mPGES-1 inhibitory activity in the low µM range [3].



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ORG-P83

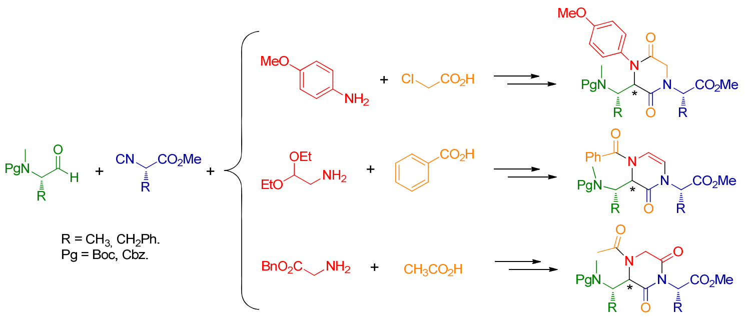
Multicomponent synthesis of piperazine based minimalist peptidomimetics

Mattia Stucchi[a], *Giordano Lesma*[a], *Alessandra Silvani*[a], *Giovanni Grazioso*[b]

[a] *Dipartimento di Chimica, Università di Milano, via Golgi 19, 20133, Milano, Italy*
[b] *Dipartimento di Scienze Farmaceutiche, Università di Milano, Via Mangiagalli 25, 20133 Milano, Italy*

mattia.stucchi@unimi.it

Statistical analyses of structurally characterized protein-protein interfaces have shown side-chain substituents to account for about 80% of the interactions; the polyamide backbone accounts for much less.[1] Compounds that present only selected side-chains to resemble peptide secondary structures are referred as *minimalist mimics* by Burgess in 2011.[2] We selected the Ugi multicomponent reaction as a powerful and versatile tool for synthesizing a small library of piperazine-based peptidomimetics. By using aldehydes and isocyanides derived from natural amino acids, and bifunctional amines and carboxylic acids suitable for post-Ugi cyclization reactions, we obtained the target compounds in good yields and diastereoselectivity. By computational studies, their ability to mimic multiple secondary structures could be assessed.



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ORG-P84

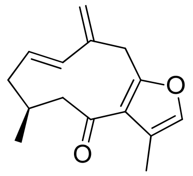
Absolute configuration of furanogermacrenones from *Commiphora erythraea* by computational analysis of ECD and ORD spectra

<u>Stefano Superchi</u>[a], *Ernesto Santoro*[a], *Federica Messina*[b], *M. Carla Marcotullio*[b]

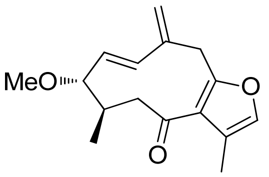
a Dipartimento di Scienze, Università della Basilicata, Via Ateneo Lucano 10,
85100, Potenza, Italy.
b Dipartimento di Scienze Farmaceutiche, Università di Perugia, via del Liceo 1,
06123 Perugia, Italy.

stefano.superchi@unibas.it

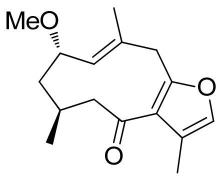
Compounds **1-4** were isolated as the major components of the resin (myrrh) of *Commiphora erythraea* (Ehrenb.) Engl. (Burseraceae), a small tree growing in the Arabian Peninsula and widespread in Ethiopia.[1] Such myrrh, locally called agarsu, has a large use in traditional medicine and compounds **1-4** were found to display different and interesting biological properties. In this study the absolute configuration (+)-(4*S*)-**1**, (+)-(3*S*,4*R*)-**2**, (-)-(2*S*,4*S*)-**3**, and (-)-(1*R*,2*R*,4*S*)-**4** was assigned, for the first time, to these bioactive furanogermacranes by DFT computational analysis of their optical rotatory dispersion (ORD) curves and electronic circular dichroism (ECD) spectra. This analysis also showed that compounds **1-4** share the same absolute configuration at the methyl substituted carbon then allowing to hypothesize a biosynthetic relationship among these structurally related metabolites.



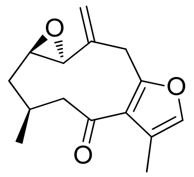
(4*S*)-**1**



(3*S*,4*R*)-**2**



(2*S*,4*S*)-**3**



(1*R*,2*R*,4*S*)-**4**

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ORG-P85

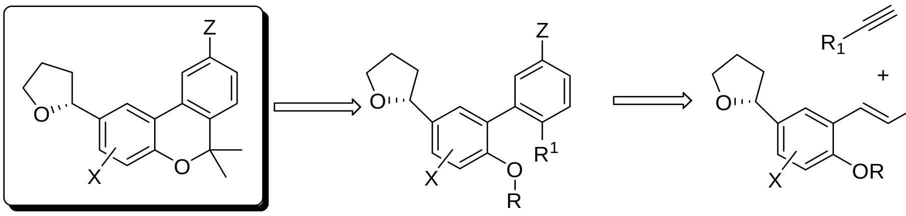
Sintesi di Composti a Struttura Cannabinoidica Tetraidrofurano-Sostituiti

Lucio Minuti[a], *Andrea Temperini*[b]

a Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia, Via Elce di Sotto 8, 06123, Perugia, Italia
b Dipartimento di Scienze Farmaceutiche, Università di Perugia, Via del Liceo 1, 06123, Perugia, Italy

andrea.temperini@unipg.it

Il nucleo del tetraidrofurano è presente in numerosi composti naturali bioattivi. In continuazioni dei nostri studi sulla sintesi e proprietà biologiche di composti a struttura cannabinoidica [1,2], riportiamo qui un approccio alla sintesi di cannabinoidi enantioarricchiti contenenti unità strutturali del tetraidrofurano.



X = OH, OMe; R = H, Me;R_1 = CO_2Me ; Z = Me, OAc

La sintesi di tali composti è basata sulla reazione di Diels-Alder di dieni tetraidrofurano-sostituiti con metil propiolato. Vista la bassa reattività di questi dieni, le reazioni sono attivate dall'alta pressione (9 kbar). Il nucleo tetraidrofuranico viene sintetizzato a partire dal corrispondente fenilseleno alcool, secondo una metodica messa a punto precedentemente nei nostri laboratori [3].

Si ringrazia la Fondazione Cassa Risparmio Perugia (Progetto 2012.0122.021) e il Ministero dell'Istruzione dell'Università e della Ricerca (MIUR), PRIN 20109Z2XRJ_010.

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ORG-P86

3,4-dihydropyrimidin-2(1H)-one as a useful scaffold for Hsp90 C-terminal inhibition

Stefania Terracciano[a], *Maria Strocchia*[a], *Maria Giovanna Chini*[a], *Antonio Vassallo*[b], *Mariacarmela Vaccaro*[a], *Fabrizio Dal Piaz*[a], *Antonietta Leone*[a], *Raffaele Riccio*[a], *Giuseppe Bifulco*[a], *Ines Bruno*[a]

a Department of Pharmacy, University of Salerno, via Giovanni Paolo II, 132, 84084 Fisciano, Italy
b Department of Science, University of Basilicata, Viale dell'Ateneo Lucano n.10, 85100 Potenza, Italy

sterracciano@unisa.it

Heat shock protein 90 (Hsp90) is a highly conserved molecular chaperone that plays a crucial role in stabilizing and activating more than 200 "client proteins", many of which are involved in signal transduction, cell cycle regulation and apoptosis [1]. Therefore a considerable interest in developing chemotherapeutic drugs that specifically disrupt the function of Hsp90 has aroused. Recently several N-terminal Hsp90 inhibitors have been identified and are currently in clinical trials, while only few C-terminal inhibitors have been reported. Here we describe the synthesis of 3,4-dihydropyrimidin-2(1H)-ones performed through a microwave-assisted Biginelli reaction [2]. These compounds have been extensively evaluated for their biological activity using several assays including surface plasmon resonance (SPR), inhibition of cell proliferation and cell cycle arrest, depletion of client proteins. From these studies a new promising molecule has emerged. In order to identify the binding site on the target protein we have performed limited proteolysis experiments which suggested the interaction of the compound with the C-terminal domain of Hsp90 and a binding mode has been proposed by molecular docking.

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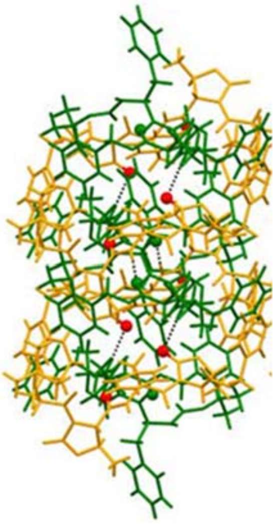
ORG-P87

Two Wrongs Make a Right: Properties in the Solid State and in Solution of Hybrid Foldamers Stereoisomeric Mixtures

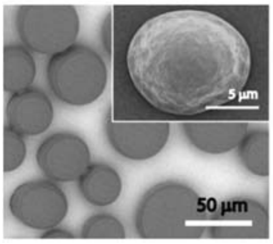
Claudia Tomasini[a], *Nicola Castellucci*[a], *Lorenzo Milli*[a]

a Dipartimento di Chimica "G. Ciamician", Università di Bologna, Via Selmi 2, 40126, Bologna, Italia

claudia.tomasini@unibo.it



On slow evaporation of a 1:1 diastereoisomeric mixture of Boc-(L-Phe-L-Oxd)$_2$-OBn **1** and Boc-L-Phe-L-Oxd-D-Phe-L-Oxd-OBn **2** in methyl *t*-butyl ether, single crystals suitable for X-ray diffraction study were obtained. In contrast, the two pure oligomers lead to the formation of amorphous solids in any crystallization condition. So the preferential conformation of both oligomers was fully elucidated in the solid phase. The preferred conformation of **1** ranges between PPII helix and β-strands and we can gather that longer and more structured oligomers will form PPII helices. The same outcome was retained in solution, as demonstrated by VCD (Vibrational Circular Dichroism) analysis.
Finally we have demonstrated that the 1:1 mixture of **1** and **2** leads to the formation of new materials with interesting properties missing in the two pure compounds, such as the tendency to form crystals, fibers and globules, depending on the solvent.



ORG-P88

Fishing Biomolecolare con *Hosts* Calixarenici

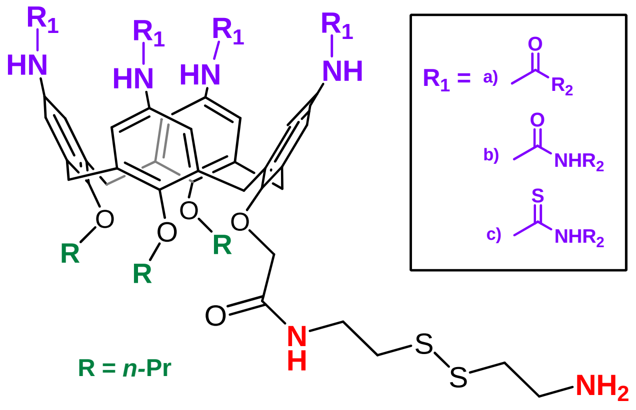
Stefano Tommasone[a], *Carmen Talotta*[a], *Carmine Gaeta*[a], *Chiara Cassiano*[b], *Agostino Casapullo*[b], *Placido Neri*[a]

a Dipartimento di Chimica e Biologia, Università di Salerno, Via Giovanni Paolo II 132, 84084, Fisciano (Salerno)
b Dipartimento di Farmacia, Università di Salerno, Via Giovanni Paolo II 132, 84084, Fisciano (Salerno)

stommasone@unisa.it

Nello sviluppo di potenziali nuovi farmaci particolarmente utile è la proteomica chimica accoppiata alla spettrometria di massa[1], nota anche come "*fishing for partners*", che permette l'individuazione dei loro target biomolecolari.

Allo scopo di estendere questa tecnica a potenziali calixareni bioattivi[2], sono stati progettati e sintetizzati dei derivati che possiedono sostituenti all'*upper rim* sia accettori che donatori di legame a idrogeno, mentre al *lower rim* è legato uno spaziatore opportunamente funzionalizzato per consentire l'ancoraggio ad un supporto solido. Tali derivati sono stati utilizzati per esperimenti di *fishing* al fine di valutare la capacità di interagire con bersagli macromolecolari di interesse biologico.



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ORG-P89

Characterization of mixed-valence state in mono-oxidized tetraferrocenylporphyrins

A.Vecchi[a], *P.Galloni*[a], *V. Conte*[a], *B. Floris*[a], *D. O. Cicero*[a],
A. G. Marrani[b], *A. Bagno*[c], *V. N. Nemykin*[d]

a Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Via della Ricerca Scientifica, 00133, Roma, Italia
b Dipartimento di Chimica, Università degli Studi di Roma "La Sapienza", P. Aldo Moro 5, 00185 Roma, Italia
c Dipartimento di Scienze Chimiche, Università degli Studi di Padova, Via Marzolo 1, 35131 Padova, Italia
d Department of Chemistry & Biochemistry, University of Minnesota-Duluth, Duluth, Minnesota 55812, USA

andrea.vecchi@uniroma2.it

We have been recently involved in the characterization of both metal free and metallated 5,10,15,20-tetraferrocenylporphyrin (H_2TFcP and MTFcP), which showed interesting mixed-valence states and reversible electrochemical behavior both in solution[1] and on surface.[2] The easy accessibility to the monocationic porphyrin ($TFcP^+$) is of particular interest because of the long-range electronic communication among ferrocenyl units, which gives rise to an intense inter-valence charge transfer (IVCT) band in the NIR region of the spectrum. This peculiar absorption can be used in the construction of redox-driven optical sensors and switches in the NIR. Both mono-oxidized TFcPs free-base and zinc complex were prepared in good yields and characterized by XPS and NMR spectroscopy. Experimental data as well as theoretical calculations support the idea of a fast electron transfer occurring among iron centers and place these cations as intermediate class II-III in the Robin and Day classification of mixed-valence species.

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ORG-P90

Composizione molecolare di *Cistus libanotis* L. della Tunisia

Venditti A.[a,b]*, Bianco A.*[a]*,Nicoletti M.*[b]*, Bruno M.*[c]*, Ben Jemia M.*[d]

a Dipartimento di Chimica, "Sapienza" Università di Roma, P.le A. Moro 5, Cap,00185 Roma,Italia
b Dipartimento di Biologia Ambientale, "Sapienza" Università di Roma, P.le A. Moro 5, Cap,00185 Roma,Italia
c Dipartimento STEBICEF, Università di Palermo, Parco d'Orleans II - 90128 Palermo, Italia
d Laboratoire des Plantes Extremophiles - Biotechnologic Center Borj-CedriaTechnopark, B.P. 901, 2050 Hammam-Lif, Tunisia

alessandro.venditti@uniroma1.it

In continuazione di recenti studi effettuati su *Cistus* sp. dal nostro gruppo di ricerca[1], è stato esaminato dal punto di vista fitochimico un campione di *Cistus libanotis* L. proveniente dalla Tunisia. L'attenzione è stata focalizzata sulla frazione a medio-bassa polarità che contiene i composti diterpenici contenuti nel labdanum, una resina utilizzata in profumeria che viene raccolta da alcune specie di *Cistus*[2,3]. L'analisi fitochimica ha permesso di identificare: due composti diterpenici, l' acido 3α,4α-diidrossi-*neo*-clerodan-15-oico[4] identificato per la prima volta in *Cistus* sp. e l'acido 18-idrossi-*cis*-clerodan-3-ene-15-oico; sei derivati flavonoidici a vario grado di metossilazione, apigenina, 7-*O*-metil-apigenina, 4',7-*O*-dimetil-apigenina, 7-*O*-metil-luteolina, 3,7,4'-*O*-trimetil-quercetina, 3,3',4',7-*O*-tetrametil-quercetina; due esteri cinnamici del borneolo isolati per la prima volta dal genere *Cistus*: *p*-cumaroil borneolo e caffeoil borneolo[5]. In conclusione il *C. libanotis* si è rivelato essere povero dal punto di vista del contenuto in composti diterpenici, sono invece risultati particolarmente abbondanti i derivati flavonoidici dell'apigenina, luteolina e quercetina a vario grado di metossilazione, due dei quali identificati per la prima volta in *Cistus* sp.

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ORG-P91

Metaboliti secondari da frutti e semi di *Gentiana dinarica* Beck e da fiori di *Gentiana lutea* L. dei Monti Ernici

Venditti A.[a,b]*, Guarcini L.*[a]*, Altieri A.*[a]*, Bianco A.*[a]

[a] *Universita di Roma "La Sapienza", Dipartimento di Chimica, Piazzale Aldo Moro, 5 00185 Roma, Italy*
[b] *Università di Roma "La Sapienza", Dipartimento di Biologia Ambientale*

alessandro.venditti@uniroma1.it

Sono stati studiati il profilo molecolare dei frutti e semi della *Gentiana dinarica* Beck e dei fiori della *Gentiana lutea* L.[1] dell' Appennino Centrale, effettuando inoltre un confronto con i dati disponibili in letteratura.

La frazione polare di frutti e semi di *G. dinarica* è risultata composta prevalentemente da iridoidi: vengono confermati sweroside, swertiamarin e gentiopicroside[2], con acido loganico e 6'-*O*-β-D-glucosyl-gentiopicroside, identificati per la prima volta. Va notata l'assenza del trifloroside che invece è un componente dei frutti di *G. lutea*[3]. La presenza di isoorientina[2] è stata confermata ma non quella del rispettivo 4'-*O*-glucoside. Nelle frazioni a più bassa polarità è stato identificato l'acido ursolico, rinvenuto per la prima volta in questa specie.

Nei fiori di *G. lutea* l'isogentisina[4] è il componente principale, mentre dal punto di vista degli iridoidi sono risultati presenti solo il gentiopicroside e l'acido loganico[3,5]. Sweroside e trifloroside[3], presenti nei semi e frutti, non sono stati rinvenuti. È stato isolato per la prima volta il 2-metil-D-*chiro*-inositolo.

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ORG-P92

Analisi fitochimica di *Juniperus phoenicea* L. subsp. *turbinata* (Guss), Nyman dall'Arcipelago de La Maddalena

Venditti A.[a,b]*, Bianco A.*[a]*, Ornano L.*[a,c]*, Ballero M.*[c]*, Sanna C.*[c]*, Bruno M.*[d]*,*
Rosselli S.[d]

a Dipartimento di Chimica, "Sapienza" Università di Roma, P.le A. Moro 5, Cap,00185 Roma, Italia
b Dipartimento di Biologia Ambientale, Università di Roma,
c Consorzio Interuniversitario CoSMeSe, Università di Cagliari,
d Dipartimento STEBICEF, Università di Palermo

alessandro.venditti@uniroma1.it

Il *J. phoenicea* L. subsp. *turbinata* (Guss),Nyman, è una specie arbustiva molto longeva a lento accrescimento della famiglia delle Cupressaceae ed un elemento costitutivo della macchina mediterranea[1]. Nella frazione polare è stata riscontrata la notevole presenza di diterpeni ed un unico composto flavonoidico. Dai dati preliminari in risonanza magnetica si può ipotizzare anche la presenza di un derivato diterpenico formilato in quanto presenti segnali caratteristici. Ulteriori studi sono in corso per stabilire la struttura di questa sostanza. Dal punto di vista chemotassonomico i composti isolati sono stati precedentemente identificati in specie correlate come *Juniperus rigida, J. communis e J. taxifolia*, confermando così le relazioni filogenetiche tra tali specie[2,3,4].

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ORG-P93

Iridoidi a scheletro spironolattonico ed epossidico da *Pentas lanceolata* (Forssk.) Deflers dell'Orto botanico di Cagliari

Venditti A.[a,b], *Guarcini L.*[a], *Bianco A.*[a], *Ballero M.*[c]

a Dipartimento di Chimica, "Sapienza" Università di Roma, P.le A. Moro 5, Cap,00185 Roma, Italia
b Dipartimento di Biologia Ambientale, Università di Roma,
c Consorzio Interuniversitario CoSMeSe, Università di Cagliari,

alessandro.venditti@uniroma1.it

La frazione polare di *Pentas lanceolata* (Forssk.) Deflers è stata esaminata dal punto di vista fitochimico ed in modo particolare sul contenuto in glucosidi monoterpenici. In dettaglio sono stati isolati dodici composti dall'estratto etanolico, di questi, dieci sono iridoidi glucosidici: asperuloside (**1**), asperulosidic acid (**2**), tudoside (**4**), *E*-uenfoside (**5**) e *Z*-uenfoside (**6**), già precedentemente identificati in *P. lanceolata*[1]. Deacetyl-asperulosidic acid (**3**), ixoside (**8**), griselinoside (**9**), 6β,7β-epoxysplendoside (**10**) sono stati identificati per la prima volta da questa specie in questo studio. Oltre i composti ritenuti marker chemotassonomici[2,3], sono stati isolati composti interessanti in quanto presentano funzionalizzazioni insolite che risultano piuttosto rare nella famiglia delle Rubiaceae[4,5], come il ponte epossidico e/o l'anello spironolattonico.

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ORG-P94

Pivaloilcodeina, un nuovo inibitore della glucuronidazione della morfina

Antonilli L.[a], Bianco A.[b], Guarcini L.[b], Nencini P.[a], Nicoletti R.[b], Sabatini G.[a], Salemme A.[a], Sanasi F.[b], Togna A.R.[a], Togna G.I.[a], Venditti A.[b,c]

[a] Dipartimento di Fisiologia e Farmacologia 'V. Erspamer' "Sapienza" Università di Roma, Piazzale Aldo Moro, 5 00185 Roma, Italy
[b] Università di Roma "La Sapienza", Dipartimento di Chimica,
[c] Università di Roma "La Sapienza", Dipartimento di Biologia Ambientale

alessandro.venditti@uniroma1.it

Da recenti studi è risultato che gli oppioidi a struttura fenantrenica, inclusa la codeina, modulano la glucuronidazione della morfina nel ratto[1]. La morfina 3-glucuronide (M3G) è un derivato morfinico privo di effetti analgesici ed in grado di attivare il sistema glutammatergico, causando effetti neuroeccitatori che contribuiscono alla comparsa dell'allodinia ed iperalgesia[2]. La morfina 6-glucuronide (M6G) è invece un analgesico potente quanto la morfina stessa e certamente contribuisce all'azione analgesica del composto progenitore[3,4]. Il controllo della glucuronidazione potrebbe essere un modo per ridurre i fenomeni eccitatori provocati dalla metabolizzazione della morfina a M3G e per contrastare la comparsa della tolleranza e dei fenomeni paradossi ad essa collegati. In questo studio sono stati preparati diversi derivati esterei in posizione 6 della codeina ed in seguito sono state testate sulla sintesi di M3G e M6G su microsomi epatici e su epatociti di ratto. Il presente studio mostra che la codeina ed i suoi derivati acetile e pivaloile agiscono da inibitori della formazione di M3G, rafforzando l'ipotesi che la struttura fenantrenica sia essenziale per modulare la glucuronidazione della morfina[5].

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ORG-P95

Analisi fitochimica di *Schizogyne sericea* (L. fil.) DC.

Venditti A.[a,b]*, Muscolo C.*[a]*, Bianco A.*[a]*, Maggi F.*[c]*, Zorzetto C.*[d]

a Dipartimento di Chimica, "Sapienza" Università di Roma, Piazzale A. Moro 5, 00185 Roma, Italia
b Dipartimento di Biologia Ambientale, Università di Roma "La Sapienza"
c Scuola di Scienze del Farmaco e dei Prodotti della Salute, Università di Camerino,
d Departamento de Medicina Física y Farmacología, Facultad de Farmacia, Universidad de La Laguna (ULL), La Laguna (Tenerife), España

alessandro.venditti@uniroma1.it

Schizogyne sericea (L. fil.) DC. (Asteraceae) è una specie arbustiva, alofita, tomentosa, endemica delle Isole Canarie (Spagna). Per approfondire le conoscenze su questa pianta è stata riesaminata la frazione polare, confermando alcuni composti precedentemente identificati[1], insieme al 2-methyl-,2-[3-[(acetyloxy)methyl]-2-oxiranyl]-5-methylphenyl isobutyrate, isolato in precedenza da *Arnica sachalinensis* (Regel) A. Gray[2] e risultato possedere una spiccata attività allergenica[3]. Tra i componenti a polarità maggiore sono stati isolati una serie di acidi dicaffeoilchinici, comuni nelle Asteraceae[4], che vengono rinvenuti per la prima volta tra i componenti di *S. sericea*. L'analisi dell'olio essenziale è stata condotta mediante gascromatografia accoppiata a spettrometria di massa (GC-MS). Il componente principale è risultato essere il *p*-cimene (40.8%), come in *S. glaberrima* DC. endemica dell'Isola Gran Canaria[5].

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ORG-P96

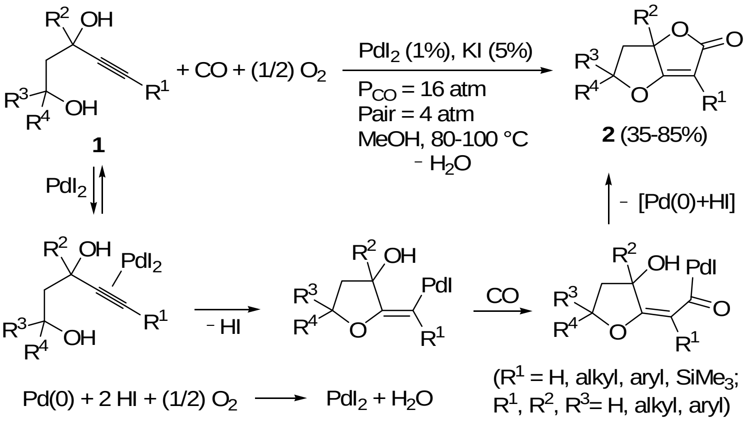
A Novel Synthesis of Dihydrofuro[3,2-*b*]furan-2(5*H*)one Derivatives by Pd-Catalyzed Oxidative Carbonylation of 4-Yne-1,3-diols

Ida Ziccarelli, Raffaella Mancuso, Donatella Armentano, Bartolo Gabriele

Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria
Via P. Bucci 12-14/C, 87036Arcavacata di Rende, Italy

idaziccarelli@gmail.com

The dihydrofuro[3,2-*b*]furan-2(5*H*)one unit constitutes the core structure of several biologically active compounds [1]. In this communication, we report a novel approach to the synthesis of dihydrofuro[3,2-*b*]furan-2(5*H*)one derivatives **2**, based on PdI_2-catalyzed oxidative carbonylation [2,3] of readily available 4-yne-1,3-diols **1**, according to Scheme 1.



Scheme 1

Reactions are carried out in MeOH at 80-100 °C and under 20 atm of a 4:1 mixture of CO-air, in the presence of catalytic amounts of PdI_2 (1 mol %) in conjunction with KI (5 mol %), to give furofuranones **2** in fair to good isolated yields (up to 85%). The structure of the products has been confirmed by X-ray crystallographic analysis.

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ORG-P97

Flash oral communication FO4

Fighting bacteria resistance: synthesis of novel indole-based efflux pump-inhibitors

S. Lepri[a]*, L. Goracci*[a]*, F. Buonerba*[a]*, G. Cruciani*[a]*, R. Ruzziconi*[a]*, G. Kaatz*[b]

a Dipartimento di Chimica, Biologia e Biotecnologie Università di Perugia, Via Elce di Sotto 8, 06123, Perugia, Italia
b Department of Internal Medicine, Division of Infectious Diseases, School of Medicine, Wayne State University and the John D. Dingell Department of Veterans Affairs Medical Center, Detroit, Michigan 48201, United States

susanlepri@gmail.com

The antibiotic resistance is a worldwide threat which has been causing serious concerns among scientific and medical communities, especially regarding the outbreak of *methicillin-resistant Staphylococcus aureus* (MRSA), responsible for several infection diseases. Bacterial resistance can rise through three main mechanisms: drug target modification, drug inactivation or export by pump efflux. While the fight against either the drug target modification or drug inactivation entails developing new classes of antibiotics, the pump efflux system represents a valid option for both its innovative character and the intrinsic advantage of recycling the by now useless antibiotics. In particular, the *S. aureus* NorA efflux pump is thought to be the main responsible for quinolone-based drug resistance by showing up extrusion of the antibacterial drug from the membrane, and thus lowering its effective concentration. Drugging the efflux-pumps seems to be not only attractive, but also a challenging strategy, due to the little information about these membrane proteins. Thus, combining data from *in silico* screening[1] and pharmacophore models, a novel class of efflux pump inhibitors have been discovered, leading to the synthesis of more efficient analogues, which were all tested for their inhibitory activity against MRSA. In addition, preliminary data on their synergistic activity with Ciprofloxacin are also reported.

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ORG-P98

Hydroxytyrosyl oleate: an anti-inflammatory booster of the natural occurring hydroxytyrosol

Pierluigi Plastina[a,b], *Mieke Poland*[b], *Jocelijn Meijerink*[b], *Renger Witkamp*[b], *Alessia Fazio*[a], *Bartolo Gabriele*[a]

a Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Via P. Bucci, 87036, Rende (CS), Italy
b Division of Human Nutrition, Wageningen University, Bomenweg 2, 6703 HD Wageningen, The Netherlands

pierluigi.plastina@unical.it

Hydroxytyrosol is one of the major phenolics found in olives and extra-virgin olive oil with well known antioxidant properties as well as antimicrobial, antitumor, and anti-inflammatory activities [1]. Lipophilic hydroxytyrosol derivatives have been suggested to be more active than hydroxytyrosol itself because of their increased metabolic stability and ability to pass membranes [2].

In the present study, hydroxytyrosol was subjected to lipase-catalyzed acylation, to afford a series of hydroxytyrosyl esters with short (C2), medium (C12) and long (C16 and C18) acyl chains.

Hydroxytyrosol and its derivatives were then evaluated for their ability to reduce the level of nitric oxide (NO) on lipopolysaccharide (LPS)-stimulated RAW264.7 macrophages. Among the compounds tested, hydroxytyrosyl oleate resulted the most promising, inducing a concentration-dependent decrease of NO production. Inhibition was also found to take place at a transcriptional level as gene expression of inducible NO synthase (iNOS) was inhibited by hydroxytyrosyl oleate.

In conclusion, lipophylization of hydroxytyrosol with an oleic acid moiety led to the formation of a compound that is more effective than hydroxytyrosol itself in the modulation of inflammation by reducing NO production and expression.

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ORG-P99

Viologen-based Ionic Liquid Crystals

Giacomo Saielli[a], *Marcella Bonchio*[b], *Mauro Carraro*[b], *Girolamo Casella*[b,c], *Valerio Causin*[b], *and Federico Rastrelli*[b]

a Istituto per la Tecnologia delle Membrane del CNR, Unità di Padova, Via Marzolo, 1 - 35131 Padova
b Dipartimento di Scienze Chimiche, Università di Padova, Via Marzolo, 1 - 35131, Padova
c Dipartimento di Scienze della Terra e del Mare (DiSTeM), Università di Palermo, Via Archirafi, 23 -90123, Palermo (Italy)

giacomo.saielli@unipd.it

Ionic liquid crystals (ILC) are expected to combine the properties and technological applications of ionic liquids and liquid crystals [1]. We extend here our investigation of monomeric viologen-based ILCs [2,3] to dimers. Thus we have synthesized symmetric dimeric viologen salts, nBPmBPn, where n is the number of carbon atoms in the end alkyl chains while m is the number of carbon atoms in the spacer. In most cases the counteranion is bis(trifluoromethanesulfonyl)amide (Tf_2N^-), but also dodecatungstosilicates have been investigated in details. The various phases exhibited have been characterized by means of TGA, DSC, X-ray diffraction, polarized optical microscopy and solid state NMR, while the behaviour in solution has been characterized by cyclic voltammetry. The modulation of the length of the alkyl chains allowed the fine tuning of the transition temperatures and thermal range of stability of the ILCs. More interestingly, the type of mesophase observed, either a SmA or an ordered SmX, was also found to depend strongly on the relative lengths of the end and middle alkyl chains [4,5].

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ORG-P100

Synthesis and Biological Activity of Phosphonated Reverse *N,O*-Nucleosides

R. Romeo,[a] C. Carnovale,[a] S.V. Giofrè,[a] C. Maniaci,[a] G. Monciino,[b] M.A. Chiacchio[b]

a Dip. di SCIFAR, Università di Messina, Viale Annunziata, 98168 Messina
b Dip. di Scienze del Farmaco, Università di Catania Viale A. Doria, 95125 Catania

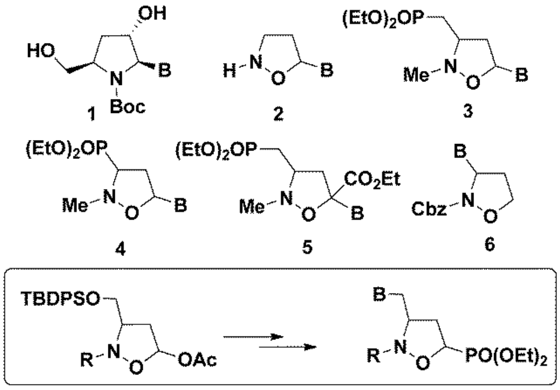
robromeo@unime.it

The nucleoside structure has proven to be an effective template for the design and development of new therapeutically useful compounds. In particular, nucleoside analogues, in which the furanose ring has been replaced by different carbon or heterocyclic systems, have attracted our interest by virtue of their biological action as antiviral and/or anticancer agents.[1] Among these, *N,O*-nucleosides **2-5**, possessing an isoxazolidinyl moiety, have emerged as an interesting class of dideoxy-nucleoside analogues with potential pharmacological activity (Fig.).

In this context, *N,O*-nucleosides **6** containing a pyrimidine nucleobase at C-3 position with a glycoside-type linkage, as HEPT analogues, have been shown to be endowed with inhibitory activity against HIV and AMV virus reverse transcriptase.[3]

In our program targeted to the discovery of new compounds able to interfere with viral replication, our interest was focused on the synthesis and evaluation of the pharmacological properties of 3-pyrimidinyl isoxazolidines characterized by the presence of a phosphonic group at C-5.

Biological evaluation of some derivatives indicates that the 3-pyrimidinyl scaffold is suitable for the development of potent NNRTTs.



B = Ty, 5-FU, U, Cy

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ORG-P101

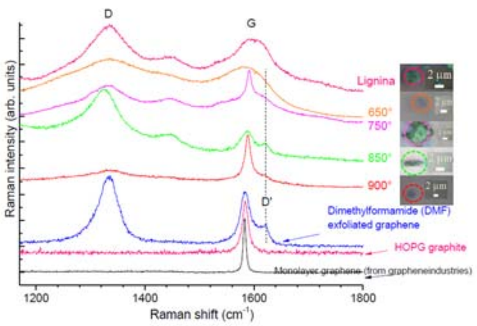
Graphenes from lignin pyrolysis

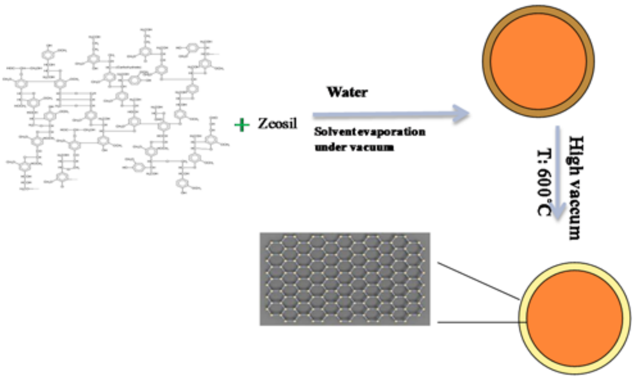
D. Dondi[a], A. Zeffiro[a], D. Vadivel[a], V. Bellani[b], A. Speltini[a], A. Buttafava[a]

[a] Dipartimento di Chimica, Università di Pavia, Via Taramelli 12, 27100, Pavia, Italy
[a] Dipartimento di Fisica, Università di Pavia, Via Bassi 6, 27100, Pavia, Italy

daniele.dondi@unipv.it

Lignin, as the most abundant aromatic natural polymer and the second richest source of organic raw material, is considered as a potential source of chemicals and energy. In this study we have demonstrated the formation of single and multiple layer graphene flakes (detected by Raman spectroscopy) from the pyrolysis of soluble Kraft lignin, a byproduct of paper pulping process. Pyrolysis was attained coating Si/SiO_2 wafers with a layer of lignin deposited by simple solvent evaporation. The vacuum pyrolysis was sufficient to yield appreciable amounts of graphene. The removal of inorganic salts and alkali from lignin led to detrimental production of graphene under the same conditions. Under similar experimental conditions, graphene and pyrolytic carbon was obtained onto silica. In that case the reactivity with oxygen, related to the simultaneous presence of both silica and carbon was extensively studied by EPR spectroscopy. This has lead to the detection of stable silicon peroxy radicals, usually considered unstable at ambient temperature [1].





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ORG-P102

Synthesis and characterization of sulfonated chars for the hydrolysis of cellulose

Roberto Paolo Marconi [a], *Daniele Dondi*[a], *Alberto Zeffiro*[a], *Armando Buttafava*[a]

a Department of Chemistry, Via Taramelli 12, 27100 Pavia, Italy

roberto.marconi@unipv.it

Lignocellulosic biomass is one of the most studied biomass for biethanol production. The possibility to increase the glucose production from cellulose has been object of several studies. In this study we evaluated the possibility to use sulphonate char of lignin as a solid acid catalyst for cellulose microwave assisted hydrolysis [1]. Kraft lignin, pyrolyzed at different times and temperatures [2], was sulphonated at ambient temperature. The microwave assisted hydrolysis by using the catalyst, was performed at 160°C for 30 minutes. The catalyst was characterized by EPR, TGA, FTIR-ATR and acid-base titration. The hydrolysis products were detected by HPLC, using different conditions. The results showed a good production of sugars with a low amount of unwanted products like furfural and hydroxymethylfurfural, that could interfere with the subsequent fermentation step. In fact, the production of sugars was comparable, if not higher, with respect to sulfuric acid in the same experimental conditions. The recyclability of the catalyst was assessed too. An explorative study on a real biomass such as alfalfa stem (Medicago sativa) was also made. The results showed that the catalyst, with respect to strong acid hydrolysis, produces less byproducts and more sugar oligomers.

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ORG-P103

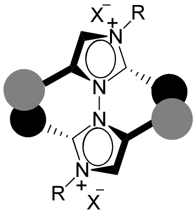
Biheteroaromatic Scaffolds to Design Unconventional Chiral Ionic Liquids

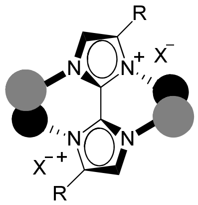
Simona Rizzo[a], *Francesco Sannicolò*[b], *Voichita Mihali*[b], *Marco Pierini*[c], *Roberto Cirilli*[d], *Patrizia Mussini*[b], *Armando Gennaro*[e]

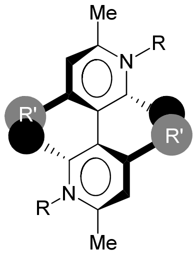
a Ist. di Scienze e Tecnologie Molecolari, Consiglio Nazionale delle Ricerche, via Golgi 19, 20133, Milano, Italia
b Univ. degli Studi di Milano, Dip. di Chimica, via Golgi 19, 20133, Milano, Italia
c Univ. degli Studi di Roma La Sapienza, Dip. di Chimica e Tecnologie del Farmaco, Piazzale A. Moro 5, 00185, Roma, Italia
d Ist. Superiore di Sanità, Dip. del Farmaco, Viale Regina Elena 299, 0016,1 Rome, Italia
e Univ. degli Studi di Padova, Dip. Scienze Chimiche, Via Marzolo, 1, 35131, Padova, Italia

simona.rizzo@istm.cnr.it

Chiral Ionic Liquids (CILs) constitute a class of solvents which got an increasing importance in the last ten years. They are used as solvents in asymmetric synthesis and in stereoselective polymerization, as chiral phases for gas chromatography, as chiral shift reagents in NMR spectroscopy and, in some cases, to generate cholesteric liquid crystals. Most of known CILs, are onium salts characterized by chiral substituents having one or several stereocenters. The aim of the research is to design, synthesize, characterize and test in electrochemical oxo-reduction processes a new family of non-conventional CILs in which the stereogenic element (a stereogenic axis) coincides with the function responsible for the IL properties. Using the successful strategy recently employed for designing “inherently chiral” oligotiophenes,[1] some “inherently chiral” CILs have been prepared based on 1,1’-, 2,2’-bisimidazolium and 3,3’-bipyridinium atropisomeric scaffolds. Structural characterization by single-crystal X-ray analysis, HPLC separation experiments, evaluation of configurational stability supported by theoretical calculations, and the investigation of the elettrochemical behaviour of the neutral precursors and of the salts have been performed. Though the double alkylation of was found rather difficult, some ILs of the new series have been isolated characterized.







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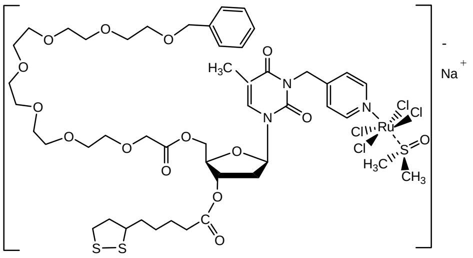
ORG-P104

Design, synthesis and characterization of multifunctional nucleolipid-based Ru(III) complexes as novel anticancer agents

Claudia Riccardi, Domenica Musumeci, Daniela Montesarchio

Dipartimento di Scienze Chimiche, Università di Napoli Federico II, Via Cintia 21, I-80126, Napoli, Italy

riccardiclaudia90@gmail.com



Ru(III) complexes are emerging as effective anticancer candidate drugs, in a promising approach, alternative to the well established Pt-based chemotherapy which is typically associated with high toxicity. Two Ru(III) complexes, *i.e.* NAMI-A and KP1019, are currently in advanced clinical trials.[1] Our most recent efforts in this research field have been addressed to the synthesis and characterization of Ru(III)-containing analogues incorporated into nucleolipidic platforms as suitable prodrugs producing, under physiological conditions, supramolecular aggregates capable of efficiently conveying the metal ions through the cell membranes.[2] Within a general, interdisciplinary research program directed at the synthesis of multifunctional nanoparticles for theranostic applications, we here report a novel design of functionalized Ru(III) salts, carrying a disulfide moiety in the nucleolipidic scaffold (see Figure) allowing its easy incorporation onto metal (Au, Zn, etc.)-based nanoparticles.

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Chimica dei Sistemi Biologici

Plenary

BIO-PL1

Research at an NMR infrastructure in Life Sciences

Claudio Luchinat
CERM and Department of Chemistry, University of Florence, Via L. Sacconi 6,
50019 Sesto Fiorentino – Italy

Developments in NMR applied to the structural and dynamic characterization of biological systems will be presented. Protein-ligand or protein-protein recognition often occur thanks to the availability of multiple conformational states of at least one of the partners. Paramagnetic NMR is a powerful tool to address the conformational freedom of proteins. We have developed a rigorous theoretical interpretation of the NMR data when averaged by conformational equilibria, that permits the detection of relevant protein conformations (1). Other average data such as SAXS can be used in the analysis, further increasing the power of the method. One can thereby calculate the "Maximum Occurrence", or MaxOcc, of any conformation in an ensemble. It can be empirically shown that the MaxOcc of a conformation correlates with the weight that this conformation has in the ensemble. Two-domain metalloproteins such as calmodulin or matrix metalloproteinases are paradigmatic examples. We have recently developed Sedimented Solutes NMR (SED-NMR) (2), based on limiting rotational diffusion of biomolecules by gravity under magic angle spinning or ultracentrifugation. SED-NMR can be used to prepare biological samples for solid state NMR experiments but also to investigate species that are not otherwise accessible to NMR, for instance to study the kinetics of formation of beta amyloid peptide oligomers. The glassy state of the sediment is also a suitable matrix for dispersing radicals for DNP experiments (3). Applications of relaxometry will be also presented, e.g. for the analysis of the spectral density of water protons in the presence of radicals to understand DNP experiments in solution (4), and to determine the reorientation times of solute molecules up to the microsecond range, so that the tumbling time of hundreds kDa proteins can be accessed (5).

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BIO-PL2

Cytochrome *c*: from an electron transfer to a (pseudo-)enzymatic globin

Paolo Ascenzi [a], *Massimo Coletta* [b,c], *Laura Fiorucci* [b], *Maria Marino* [d], *Fabio Polticelli* [d,e], *Federica Sinibaldi* [b], *Roberto Santucci* [b]

[a] *Interdepartmental Laboratory of Electron Microscopy, Roma Tre University, Roma, Italy*
[b] *Department of Clinical Sciences and Translational Medicine, University of Roma "Tor Vergata", Roma, Italy*
[c] *Interuniversity Consortium for the Research on the Chemistry of Metals in Biological Systems, Bari, Italy*
[d] *Department of Science, Roma Tre University, Roma, Italy*
[e] *National Institute of Nuclear Physics, Roma Tre Section, Roma, Italy*

ascenzi@uniroma3.it

Cytochrome *c* (cyt*c*) is a small heme-protein located in the space between the inner and the outer membrane of the mitochondrion that transfers electrons from cytochrome *c*-reductase to cytochrome *c*-oxidase. The hexa-coordinated heme-Fe atom of cyt*c* displays a very low reactivity toward ligands and does not exhibit catalytic properties. However, upon cardiolipin (CL) binding, cyt*c* achieves ligand binding and enzymatic properties reminiscent of those of heme-globins and heme-enzymes. In particular, the peroxidase activity of CL-cyt*c* is critical during the early stages of the apoptotic process generating CL hydroperoxides that favor the dissociation of CL-cytc and the release of CL-free soluble cyt*c* into the cytosol. Remarkably, cytoplasmatic cyt*c* actively participates in the execution of the programmed cell death by binding to the apoptosis protease activation factor 1 (*i.e.*, APAF-1) with the subsequent activation of pro-caspase-9. However, ligand (*e.g.*, CO and NO) binding to the heme-Fe-atom of CL-cyt*c* and the heme-Fe-based scavenging of reactive nitrogen and oxygen species participate to the impairment of apoptosis. Here, the ligand binding and enzymatic properties of CL-cyt*c* are examined to highlight the role of CL in modulating pro- and anti-apoptotic roles of cyt*c*.

BIO-PL3

Molecular determinants of infectious diseases: protein structures at the service of biology

Rita Berisio

Institute of Biostructures and Bioimaging, Italian Research Council

There is an overall consensus that to develop improved drugs and vaccine control strategies, we need to gain a better understanding of the biology of involved pathogens. Innate immune recognition of bacterial pathogens is based on the detection of constitutive and conserved products of microbial metabolism on the bacterial cell surface. Lipopolysaccharides, lipoproteins, peptidoglycan and lipoteichoic acids are all unique molecules synthesized by bacteria but not eukaryotic cells. These products, denominated Pathogen Associated Molecular Patterns, are considered as the key molecular signatures of microbial invaders by the innate immune system and their recognition signals the presence of infection. The molecular arsenal of human host immune responses and small molecule mediators together define a dynamic host-pathogen interactome. Therefore, targeting proteins involved in host-pathogen interactions is a promising strategy for the development of new and effective anti-microbial drugs. Structural biology, including molecular biology, biochemistry, and biophysics concerned with the three-dimensional structure of biological macromolecules, is of great interest to biologists, since macromolecules carry out most of the cellular functions. As such, it has enormous impact on biomedical research and on biology in general. A tour through applications of structural biology to the understanding of molecular determinants of cellular processes will be presented.

Chimica dei Sistemi Biologici

Keynote

BIO-K1

The double life of PHD fingers: epigenetic readers or structural hubs for multiple interactions?

Giovanna Musco
Biomolecular NMR Unit c/o S. Raffaele Scientific Institute, Via Olgettina 58 20132, Milano

In recent years the PHD finger domain, one of the most recurrent domains in nuclear proteins, has been extensively investigated from both the structural and functional point of view. This small Zn2+binding motif has emerged as a robust conserved scaffold with diversified activities: it can work not only as an epigenetic reader sensing the modification status of histone H3, but can also function as a general protein–protein interaction motif, thereby expanding its role in diverse cellular processes including transcriptional regulation and/or signal transduction. Its high functional versatility relies on the low secondary structure content and on subtle but significant changes in amino acid compositions contributing to the domain functional and structural plasticity. Herein I will discuss two paradigmatic examples (AIRE-PHD and Sp140-PHD) for the structural and functional versatility attributed to this domain.

BIO-K2

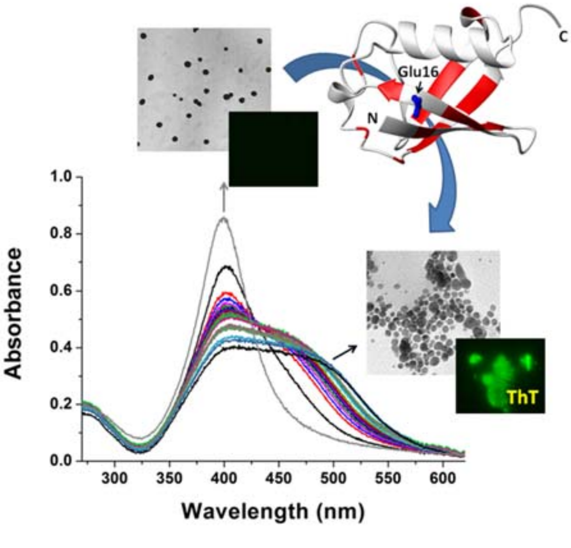
Amyloid Transition of Ubiquitin on Silver Nanoparticles

Fabio Arnesano

Department of Chemistry, University of Bari "Aldo Moro", via E. Orabona 4,
70125 Bari, Italy

fabio.arnesano@uniba.it

The interaction of nanoparticles with proteins has emerged as a key issue in addressing the problem of nanotoxicity. We investigated the interaction of silver nanoparticles (AgNPs), produced via laser ablation, with human ubiquitin (Ub), a protein essential for degradative processes in cells. The surface plasmon resonance peak of AgNPs indicates that Ub is rapidly adsorbed on the AgNP surface yielding a protein corona; the Ub-coated AgNPs then evolve into clusters held together by an amyloid form of the protein, as revealed by binding of thioflavin T fluorescent dye. Transthyretin, an inhibitor of amyloid-type aggregation, impedes aggregate formation and disrupts preformed AgNP clusters. In the presence of sodium citrate, a common stabilizer which confers an overall negative charge to the NPs, Ub is still adsorbed on the AgNP surface, but no clustering is observed. Ub mutants bearing a single mutation at one edge β strand (i.e. Glu16Val) or in loop (Glu18Val) behave in a radically different manner [1].



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BIO-K3

Lipid selection and catalysis in FAAH for endocannabinoid degradation

Marco De Vivo

Drug Discovery and Development (D3) – D3 Computation
Italian Institute of Technology
Via Morego, 30 – Genoa, IT

marco.devivo@iit.it

Anandamide is one of the main neurotransmitters involved in the endocannabinoid-mediated control of pain. Its biological functions are mainly regulated by the fatty acid amide hydrolase (FAAH) that cleaves anandamide to generate arachidonic acid via a specific mechanism of hydrolytic degradation.1 The enzymatic mechanism for lipid selection to specifically hydrolyze anandamide, rather than similar bioactive lipids, remains elusive. To clarify the regulatory mechanisms of lipid degradation in the endocannabinoid system, we comparatively analyzed microsecond-long molecular dynamics (MD) simulations of both wild-type and mutated FAAH, in complex with fatty acid substrates having different rates of hydrolysis (anandamide > oleamide > palmitoylethanolamide), embedded in a realistic membrane/water environment.2 Findings from MD simulations have been integrated with mutagenesis and kinetics experiments, confirming a structural framework for a lipid selection mechanism mediated by structural flexibility and gating residues between multiple binding cavities, as found in FAAH. Also, quantum mechanics/molecular mechanics (QM/MM) simulations have been used to unravel the whole catalytic cycle of FAAH in complex with its main substrate anandamide. We quantitatively describe the energetic cost of an exquisite catalytic strategy of FAAH to induce amide bond distortion,3 reactive nitrogen inversion, and amide bond hydrolysis in anandamide, promoting catalysis to completion. These mechanistic insights for lipid selection and degradation in FAAH might also favorably impact de-novo enzyme design or drug discovery efforts.

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BIO-K4

La Proteomica nello studio dei meccanismi cellulari

Piero Pucci
Dipartimento di Scienze Chimiche e CEINGE Biotecnologie Avanzate, Università di Napoli Federico II, Napoli, Italy

Con l'aumento dei numerosi progetti di sequenziamento dei genomi, si è verificata una concomitante crescita esponenziale del numero di sequenze proteiche la cui funzione biologica è ancora sconosciuta. Le scienze biologiche si trovano quindi ad affrontare una sorta di situazione paradossale in cui la sequenza proteica, il corrispondente gene che codifica per esse, la sua localizzazione cromosomica ed anche il meccanismo di regolazione possono essere definiti ma rimane completamente sconosciuto il ruolo biologico che svolge la proteina all'interno della cellula.

La Proteomica Funzionale può fornire un contributo basilare alla definizione della funzione biologica di una proteina mediante l'identificazione dei partners con cui essa interagisce. E' ormai chiaro, infatti, che i processi cellulari vedono la partecipazione di una moltitudine di proteine che si assemblano in modo rapido e transiente a formare grandi complessi funzionali in cui le componenti proteiche stabiliscono delle interazioni specifiche che intervengono a condizionare la realtà funzionale di una data proteina, che poi dissociano liberando singoli componenti proteici. Una singola proteina può assemblare con partners diversi a costituire complessi funzionali diversi, ognuno dotato di una propria specifica funzione biologica. Ne consegue che una proteina può possedere una sola attività ma molte funzioni biologiche. L'associazione di una proteina sconosciuta con partners che appartengono ad uno specifico complesso multiproteico coinvolto in un determinato meccanismo cellulare è quindi fortemente indicativa della sua funzione biologica.

La filosofia del metodo consiste nella possibilità di esprimere la proteina di interesse (esca) in forma ricombinante modificata con uno specifica marcatura (tag); il complesso dei partners molecolari della proteina esca può quindi essere purificato dall'intero estratto cellulare mediante tecniche basate sulla cromatografia di affinità utilizzando l'opportuno ligando (anti-tag) immobilizzato su un supporto insolubile. Una strategia alternativa prevede l'utilizzo di metodologie di immunoprecipitazione in cui la proteina esca forma in vivo i complessi multiproteici interagendo con i suoi partners specifici. Una volta formatisi, tali complessi vengono immunoprecipitati utilizzando un anticorpo specifico per l'epitopo (tag) con cui è stata marcata la proteina esca. In entrambi i casi, le proteine costituenti i complessi funzionali sono frazionate mediante SDS-PAGE ed identificate utilizzando metodologie di spettrometria di massa tandem accoppiate a cromatografia liquida capillare (nanoLC-MS/MS).

Saranno descritti alcuni esempi dell'applicazione di studi di proteomica funzionale alla definizione di meccanismi cellulari quali la trascrizione genica e il trasporto di rame.

Chimica dei Sistemi Biologici

Oral

BIO-O1

From Lipid A-like structures to simplified small molecules active on TLR4

Valentina Calabrese[a], *Francesco Peri*[a], *Carlotta Ciaramelli*[a], *Stefania Sestito*[a], *Roberto Cighetti*[a]

a Dipartimento di Biotecnologia e Bioscienze, Università di Milano-Bicocca, Piazza della Scienza 2, 20126, Milano, Italy.

valentina.calabrese@unimib.it

Toll-like receptors play a critical role in the recognition of conserved pathogen-associated molecular patterns (PAMPs) derived from various microbial pathogens. Among these TLR4 recognizes a broad variety of substances from viruses and mycoplasma, and is also activated by endogenous factors. TLR4 antagonists that reduce TLR4 activation by bacterial endotoxin (LPS), are hit compounds to develop drugs against sepsis and septic shock. Otherwise compounds that behave as TLR4 agonists could be used as vaccine adjuvants. Lipid A is the endotoxic portion of LPS, the natural TLR4 ligand, and has been used for decades as a model scaffold to synthesize a large variety of TLR4 modulators. However the syntheses of Lipid A mimetics are really challenging and provide poorly soluble products which forms aggregates that complicates their use *in vitro* and *in vivo*. We synthesized several small molecules active as TLR4 modulators, with the aim of simplifying the synthesis by reducing the chemical complexity of the compounds, thus preserving their activity on the TLR4 activation pathway[1-3]. The syntheses, the biological activity and the binding studies on purified receptors of these compounds will be presented.

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BIO-O2

Single molecule approach to study pore formation in membranes by Bcl-2 proteins

Katia Cosentino, Yamuna Subburaj, Joseph D. Unsay, Ana J. García-Sáez

Max Planck Institute for Intelligent Systems, 70569 Stuttgart, Germany
Interfaculty Institute of Biochemistry, University of Tuebingen, 72076 Tuebingen, Germany

cosentino@is.mpg.de

The Bcl-2 proteins are essential regulators of the mitochondrial outer membrane permeabilization (MOMP) process by forming pores [1, 2]. These pores allow the release of apoptotic factors into the cytosol, such as cytochrome c, inducing caspase activation and mediating cell death [3]. The dysregulation of this function has an important role in the onset of tumors and neurodegenerative diseases [4].

Despite extensive studies, the molecular mechanism of membrane permeabilization by pore formation remains to be clarified.

Here, we studied the assembling mechanism of Bax, a proapoptotic member of the Bcl-2 protein family, which executes pore formation. By using membrane models and a single molecule approach, we found that Bax molecules assembled mainly in dimers, tetramers and hexamers, supporting the hypothesis of Bax oligomerization by dimer condensation. In addition, in the presence of the antiaptototic Bcl-xL protein, a decrease number of oligomeric Bax species was observed, confirming the inhibitory effect of this protein in inducing mitochondrial apoptosis [5].

Furthermore, in order to elucidate the role of lipids in MOMP, we studied the molecular effects of cardiolipin (CL), a lipid mainly found in mitochondrial membranes, on model systems. We found that CL induced membrane reorganization by formation of non-lamellar structures, similar to those found in mitochondrial contact sites, supporting an involvement of this lipid in membrane permeabilization by pore formation [6].

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BIO-O3

The Spectroscopic Probe *p*CN-Phe for Studying Peptide-Membrane Interactions

M. De Zotti[a], *S. Bobone*[b], *L. Stella*[b], *C. Toniolo*[a], *F. Formaggio*[a]

a ICB, Padova Unit, CNR, Department of Chemistry, University of Padova, Via Marzolo 1, 35131, Padova, Italy
b Department of Chemical Sciences and Technologies, University of Rome "Tor Vergata", Via della Ricerca Scientifica 1, 00133, Rome, Italy

marta.dezotti@unipd.it

Nitrile-derivatized amino acids have been successfully employed as combined fluorescence (*e.g.*, Phe) and IR (-CN) absorption probes for investigating their local environments in proteins [1,2]. Indeed, it is known that the CN stretch frequency shifts, and its spectral lineshape changes, when this group is exposed to solvents of different polarity. On this basis, we decided to insert nitrile-containing α-amino acid residues (Fig. 1) at different positions in the sequences of two peptaibiotics, trichogin GA IV and alamethicin F50/5. These two peptides are able to interact with biological membranes through mechanisms not yet completely understood. By exploiting both IR absorption and fluorescence spectroscopies, we studied the peptide behavior in the presence of liposomes. Our results offer a picture of peptide insertion into the membrane and allow an assessment of the effectiveness of the chosen probe for the investigation of peptide-membrane interactions. Moreover, they highlight its sensitivity to different (water *vs*. membrane) environments when incorporated into a peptide.

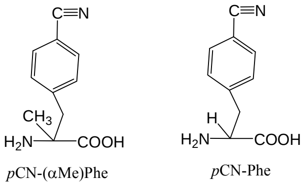

Fig. 1 Chemical structure of the *p*CN-containing, α-amino acids employed in this work.

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BIO-O4

Trehalose-conjugated peptides as inhibitors of Aβ(1-42) oligomerization

Michele Saviano[a], *Ida Autiero*[b], *Emma Langella*[b], *Maria Laura Giuffrida* [c], *Giuseppe Pappalardo* [c], *Paolo De Bona*[d]

a Istituto di Cristallografia, CNR, Via Amendola 122/O , 70126, Bari, Italy
b Istituto di Biostrutture e Bioimmagini UOS Napoli, CNR, Via Mezzocannone 16, 80134, Napoli, Italy
c Istituto di Biostrutture e Bioimmagini UOS Catania, CNR, Via Paolo Gaifami,18, 95126, Catania, Italy
Department of Biochemistry and Molecular Biophysics, Washington University School of Medicine, 660 S. Euclid Ave., MO 63110, St. Louis, USA

michele.saviano@ic.cnr.it

Alzheimer's disease (AD) is currently one of the most common and devastating forms of dementia correlated with β-amyloid peptide (Aβ) accumulation in human brain tissue. Inhibiting Aβ self-oligomerization might, therefore, provide a useful approach to treating and controlling the pathogenic pathways underlying AD. Several small molecules capable of binding to Aβ have been identified, among these trehalose and the pentapeptide LPFFD have been reported to have effects on the aggregation as well as on Aβ neurotoxicity. We hypothesized that the conjugation of trehalose with the pentapeptide LPFFD would result in new compounds with higher affinity for Aβ thereby acting as new effective inhibitors of Aβ's cellular toxicity.

In this communication, we report the synthesis and the spectroscopic characterization of three new trehalose conjugates with the LPFFD peptide. All the synthesized compounds were tested as inhibitors of both Aβ's fibrillogenesis and toxicity toward pure cultures of rat cortical neurons. In addition, the effects of these glycopeptides on the morphology of Aβ aggregates were analysed by AFM microscopy. In addition, a molecular dynamics approach was used to investigate the interaction between trehalose-conjugates and the Aβ (1-42) penta-oligomer system focusing on *i)* the binding modes of the ligands, *ii)* the resulting destabilizing effects on the global amyloid structure, and *iii)* the role of the trehalose moiety. Our results would be useful starting points for the rational design of new promising candidates with improved anti-aggregating features.

BIO-O5

Studies of the interactions of antimicrobial peptides with *E.coli* cells

Alessandra Romanelli

Dipartimento di Farmacia, Università di Napoli "Federico II", Via Mezzocannone 16, 80134, Napoli, Italia

alessandra.romanelli@unina.it

The mechanism of action of antimicrobial peptides has been investigated by different biophysical techniques using model systems, as lipid mixtures, to reproduce the outer leaflet of bacterial membranes. Studies carried out by solid state NMR and time lapse fluorescence revealed that the behavior of the peptides on the membranes depends on the composition of the membrane[1,2]. Thus the choice of the model system for the bacterial cells is not an easy task; we will likely have a deeper understanding of the mechanism by which antimicrobial peptides kill bacterial cells studying the interactions of such peptides with whole cells. We recently reported secondary structure studies of two antimicrobial peptides, magainin 2 and cecropin A, in the presence of *E.coli* cells by Circular Dichroism (CD) [3]. In this work we explored the interactions of peptides belonging to the temporin family (TB and the analogue TB_KKG6A) with *E.coli* cells by CD. Furthermore NMR studies on TB_KKG6A, previously developed by us [4], were carried out demonstrating that upon interaction with *E.coli* the peptide adopts a helical conformation; some structural differences with the structure obtained in the presence of LPS were found.

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BIO-O6

Identification of peptidomimetic compounds targeting tumor angiogenesis through MMP2 inhibition

Chiara Calugi[a], Francesca Bianchini[b], Gloria Menchi[a], Antonio Guarna[a], Lido Calorini[b], Andrea Trabocchi[a]

a Department of chemistry "Ugo Shiff", University of Florence, Via della Lastruccia 13,50059, Sesto Fiorentino, Italy
b Departement of clinical and experimental biomedical science, "Mario Serio", University of Florence, Viale Morgagni 50, 50134, Florence, Italy

chiara.calugi@unifi.it

Matrix metalloproteinases (MMPs) are zinc-dependent proteinases involved in the turnover and remodeling of the extracellular matrix on both normal and pathological processes. Among them, MMP2 plays a central role in pathological events leading to cancer, inflammatory and cardiovascular diseases and neurological disorders [1]. Owing to its crucial role, pharmacological regulation of MMP2 has been extensively studied and several inhibitors mainly characterized by the presence of a hydroxamate Zn-binding group have been developed. We recently reported the identification of a small library of D-proline-derived hydroxamic acids as anthrax lethal factor inhibitors [2]. Taking advantage of the structural similarity between these two metalloproteinases, we envisaged the possibility to exploit such library in order to target MMP2. One of these D-proline compounds, containing two hydrophobic groups at position 1 and 4 of the pyrrolidine ring, proved to be an effective MMP2 inhibitor, resulting in the blockade of neoangiogenesis *in vivo*. Moreover, docking studies were performed in order to investigate the possible binding mode of this class of compounds within the MMP2 catalytic site and to determine the structural determinants crucial for inhibition.

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BIO-O7

Structural bioinformatics of metalloproteins

Antonio Rosato[a,b], *Claudia Andreini*[a,b], *Yana Valasatava*[b]

a Dipartimento di Chimica, Università di Firenze, Via della Lastruccia 3, 50019, Sesto Fiorentino, Firenze
b Centro di Risonanze Magnetiche, Università di Firenze, Via Luigi Sacconi 6, 50019, Sesto Fiorentino, Firenze

rosato@cerm.unifi.it

Bioinorganic or biological inorganic chemistry is the discipline dealing with the interaction between inorganic substances and molecules of biological interest. The interaction between metal ions or metal-containing cofactors and biological macromolecules is often addressed at the 3D structural level, with atomic detail. These studies constitute an intersection between bioinorganic chemistry and structural biology. If the 3D structure of a metalloprotein is known, then it can be used to gain a deep insight into functional features. We showed that the functional/biochemical relevance of the interaction between the metal ion(s) and the biological macromolecule is better understood when one goes beyond the details of the metal coordination sphere. In a metalloprotein, a suitable object for this purpose is the ensemble of atoms containing the metal ion or cofactor, its ligands and any other atom within 5 Å from a ligand. We call this a Minimal Functional Site (MFS). The MFS describes the local 3D environment around the cofactor, independently of the larger context of the protein fold in which it is embedded. A database of all MFS's is available at http://metalweb.cerm.unifi.it/. MFS's can be compared in a pairwise manner, across a family or various families of metalloproteins/enzymes, or can be searched in order to find structural matches to new sites. The kind of information that can be gained from these approaches will be described.

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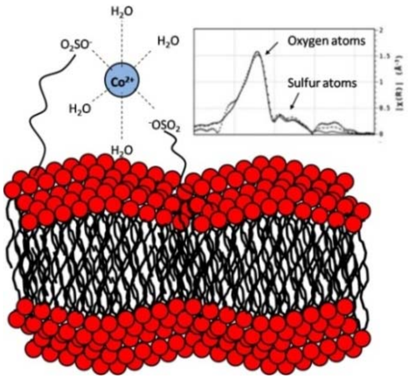
BIO-O8

How cobalt binds to photosynthetic bacterium *R. sphaeroides*: a XAS study

Benny Danilo Belviso[a], *Rocco Caliandro*[a], *Francesca Italiano*[b], *Benedetta Carrozzini*[a], *Alessandra Costanza*[c], *Massimo Trotta*[b]

[a]*CNR – Istituto di Cristallografia, Via Amendola 122/o, 70126, Bari, Italy*
[b]*CNR – Istituto per i Processi Chimico Fisici, Via Orabona 4, 70126, Bari, Italy*
[c]*CNR - Istituto di Produzione delle Piante, Via Amendola 122/o, 70126, Bari, Italy*

danilo.belviso@ic.cnr.it



Cobalt ion is required for cell activities of bacterial organisms; however, at high concentrations, this heavy metal ion is toxic because increases the oxidative stress and hinder correct macromolecular functions, modifying the ion transport[1]. The photosynthetic bacterium *Rhodobacter sphaeroides* (*Rs*) tolerates high cobalt concentrations and can accumulates it mostly on cellular surface. This characteristic makes *Rs* a potential candidate for cobalt bioremediation process. The mechanisms involved in the interaction between a *Rs* and cobalt ion together with the fate of bioassorbed coabalt are relevant for bioremediation development but, at the present, they are still unknown. Here we present the results of an X-ray absorption spectroscopy (XAS) study conducted to unravel the binding sites of the cobalt ion on the cellular components of *Rs*[2]. This study shows that cobalt binds to carboxylate in the soluble portion of the cell while, on the photosynthetic membrane, it binds to oxygen atoms of a sulfonic group, suggesting that sulfolipids are present in cobalt-exposed cells and are involved in a typical response mechanism of the photosynthetic membrane of *Rs* to high cobalt concentration.

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BIO-O9

Porphyrin-proteasome interaction: a kinetic, spectroscopic and modeling approach

Santoro A.M.,[a] *Cunsolo A.,*[b] *D'Urso A.,*[b] *Coletta M.,*[c] *Sbardella D.,*[c] *Tundo G. R.,*[c] *Diana D.,*[d] *Fattorusso R.,*[e] *Fattorusso C.,*[f] *Persico M.,*[f] *Milardi D.,*[a] *Purrello R.*[b]

[a] *Istituto di Biostrutture e Bioimmagini - CNR UOS di Catania c/o Dipartimento di Scienze Chimiche, Viale Andrea Doria 6, 95125 Catania (Italy)*
[b] *Dipartimento di Scienze Chimiche, Università di Catania, Viale Andrea Doria 6, 95125 Catania (Italy)*
[c] *Dipartimento di Scienze Cliniche e Medicina Traslazionale, Università di Roma Tor Vergata, Via Montpellier 1, I-00133 Roma (Italy)*
[d] *Istituto di Biostrutture e Bioimmagini, CNR, Via Mezzocannone 16, Napoli, Italy*
[e] *Dipartimento di Scienze Ambientali, Seconda Università di Napoli, Via Vivaldi 46, Caserta, Italy*
[f] *Dipartimento di Farmacia, Università di Napoli, Università di Napoli* **"** *Federico II*****"***, Via D. Montesano, 49 I-80131 Napoli, Italy*

amsantoro@unict.it

Proteasome inhibition is an attractive anticancer strategy because protein homeostasis is crucial to cancer cell survival. We recently [1] found that cationic porphyrins reversibly inhibit the three main protease activities of proteasome. Actually porphyrins are already used in anticancer photodynamic therapy (PDT), and a combination of PDT with proteasome inhibitors has been shown to remarkably enhance tumor cells cytotoxicity. Understanding the molecular bases of such inhibition represents a crucial step for the identification of new drug candidates. The unique spectroscopic features of porphyrins make them excellent probes for the interactions of proteasome with other inhibitors, thus, we investigated the inhibition mechanism using a combination of spectroscopic and computational techniques. We performed stopped –flow UV-Vis analysis, NMR and molecular docking studies to understand porphyrin binding onto 20S proteasome. Finally, a preliminary investigation to verify inhibitor proteasome activity on cell cultures has been booted.

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BIO-O10

Looking for new efficient G-quadruplex binders

Jussara Amato[a], *Domenica Musumeci*[b], *Antonio Randazzo*[a], *Ettore Novellino*[a], *Concetta Giancola*[a], *Daniela Montesarchio*[b], *Bruno Pagano*[a]

a Dipartimento di Farmacia, Università di Napoli "Federico II", Via D. Montesano 49, 80131, Napoli, Italy
b Dipartimento di Scienze Chimiche, Università di Napoli "Federico II", Via Cintia 4, 80126, Napoli, Italy

jussara.amato@unina.it

The discovery of small organic molecules efficiently recognizing G-quadruplex (G4) DNA is one of the "hottest" research areas in the study of these unusual nucleic acids structures, particularly motivated by the need for effective anticancer agents.[1] In fact, G4 structures in telomeres and oncogene promoters have been recognized as key elements in the regulation of cancer cell proliferation.[2] Thus, considerable efforts are currently devoted to the design of novel compounds able to target them. Our research group, together with our partners, is contributing to the search of molecules specifically recognizing peculiar G4 structures, with the aim of finding suitable candidate drugs. To this end, we are focusing on the identification of drug-like molecules able to modulate the stability of G4 structures or promote their formation under physiological conditions in order to fine-tune their properties. This exceptional impulse is producing a huge number of putative ligands, for which fast and reliable screening methodologies are urgently required. For this purpose, we have recently developed a simple, cheap and highly reproducible affinity chromatography-based method, based on a G4-functionalized resin, enabling a rapid and efficient identification of G4-specific ligands.[3] The devised protocol allows us to identify small molecules specifically interacting with a G4 structure, capturing and then releasing them through a cation-induced control of the folding/unfolding processes of the immobilized G4-forming sequence.

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BIO-O11

Self-assembly of the newly discovered DNA base 5-carboxylcytosine on graphite

S. Irrera[a], D. Passeri[b], M. Reggente[b], M. Rossi[b] and G. Portalone[a]

[a]Department of Chemistry , 'Sapienza' University, P.le A. Moro 5, I-00185 Rome, Italy

[b]Department of Basic and Applied Sciences for Engineering, 'Sapienza' University, Via A. Scarpa 14, 00161 Rome, Italy

5-carboxylcytosine (caC) has been recently detected in mammalian cells and proposed as the eight DNA base [1], but its functions and biological roles still remain unknown. The only accurate structural information on caC relies on its chloride, bromide, nitrate and phenylbiguanidium salts determined by X-ray single-crystal diffraction (XRD) [2]. Self-assembling of caC into adlayers has many applications, as it can transfer molecular properties to the adsorbing surface which can be used in nanotechnology and nanomedicine, i.e. exploiting nucleobase intermolecular forces in molecular recognition through base-pairing [3]. Here we report a combined approach of XRD, scanning tunneling microscopy (STM) and atomic force microscopy (AFM) on the adsorption of caC on highly oriented pyrolytic graphite (HOPG) surface by drop-casting from a water solution of calcium hydroxide (Fig. 1). AFM shows networks formed by caC on the surface as monolayers and one-molecule filaments. STM images gives insights into the role of calcium ions in the adsorption.

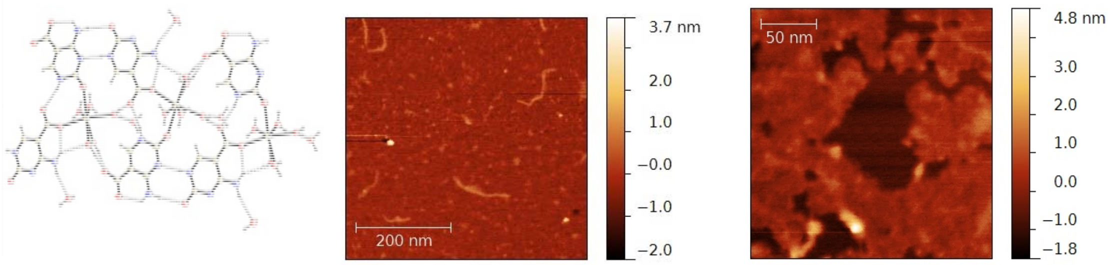

Fig 1: Crystal structure of 5-carboxylcytosinate calcium eptahydrate (left). 2D self-assembly of caC on HOPG: 1nm (z) filaments (central) and monolayer (right).

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BIO-O12

Enantioselective extraction mediated by a chiral silicon surface

<u>A. D'Urso,</u>[a] *C. Tudisco,*[ab] *F.P. Ballistreri,*[a] *G.G. Condorelli,*[ab] *R. Randazzo,*[a] *G.A. Tomaselli,*[a] *R.M. Toscano,*[a] *G. Trusso Sfrazzetto,*[a] *A. Pappalardo*[a]

a Dipartimento di Scienze Chimiche, Università di Catania, V.le A. Doria 6, 95125, Catania, Italy.
b INSTM Udr of Catania, Viale Andrea Doria 6, 95125, Catania, Italy

adurso@unict.it

Chirality is a property of matter that plays a key role in several branches of science, from optics to medicine.[1] Many biological processes involve chiral molecules in order to achieve highly specific and selective interactions. The separation of chiral isomers is an appealing burgeoning field that captures the interest of many researchers.[2] An interesting approach for harnessing the full potential of molecular receptors consists of their arrangement in monolayers hosted on an inorganic surface.[3] A chiral organic–inorganic hybrid material, based on a porous silicon surface functionalized with a chiral cavitand, was designed and synthesized.[4] The affinity of this device in water toward a bromine-marked alkyl-ammonium salt has been evaluated using XPS detection. UV and CD measurements highlight the enantioselective extraction from a racemic mixture in water of the S-enantiomer of the selected guest.[5]

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BIO-O13

Synthetic glycolipids active on TLR4 receptor: a new generation of therapeutics

Francesco Peri[a], *Valentina Calabrese*[a], *Carlotta Ciaramelli*[a], *Stefania Sestito*[a], *Roberto Cighetti,*[a]

[a]*Dipartimento di Biotecnologie e Bioscienze, Università di Milano Bicocca, P.zza della Scienza, 2 , 20126, Milano, Italy.*

francesco.peri@unimib.it

Toll-like receptor 4 (TLR4) is the human receptor for bacterial endotoxin (lipopolysaccharide, LPS). TLR4 in combination with other receptors (LBP, CD14, MD-2) detect minute amounts of LPS aggregates and activates the immune and inflammatory responses to pathogen infections. However, excessive and deregulated TLR4 activity leads to serious syndromes such as septic shock and sepsis, and other inflammatory and autoimmune diseases. Small molecules active in modulating TLR4 activity are therefore lead compounds for a new generation of therapeutics. Over the last 7 years our group rationally designed and synthesized glycolipids active in modulating the TLR4 activity as agonists and antagonists.[1] Cationic glycolipids[2] and anionic lipid A mimetics[3,4] inhibit endotioxin-induced cytokine production in innate immunity cells. Some of these molecules are in preclinical phase as anti-septic shock agents and as drugs against other TLR4-dependent pathologies.[5] The mechanism of action of these compounds and nanoparticles in blocking TLR4 signal has been studied, and will be presented in the communication.[6]

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BIO-O14

Charged selective membranes for protein separation with similar molecular weight on the basis of size and electrostatic interactions

Rosalinda Mazzei[a], *Anna Maria Szymczak*[a], *Enrico Drioli*[a], *Mohamed Al-Fageeh*[b], *Mohammed Aljohi*[b], *Lidietta Giorno*[a]

[a]*Institute on Membrane Technology, CNR-ITM C/o University of Calabria, Via P. Bucci 17C, 87036 Rende (CS), Italy*
[b]*National Centre for Biotechnology, King Abdulaziz City of Science and Technology (KACST), P.O. Box 6086, Riyadh 11442, Saudi Arabia*

r.mazzei@itm.cnr.it

The fractionation of proteins that do not differ in molecular mass is an high challenge to be reached. By ultrafiltration (UF) process the complete separation is only possible for proteins that differ in molecular mass by at least a factor of 10. In the recent literature more attention was given on careful adjustment of physicochemical parameters, like pH or ionic strength of the solution, that can improve the process[1][2][3].
In this work a complete separation of α-lactalbumin (ALA, 14.4 kDa) from β-lactoglobulin (BLG, 18.4 kDa) with an high recovery factor was achieved starting from binary protein mixture. By properly tuning membrane surface, protein charge, ionic strength as well as optimizing fluid dynamic conditions, it was possible to obtain high selectivity and high recovery factor. The transport through the membrane is promoted by a combination between convection, electrostatic repulsion as well as protein aggregation state.

This work has been financially supported by the project "Membrane systems in regenerative medicine, tissue engineering, and biotechnology" AGREEMENT No. KACST- ITM-CNR/03.

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BIO-O15

Didymin rescues neuronal cells from oxidative damage in a biohybrid membrane system

S. Morelli, A. Piscioneri, S. Salerno, E. Drioli, L. De Bartolo

National Research Council - Institute for Membrane Technology (ITM–CNR), cubo 17C, Via Pietro BUCCI, 87036 Rende CS, Italy

s.morelli@itm.cnr.it

Oxidative stress plays an important role in Alzheimer's disease and other neurodegenerative disorders. Didymin is a novel flavonoid glycoside richly expressed in citrus fruits, with anticancer properties but its neuroprotective property is not yet well-characterized.

For the first time in this study the neuroprotective effect of didymin against hydrogen peroxide (H_2O_2)- induced damage in neuronal cells was investigated.

A biohybrid membrane system constituted by biodegradable membranes and neuronal cells [1-2] was used as model system for the *in vitro* induction of oxidative stress to investigate the neuroprotective effect of didymin. Cells were exposed to different concentrations of didymin after H_2O_2 insult.

Treatment with didymin markedly decreased intracellular ROS generation and attenuated H_2O_2-induced cell viability loss and apoptotic cell death in a dose-dependent manner. The mechanisms by which didymin protected neuron cells from oxidative stress included the induction of several antioxidant enzymes, Catalase, SOD and GPx. Furthermore, didymin dose-dependently restored H_2O_2-induced loss of mitochondrial membrane potential and inhibited apoptotic features such as p-JNK and Caspase-3 activation. This study showed the ability of didymin to suppress and/or reverse H_2O_2-induced damage in neuronal cells by using a membrane system as an *in vitro* model.

These data suggest that didymin may be a potential therapeutic molecule for the treatment of neurodegenerative disorders associated with oxidative stress, or employed in physiological conditions as anti-aging molecule.

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BIO-O16

Unfolding mechanism characterization of prokaryotic zinc finger domain

Palmieri M.[a], Russo L.[a], Malgieri G.[a], Rivellino A.[a], J.V. Caso[a], de Paola I.[b], Zaccaro L.[b], Sciacca M. F.M.[c], Majewska R.[a], De Stefano M.[a], Pedone P.V.[a], Isernia C.[a], Milardi D.[c], Fattorusso R.[a]

a Department of Environmental, Biological and Pharmaceutical Science and Technology,
Second University of Naples, Via Vivaldi 43,81100 Caserta, Italy
b IBB-CNR ,Via Mezzocannone 16,80134 Naples, Italy
c IBB-CNR ,Viale A. Doria 6, 95125 Catania, Italy

maddalena.palmieri@unina2.it

Given their abundance and frequent occurrence in many biological processes, it is important to clarify the molecular roles of metal ions in protein folding reactions. The aim of this study is to explore the mechanisms through which a cofactor influences the protein folding reaction. Starting from two homologous proteins, Ros87, containing a prokaryotic zinc finger domain, and $Ml4_{52-151}$, lacking the zinc ion, we have described the thermal unfolding mechanisms of three homologs proteins (Ml1, Ml2, Ml3) having an atypical metal coordination sphere. Our data illustrate that not only the presence of the zinc ion but also the different metal coordination sphere can stabilize, through a partly downhill folding mechanism, a conformational intermediate state [1]. Fully downhill folding proteins have been predicted to be rather rare in nature, because they miss a large folding barrier that can guard against aggregation and proteolysis in keeping unfolded structures less populated. On the other hand, partly downhill folding pathways driven by the metal coordination could be diffused among metal binding proteins. Moreover, one can infer that a native protein folding pathway could be modified in the presence of metal ions, switching it to a more delicate downhill mechanism. This would enhance the possibility of misfolding events, also through the stabilization of intermediate states that have been proven to be relevant in many pathological processes.

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BIO-O17

Microrespirometria analitica: applicazione in condizione di microgravità

L.Campanella[a], *G.Merola*[a], *S.Plattner*[a], *M.Perelli*[b], *A.Negri*[b], *G.Pepponi*[b]

a Dipartimento di Chimica, Università di Roma Sapienza, Piazzale A.Moro 5, 00185, Roma, Italia
b IMT srl, Via Carlo Bartolomeo Piazza 8, 00161, Roma, Italia

luigi.campanella@uniroma1.it

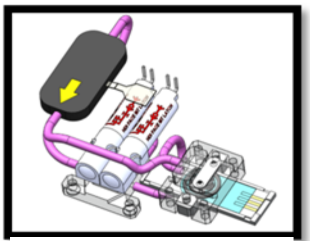

Fig.: Sistema di misura miniaturizzato

La respirometria è un metodo sperimentale che ha trovato rilevanti e significative applicazioni in vari settori delle scienze, dalla chimica alla tossicologia, dalla biologia vegetale alle scienze agrarie, dalla sensoristica alle scienze ambientali. Consiste nella misura della respirazione di un sistema biologico aerobico, correlando i relativi risultati alle finalità applicative specifiche e diverse da caso a caso. La misura impiega tre possibili differenti elettrodi indicatori: l'elettrodo di Clark e sue derivazioni per la misura dell'ossigeno, un elettrodo a diffusione gassosa per la determinazione della CO_2, un elettrodo del tipo FET per la misura del pH. Una delle recenti più innovative applicazioni di questo metodo sperimentale è in relazione alla sua implementazione in missioni spaziali per rispondere alle domande: come la respirazione di un sistema biologico aerobico, costituito da cellule di lievito Saccaromyces Cerevisiae, è influenzata da condizioni di microgravità? Come un sistema respirometrico potrebbe essere impiegato per rilevamenti ambientali e metabolici di interesse di missioni spaziali? Di certo questa applicazione automatizzata ha obbligato, in relazione al ridotto spazio disponibile nel satellite ospitante, alla miniaturizzazione della cella e del sistema elettrodico, alla ottimizzazione in termini di tempi e metodi della sospensione delle cellule di lievito e delle condizioni sperimentali, in particolare del flusso della soluzione di alimentazione e della pulizia superficiale degli elettrodi. Il tempo di misura viene dilatato a circa 1' rispetto ai tradizionali 30" e le alterazioni alle curve respirometriche da parte di tossici richiedono in preferenza l'approccio cinetico, introducendo la relativa soluzione di questi durante la registrazione della curva respirometrica e rilevando la relativa variazione di pendenza.

BIO-O18

Premio Italfarmaco

On the roles of metal ions within complex biological pathways: the contribution of quantum mechanical methods

Marta E. Alberto

Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria,
Via P.Bucci ,87036, Arcavacata di Rende (CS), Italy

marta.alberto@unical.it

The role of metals in biology and medicine spans a remarkable functional range, from fundamental chemical reactions, such as hydrolysis, group transfer, dioxygen transport and activation promoted by metalloenzymes, to processes in which metal complexes induce apoptosis in tumor cells, to photophysical processes involved in the non-invasive medical photodynamic therapy. The proper description of metal containing systems remains a challenge for quantum chemistry and today is almost synonymous with DFT for medium-sized molecules. The power of the methodology for the modeling of metal-containing biological systems it is illustrated by presenting few representative applications in the above mentioned fields.
In particular, the outcomes of theoretical investigations on *i)* binuclear metallohydrolases reaction mechanisms [1] *ii)* mechanisms of action of classical and non-classical anticancer drugs [2] *iii)* design of molecular devices for photodynamic therapy [3] will be briefly discussed.

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BIO-O19

Lipase from Candida Rugosa immobilization on cellulose functionalized membrane

Francesca Militano, Emma Piacentini, Teresa Poerio, Rosalinda Mazzei*, Lidietta Giorno*

Istituto per la Tecnologia delle Membrane (ITM–CNR) c/o Università della Calabria, Via Pietro Bucci, 87030, Rende, Italia

t.poerio@itm.cnr.it, r.mazzei@itm.cnr.it

Enzyme immobilization is mainly performed to enable enzyme re-use and thereby changing the economics of the process towards a viable situation. Enzyme immobilization, in many cases, reduces the complexity of the industrial production processes, allowing continuous operation as well as better control of the catalytic process. Currently the production of high fructose corn syrup is probably the largest industrial process which uses immobilized enzymes [1]. To enhance the use of immobilized enzyme at industrial level, one of the major challenge is to find the immobilization technique that suit the ground requirements.

Polymeric membranes are efficient carriers for enzymes immobilization and often a modification of the membrane surface is necessary in order to introduce binding sites for the enzymes linkage. In this work is presented the immobilization of Lipase from *Candida Rugosa* on regenerated cellulose membrane by covalent attachment. The membrane was firstly activated by periodate oxidation in order to introduce dialdehyde groups on the membrane surface. Lipase was immobilized both directly on the activated membrane and also through two spacers of different length by using glutaradehyde as bifunctional binding agent. The amount of the immobilized enzyme and the catalytic activity were evaluated.

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BIO-O20

Chemical modification of PVDF Membranes for Tyrosinase Immobilization

C. Algieri, L. Donato, L. Giorno

National Research Council - Institute for Membrane Technology (ITM–CNR) c/o The University of Calabria, cubo 17C, Via Pietro BUCCI, 87036 Rende CS, Italy

c.algieritm@cnr.it

Polyvinylidene fluoride (PVDF, provided by GVS-Italy) membranes were chemically activated to have a suitable surface for covalent enzyme immobilization. The study was carried out using the tyrosinase as enzyme model [1-3]. The process was performed by grafting the membrane surface with 1,4-diaminobutane and subsequently by activating it with glutarhaldehyde. The acrtivated PVDF membranes were used to immobilize covalently the enzyme. The chemico-physical properties of un-modified and modified PVDF membranes were investigated by infrared spectroscopy, scanning electron microscopy and static contact angle measurement. The specific activity of free and immobilized enzyme was determined following the production of the L-DOPA in the time. The experimental results showed as the specific activity of the immobilized tyrosinase All these results showed as the modified PVDF is a promising material to use in enzyme immobilization processes.

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BIO-O21

Potenziale applicazione di Etosomi modificati per somministrazioni diverse da quella topica.

Cristiano M.C.[a], *Trapasso E.*[a], *Pasqua A.*[a], *Cilurzo F.*[a], *Di Marzio L.*[b], *Fresta M.*[a], *Paolino D*[a].

[a]*Dipartimento di Scienze della Salute, Università "Magna Graecia" di Catanzaro, Viale Europa – loc.Germaneto, 88100 Catanzaro, Italia.*
[b]*Dipartimento di Farmacia, Università "G. d'Annunzio" di Chieti, Via dei Vestini 31, 66100 Chieti, Italia*

mchiara.cristiano@unicz.it, paolino@unicz.it

Gli etosomi sono sistemi vescicolari colloidali innovativi contenenti concentrazioni elevate di etanolo[1]. Quest'ultimo, utilizzato come *penetration enhancer*, è responsabile della loro deformabilità; esso, ad elevate concentrazioni (35-45% p/p), a causa della sua potenziale tossicità, non può essere utilizzato per applicazioni diverse da quella transdermica. Nel presente lavoro sono stati realizzati etosomi contenenti basse concentrazioni di etanolo, tali da poter essere somministrati mediante per esempio iniezione intra-articolare di principi attivi per il trattamento dell'artrite reumatoide. La formulazione migliore è risultata essere quella contenente il 15% di etanolo. Essa ha evidenziato ottime caratteristiche chimico-fisiche: dimensioni medie pari a 190 nm, indice di polidispersione di ~0.14, potenziale zeta pari a circa -25.8 mV e una buona stabilità nel tempo. Inoltre, gli studi di efficienza di incapsulazione (EI%) hanno palesato una scarsa capacità delle vescicole di incapsulare i farmaci idrofili come l'ammonio glicirizzinato (EI=26%), ma nello stesso tempo una significativa capacità di veicolare molecole lipofile come l'oil-Red-O (EI=81%) e il desametasone (EI=80.50%). In una seconda fase del lavoro, etosomi privi di principio attivo sono stati incubati con concentrazioni crescenti di acido ialuronico ad elevato peso molecolare per ottenere una struttura gel-like da iniettare. Il polisaccaride è stato scelto per le sue importanti funzioni nei processi flogistici a carico delle sinovie. A tale proposito è stato studiato il comportamento reologico di questi sistemi mediate Kinexus Rotation Rheometer.

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BIO-O22

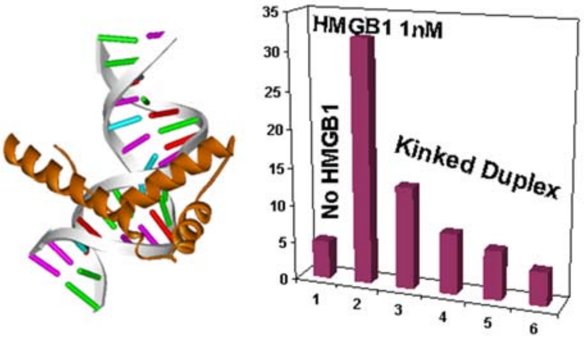
Inhibition of HMGB1 cytokine activity by use of DNA-based strategies

Domenica Musumeci[a,b], *Daniela Montesarchio*[a], *Giovanni N. Roviello*[b]

a Dipartimento di Scienze Chimiche, Università di Napoli ''Federico II'', 80126, Napoli, Italy
b Istituto di Biostrutture e Bioimmagini – CNR, 80134 Napoli, Italy

domenica.musumeci@unina.it

In the search for effective inhibitors of HMGB1, a nuclear protein involved in the architecture and reorganization of chromatin and that acts as a cytokine in a number of different inflammatory diseases [1], we recently proposed a novel approach based on the use, as HMGB1 ligands, of bent oligonucleotide duplexes [2]. We have found that the examined duplexes recognized HMGB1 with high affinity, and inhibited some cellular effects induced by the protein in a concentration dependent manner. Successive optimization has involved the study of unimolecular systems (kinked hairpin-loop DNA), with best response when derivatized with oligo-ethylene glycol moieties at the 5'-end and loop positions of the natural hairpin DNA [3]. These modifications confer improved enzymatic stability and structuring capability to analyzed system, as well as potentially enhanced pharmacokinetic properties, in view of future in vivo tests.



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BIO-O23

Anti-miR PNA as tools in cancer studies and therapy

Alex Manicardi[a], Massimiliano Donato Verona[a], Enrica Fabbri[b], Eleonora Brognara[b], Nicoletta Bianchi[b], Alessia Finotti[b], Roberto Gambari[b], Roberto Corradini[a],

a Dipartimento di Chimica, Università di Parma, Parco Area delle Scienze 17/1 , 43124,Parma, Italy
b Dipartimento di Scienze della Vita e Biotecnologie, Università di Ferrara, Via Fossato di Mortara n.74, 44100 Ferrara

Micro-RNAs (miRs) are regulatory short (19-23 bp) dsRNAs which modulate gene expression related to highly relevant biological functions such as differentiation, cell cycle, and apoptosis. Inhibition of miR activity (anti-miR approach) can lead to new treatments of several pathologies [1,2]. In this context, anti-miR peptide nucleic acids (PNAs) and their analogues are of great interest in drug development, and as a tool for the up-regulation of genes targeted by miR [3]. We here describe the synthesis of anti-miR PNAs of high affinity and high specificity for miR221 and miR222, which target important regulatory genes involved in tumor progression. A systematic study on the effect length and sequence of these PNA, and the development of suitable carrier systems which can deliver PNA to cancer cells have been carried out. These systems were found to up-regulate antitumor proteins such as P^{27}Kip1 and were used for the regulation of this and other key genes in breast cancer [4] as well as glioma [5] cells.The PNA were shown to increase the number of apoptotic cells in drug-resistant cell lines. Modifications of the PNA structure which allow better performances in anti-miR strategy will also be described.

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BIO-O24

Antibacterial peptides covalently bound to cotton garments

Andrea Orlandin[a], *Geta Hilma*[b,c], *Diana Coman*[c], *Simona Oancea*[b], *Fernando Formaggio*[a], *Cristina Peggion*[a]

[a] *ICB-CNR-Padova, Chemistry Department, University of Padova,35131 Padova, Italy*
[b] *Public Health Directorate of Sibiu, 551130 Sibiu, Romania*
[c] *University "Lucian Blaga" of Sibiu, 550012 Sibiu, Romania*

fernando.formaggio@unipd.it

We recently started the preparation of cotton fabrics characterized by covalently-bound, antibacterial peptides [1]. The production of garments able to protect from infections is highly desired for health care workers and patients [2]. The commercially available garments functionalized with silver-based compounds might display harmful effects [3]. In addition, the antimicrobial protection is limited in time due to the gradual release of the active ingredient. In this contribution we describe the preparation and the antibacterial effectiveness of cotton samples to which three antimicrobial peptides were covalently bound. The peptides were modeled after the peptaibiotics trichogin GA IV [4,5], halovir [6], and peptaibolin [7]. The activity of our cotton fibres against Gram-positive and Gram-negative bacteria was investigated with an appropriately modified experimental set-up.

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Chimica dei Sistemi Biologici

Poster

BIO-P1

NMR identification of natural compounds against neurodegenerative diseases

Erika Sironi, [a] *Cinzia Guzzi,* [a] *Francesco Nicotra,*[a] *Cristina Airoldi*[a]

a Dipartimento di Biotecnologie e Bioscienze, Università degli Studi di Milano-Bicocca,
P.zza della Scienza 2 ,20126, Milano, Italia

cristina.airoldi@unimib.it

In this communication we will show the potential of NMR approaches for the screening of natural product mixtures obtained from plant extracts, aimed at the discovery of new bioactive compounds. In particular we focused our interest on the identification of new ligands of amyloidogenic peptides and proteins involved in Alzheimer's,[1] mammalian prion[2] and Machado-Joseph's neurodegenerative diseases.[3] Due to the severe impact of these pathologies on the quality of life of the patients and their families, their massive economic burden, and the lack of effective therapies and diagnostic tools, there is an urgent need for effective molecules for their treatment and diagnosis. In this context, the availability of new screening methods is strategic.

Exploiting STD NMR experiments we were able to identify ligands of amyloid peptides and proteins in *Salvia sclareoides*,[4] *Genista tenera*[5] and green tea extracts.[6] The interaction of the best ones was further investigated at molecular level working on the purified molecules by combining NMR with other biophysical techniques such as AFM, CD, TEM and fluorescence.

Our data provide fundamental information for the rational design of new anti-amyloidogenic molecules.

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BIO-P2

New carnosine glycoconjugate as a metal-chelating and antiglycating compound

Giuseppa Ida Grasso[a], *Francesco Bellia*[a], *Graziella Vecchio*[b], *Giuseppe Arena*[b], *Enrico Rizzarelli*[a]

a Istituto di Biostrutture e Bioimmagini, CNR, Viale A. Doria 6, 95125, Catania, Italia
b Dipartimento di Scienze Chimiche, Università degli Studi di Catania, Viale A. Doria 6, 95125, Catania, Italia

francesco.bellia@cnr.it

Carnosine is an endogenous dipeptide widely and abundantly distributed in muscle and nervous tissues of numerous animal species. Many functions have been proposed for this compound, such as antioxidant, antiaggregant, antiglycating agent and metal ion-chelator, especially for copper(II) and zinc(II). The administration of carnosine provides benefits in Alzheimer's disease and other neurodegenerative disorders. However, the main limitation on therapeutic use of carnosine is associated with the hydrolysis by the specific dipeptidase carnosinase. The glycoconjugation has been found to be a promising approach to protect the dipeptide moiety in this respect. A number of glycoside derivatives of carnosine have also been characterized in terms of their binding features for copper(II) [1-4]. Here, we report the chemical and functional characterization a new carnosine derivative with trehalose, a multifunctional sugar tested for the treatment of Huntington's disease, Parkinson disease and several tauopathies. The copper(II) binding properties, as well as the antiaggregant and antiglycating actions make the new carnosine conjugate a promising agent for the treatment of a wide class of degenerative disorders.

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BIO-P3

Dynamics of PASTA domain of PonA2, a PBP from *Mycobacterium tuberculosis*

Luisa Calvanese[a], *Lucia Falcigno*[b], *Rita Berisio*[c], *Gabriella D'Auria*[b]

a CirPeb, Università di Napoli Federico II, Via Mezzocannone 16, 80134, Napoli, Italy
b Dipartimento di Farmacia, Università di Napoli Federico II, Via Mezzocannone 16, 80134, Napoli, Italia
c Istituto di Biostrutture e Bioimmagini,CNR, via Mezzocannone 16, I- 80134 Napoli, Italia

luisa.calvanese@unina.it

PASTA domain, a 65-70 a.a. motif, is frequently found in single or multiple copies at the C-terminal end of bacterial enzymes belonging to two different classes: penicillin binding proteins (PBPs) and Ser/Thr kinases (STPKs). It was suggested that PASTA might work as a sensor domain able to activate PBPs and STPKs by recognition of peptidoglycan fragments (i.e. muropeptides).[1] On this ground, PASTA-containing proteins have been often proposed as interesting targets for the design of new antimicrobials. Several studies dedicated to the binding and functional properties of PASTA motives confirm the role of sensor for PASTA units belonging to STPKs.[2] However, in our recent study dedicated to PASTA domain of ponA2, a PBP from *Mycobacterium tuberculosis* (the etiologic agent of tuberculosis) we found that while the domain adopts the typical PASTA topology, it does not show measurable binding abilities for muropeptides or their mimics.[3] These results suggest that the role of sensor may be not a general PASTA property. A detailed dynamic characterization of isolated PASTA motif is not yet available in literature. Here we report the backbone dynamics of PonA2 PASTA performed *via* NMR relaxation data and molecular dynamics simulation. This study can be useful to understand the differences in binding properties observed for different PASTA motives.

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BIO-P4

Molecular inclusion of peptides containing aromatic amino acids and β-cyclodextrin

Caso J.V. [a], *Russo L.* [a], *Malgieri G.* [a], *Palmieri M.* [a], *Galdiero S.* [b], *Falanga A.* [b], *Iacovino R.* [a] *and Isernia C.* [a]

a Department of Environmental, Biological and Pharmaceutical Sciences and Technologies,
Second University of Naples, Via A. Vivaldi 43, 81100 Caserta, Italy
b Department of Pharmacy, University of Naples Federico II, Via Mezzocannone 16, 80134,
Napoli, Italy

valentina.caso@unina2.it

The use of peptides and proteins as industrial and clinical compounds is limited by low solubility and formulation instability. Cyclodextrins (CDs) are quite interesting in this context because they have been shown to have an effect on protein solubility, thermal and proteolytic stability, refolding yield and taste masking [1-2]. Literature data indicate that aromatic side chains are primarily responsible for the interaction of proteins/peptides with cyclodextrin [3-4]. Here, the formation of β-cyclodextrin (β-CD) inclusion complexes with the aromatic residues, in nine oligopeptides, investigated by using UV-Vis, NMR spectroscopy and Molecular Docking techniques is reported. The synthesized oligopeptides, consisting of three amino acids, are composed of L-alanine (A) and one aromatic amino acid (F, W, Y) positioned, respectively, at the N-terminus, C-terminus and central position. In order to evaluate the affinities of the β-CD for each tripeptide we estimated all the binding constants. Then, we highlighted the structural details of each inclusion complex by using NMR data and Molecular docking studies. Finally, the influence of the aromatic residue along the peptide sequence on both binding affinity constant and geometry of guest-CD complexes is discussed.

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BIO-P5

Probing the helical stability in a proangiogenic peptide

V. Celentano[a], *D. Diana*[a], *D. Milardi*[b], *R. Fattorusso*[c] *and L.D. D'Andrea*[a]

a Istituto di Biostrutture e Bioimmagini, CNR, 80134 – Napoli
b Istituto di Biostrutture e Bioimmagini, CNR, 95125 – Catania
c Dipartimento di Scienze e Tecnologie Ambientali, Biologiche e Farmaceutiche -Seconda Università di Napoli, 81100-Caserta

ldandrea@unina.it

Protein folding represents one of the most important studied phenomena of recent times.

In the last years, we reported the structural and biological characterization of a designed peptide, named QK, which corresponds to the helix region 17-25 of the VEGF.[1] The peptide QK interacts with VEGF receptors and has a proangiogenic biological profile. It shows an unusual high thermal stability, which structural determinants were investigated.[2,3] We identified the hydrophobic interaction between Leu7 and Leu10 as crucial for stabilizing the helical fold of QK.

In order to correlate the relationships between hydrophobic interaction and helical stability in peptide QK, we synthesized eight QK analogue peptides where Leu10 was replaced by phenylalanine (F), isoleucine (I), valine (V), phenylglycine (Phg), norleucine (Nle), norvaline (Nva), tert-leucine (Tle) and amino butyric acid (Abu).

The structure and the effect of the temperature on the QK analogues was examined using circular dichroism, NMR spectroscopy and differential scanning calorimetry.

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BIO-P6

Co-Incapsulazione di Everolimus e Gemcitabina in sistemi liposomiali: preparazione e caratterizzazione chimico-fisica

Cristiano M.C.[a], *Pasqua A.*[a], *Cosco D.*[a], *Russo D.*[a], *Celia C.*[b], *Paolino D.*[a], *Fresta M*[a].

[a]*Dipartimento di Scienze della Salute, Università "Magna Graecia" di Catanzaro, Viale Europa – loc.Germaneto, 88100 Catanzaro, Italia.*
[b]*Dipartimento di Farmacia, Università "G. d'Annunzio" di Chieti, Via dei Vestini 31, 66100 Chieti, Italia*

mchiara.cristiano@unicz.it, *fresta@unicz.it*

L'everolimus è uno dei più utilizzati inibitori di mTOR (mammalian target of rapamycin), chinasi che fosforila serina e treonina, regolando, così, la crescita, la proliferazione, la motilità e la sopravvivenza delle cellule. L'everolimus lega una proteina intracellulare, FKBP-12, formando un complesso inibente mTOR. Le diverse applicazioni del farmaco sono, purtroppo, limitate dalla sua scarsa solubilità in acqua e dalla sua ridotta biodisponibilità. Lo scopo del presente lavoro è stato quello di preparare liposomi contenenti l'everolimus al fine di superare i problemi legati alle caratteristiche fisico-chimiche del farmaco e facilitarne l'interazione con il suo target cellulare. Inoltre, dopo aver caratterizzato i sistemi vescicolari contenenti l'inibitore di mTOR, si è deciso di potenziarne l'attività farmacologica co-incapsulando la gemcitabina [1-2], un farmaco antineoplastico analogo della citosina e in grado di inibire la DNA polimerasi con conseguente blocco della crescita tumorale. I sistemi liposomiali contenenti i due principi attivi sono stati caratterizzati da dimensioni medie pari a 130 nm (D.S. = 0.6), indice di polidispersione di 0.09 (D.S. = 0.01) e potenziale Zeta uguale a -7.88 mV (D.S. = 0.628), parametri compatibili con una plausibile somministrazione sistemica della formulazione. L'efficienza di incapsulazione è stata elevata per entrambi i farmaci, con valori pari al 90% per l'everolimus e al 84% per la gemcitabina. Studi *in vitro* sono ad oggi in corso per confermare l'esistenza di una sinergia d'azione dei due farmaci co-incapsulati nei sistemi liposomiali nel trattamento dei tumori tiroidei.

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BIO-P7

The role of peripheral substituents in modulating the antiproteasome potential of porphyrins.

A.Cunsolo[a], A.M.Santoro[b], A.D'Urso[a], C.Gangemi[a], M.Stefanelli[c], G. Tomaselli[a], M.Gobbo[d] , R.Paolesse[c] , R.Purrello[a], D.Milardi[b]

a Dipartimento di Scienze Chimiche, Università di Catania, 95125, Catania
b Istituto di Biostrutture e Bioimmagini, CNR, 95125, Catania
c Dipartimento Scienze Chimiche, Università di Roma TorVergata,00133, Roma
d Dipartimento Scienze Chimiche, Università di Padova, 35131, Padova

acunsolo@unict.it

The main function of the proteasome, is to degrade unneeded or misfolded proteins. To emphasize its essential role in numerous cellular processes, inhibition of the proteasome has been investigated in the treatment of several diseases including cancer. Bortezomib and the other proteasome inhibitors (PIs) that are currently under clinical investigation, bind to the catalytic sites of proteasomes and are competitive PIs. It's conceivable that proteasome inhibitors that act through a noncompetitive mechanism might overcome some forms of bortezomib resistance. Thus, there is a crying urgency to develop new noncompetive PIs with an improved pharmacological profile. [1] Cationic porphyrins are reversible PIs with a putatively competitive mechanism. [2] The lack of information about the relationship between the molecular structure of cationic porphyrins and their antiproteasome activity is a major drawback in the establishment of novel therapeutic strategies based on the development of multi-target photosensitizers. Here, we report the antiproteasomal activity and the inhibition mechanism of new molecules obtained by conjugating the porphyrin core to: i) phenylpyridines, ii) peptide apidaecin (MTPyP-APi); iii) or spermines. Our results evidence that both inihibitor potency (IC_{50}) and mechanism can be regulate by the number and the nature of peripheral substituents .

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BIO-P8

Nociceptin and dendritic cells: a spectroscopic study of their interaction

D’Abrosca G.[a], *Spaziano G.*[b], *Fattorusso R.*[a], *Palmieri M.*[a], *Isernia C.*[a], *Russo L.*[a], *Pedone P.V.*[a], *Matteis M.*[b], *D’Agostino B.*[b] *and Malgieri G.*[a]

a Dipartimento di Scienze e Tecnologie Ambientali, Biologiche e Farmaceutiche,Seconda Università di Napoli, Via Vivaldi 43, 81100, Caserta, Italia
b Dipartimento di Medicina Sperimentale - Sezione di Farmacologia, Seconda Università di Napoli, Via Santa Maria di Costantinopoli 16 , 80138, Napoli, Italia

gianluca.dabrosca@unina2.it

Nociceptin/Orphanin FQ (N/OFQ) is an endogenous heptadecapeptide[*1*] that selectively binds the NOP receptor, a G-protein coupled receptor (GPCR) that belongs to the opioid family and that is widely distributed in different human tissues. Activation of the N/OFQ-NOP system leads to a modulation of a wide spread physiological responses at both central - like pain, analgesia, locomotion, cognitive process and feeding - and peripheral level[*2*]. Even if to date there are no evidences for the expression of N/OFQ and its receptor NOP in the human airways, experimental data in various animal models indicate that N/OFQ is involved in the airways physiology[*3*], suggesting its potential implication in the regulation of the inflammatory response that is a crucial component of most manifestation of allergic asthma[*4*]. Here we report a preliminary spectroscopic study of the N/OFQ interaction with the membrane of immune cells involved in the inflammation response in the airways. Our data show that N/OFQ interacts with dendritic cells of sensitized mice in a manner that appears to be dependent on the NOP receptor concentration. Our results confirm and complement previous biological data[*5*] that demonstrate how the regulation of expression of NOP receptor and its activation by N/OFQ significantly modulates the inflammatory response, validating the thesis of an immunoregulatory role of this neurotransmission pathway.

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BIO-P9

Molecular characterization in solution of a bis-histidine-peptide complexed to Re(I)-tricarbonyl

Luca D. D'Andrea[a], *Gaetano Malgieri*[b], *Gaetano De Tommaso*[c], *Veronica Celentano*[a], *Alessandra Romanelli*[d], *Mauro Iuliano*[c] *and Carla Isernia*[b]

a Istituto di Biostrutture e Bioimmagini, CNR, Via Mezzocannone 16, 80134, Napoli, Italy
b Dipartimento di Scienze e Tecnologie Ambientali, Biologiche e Farmaceutiche, Seconda Università di Napoli, Via Vivaldi 43, 81100, Caserta, Italy
c Dipartimento di Scienze Chimiche, Università di Napoli "Federico II", Via Cintia 21, 80126, Napoli, Italy
c Dipartimento di Farmacia, Università di Napoli "Federico II", Via Mezzocannone 16, 80134, Napoli, Italy

ldandrea@unina.it
carla.isernia@unina2.it

Radiolabeled peptides are useful in the diagnosis and therapy of a variety of human disease characterized by overexpression of peptide receptors. Several radiometals are being used in nuclear medicine and ^{99m}Tc(I) is rapidly gaining in popularity since the introduction of mild synthetic procedure to prepare stable Tc(I)- or Re(I)-complexes $[Tc(H_2O)_3(CO)_3]$ (TcCO) or $[Re(H_2O)_3(CO)_3]$ (ReCO). Ligands replacing all water molecules can form very stable complexes, avoiding trans-chelation reactions which may occur in vivo and the generation of free metal. Histidine is considered a good ligand for TcCO/ReCO and when positioned at the N-terminus of a peptide it acts as bidentate ligand. We reported the in vitro and in vivo characterization of the peptide CCK8 decorated with an histidine based chelator labeled with 99mTc-tricarbonyl [1]. In the present work, we analyze the solution properties of the histidine-based chelator complexed to ReCO by NMR and other spectroscopic techniques in order to highlight the molecular properties of the complex.

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BIO-P10

Peptides mimicking a discontinuous VEGF binding epitope

L. De Rosa[a], *F. Finetti*[b], *L. Morbidelli*[b], *M. Ziche*[b] *and L.D. D'Andrea*

a Istituto di Biostrutture e Bioimmagini, CNR, Via Mezzocannone 16, 80134, Napoli, Italia
b Dipartimento di Science della vita, Università di Siena, Via Aldo Moro 2, 53100, Siena, Italia

ldandrea@unina.it

All biological processes are finely regulated by a network of protein-protein interactions whose characterization at the molecular level can promote the design of novel drug therapeutics working as protein binding modulators. The development of such molecules remains a challenging task because of the complex nature of protein binding sites, which often consist of multiple discontinuous epitopes. Peptide-based mimics of protein binding sites designed to reproduce multiple discontinuous epitopes are promising candidates for this purpose. Here we describe the design, synthesis, structural and biological characterization of a series of peptides mimicking two binding epitopes of Vascular Endothelial Growth Factor (VEGF) with its receptor (Flt-1). VEGF is the main regulator of angiogenesis, a biological process involving the growth of new blood vessels from pre-existing vessels. Angiogenesis is strictly tuned by several pro- and anti-angiogenic factors. An imbalance between such factors contributes to the onset, development and progression of several common and lethal human diseases, including cancer, cardiovascular disorders, retinal degeneration and chronic inflammation. Thus, the design of new, safe and effective angiogenic modulators is gaining a big interest for therapeutic and diagnostic applications.[1, 2] On the basis of the crystal structure of Vascular Endothelial Growth Factor (VEGF) with its receptor (Flt-1), we designed seven peptides mimicking two discontinuous binding epitopes of VEGF (helix 17-25 and β-hairpin 79-92). The two linear epitopes were synthesized by solid-phase peptide synthesis and conjugated by chemical ligation. The peptide series has been structurally characterized by NMR and their biological activity has been investigated.

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BIO-P11

VEGF/VEGF receptor interaction: a structural analysis on living cells

R. Di Stasi [a], *D. Diana* [a], *R. Fattorusso* [b] *& L. D. D'Andrea* [a]

a IBB-CNR, Via Mezzocannone, 16 – 80134, Napoli (Italia)
b Dipartimento di Scienze e Tecnologie Ambientali, Biologiche e Farmaceutiche - Seconda Università di Napoli, Via Vivaldi, 43 – 81100, Caserta (Italia)

rossella.distasi@cnr.it; ldandrea@unina.it

VEGF-A is a highly specific mitogen for vascular endothelial cells and plays a fundamental role in regulating both physiologic and pathological angiogenesis [1]. Its biological activity is mediated through the binding to two membrane receptors belonging to the tyrosine kinase family (VEGFR1 and VEGFR2) and to a co-receptor, neuropilin1, that enhances VEGF-A chemotactic and mitogenic activity [2]. Both VEGFR1 and VEGFR2 bind VEGF with high affinity, although only VEGFR2 modulates the mitogenic/angiogenic response [3]. In 1997, the crystal structures of free VEGF receptor-binding domain ($VEGF_{8–109}$) [4] and in complex with VEGFR1 domain 2 [5] were obtained. In the same year, the structural analysis in solution of VEGF fragment 11-109 was reported [6]. Up to know, no structural information on the interaction between VEGF-A and VEGFR2 has been reported. In order to fill this gap we intend to characterize the structure of VEGF-A in complex with VEGFR2 in the cellular environment. To this aim, the double labeled $hVEGF_{11-109}$ protein was expressed in minimal medium, in presence of $^{15}NH_4Cl$ and ^{13}C-glucose as unique sources of nitrogen and carbon. Fast $^{15}N/^{13}C$-edited NMR experiments were carried out by adding the isotopically enriched $^{15}N/^{13}C$-$hVEGF_{11\_109}$ to a suspension of Porcine Aortic Endothelial cells overexpressing VEGFR2 receptor. As negative control, 2D[^{1}H-^{15}N-^{13}C] HSQC spectra of $^{15}N/^{13}C$-$hVEGF_{11\_109}$ in the presence of WS1 fibroblasts lacking VEGF receptors were also performed. The resulting data showed the power of a direct spectroscopic approach in the identification of VEGF region immobilized upon binding to the receptors localized on cellular membrane, representing the first step towards the analysis of the receptor-bound VEGF structure.

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BIO-P12

Biological identity of liposomes in mice and humans

Giorgia La Barbera[a], Anna Laura Capriotti[a], GiulioCaracciolo[b,c], Valentina Colapicchioni[a,c], Daniela Pozzi[b,c], Salvatore Ventura[a], Riccardo Zenezini[a], Aldo Laganà[a]

a Department of Chemistry, Sapienza University of Rome, Piazzale Aldo Moro 5,00186, Rome, Italy
b Department of Molecular Medicine, Sapienza University of Rome, Via Regina Elena 291, 00161, Rome, Italy
c Italian Institute of Technology, Center for Life Nanoscience@Sapienza, Viale Regina Elena 291, 00161, Rome, Italy

giulio.caracciolo@uniroma1.it

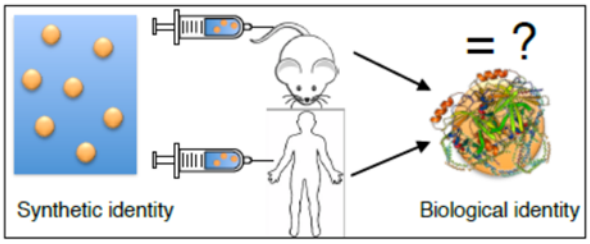

Figure 1: When nanoparticles are injected in vivo, does the nanoparticle-protein corona depend on the physiological environment?

As soon as nanoparticles (NPs) are injected into a physiological environment they are rapidly covered by a rich coating of biomolecules known as the “protein corona”. This protein dress affects the interaction of NPs with living systems[1]. Whether interaction of liposomes with biological fluids from different species could affect the NP-protein corona remains underinvestigated[2]. In this work, we investigated the interaction of PEGylated 1,2-dioleoyl-3-trimethylammonium-propane (DOTAP) liposomes with mouse plasma (MP) and human plasma (HP) by dynamic light scattering, microelectrophoresis and nanoliquid chromatography tandem mass spectrometry. The complexity of the NP-protein corona was found to be strongly dependent on the biological environment. In MP, liposomes were found to be larger, more negatively charged, less enriched in opsonins and appreciably more enriched in apolipoproteins than their counterpart in HP. Collectively, our results suggest that frequent failure to translate findings in mice to patients may be explained in part by the different biological identity of NPs in mice and humans.

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BIO-P13

Structure and dynamics of a Resuscitation promoting factor from *M. tuberculosis*

Maione V.[a], *Ruggiero A.*[b], *Malgieri G.*[a], *De Simone A.*[c], *Berisio R.*[b], *Isernia C.*[a]

a Di.S.T.A.Bi.F., Seconda Università di Napoli, Via Vivaldi 43, 81100, Caserta, Italia
b Ist. di Biostrutture e Bioimmagini, CNR , Via Mezzocannone 16, 80134, Napoli, Italia
c Division of Molecular Biosciences, Imperial College, London SW7 2AZ, UK

vincenzo.maione@unina2.it

It has been estimated that one third of world population is infected by *Mycobacterium tuberculosis* (*Mtb*). In most infected individuals, *Mtb* persists in a latent state for years until host conditions favor reactivation. A family of enzymes, called resuscitation promoting factors (Rpfs), plays a central role in mycobacteria reactivation. Rpfs, containing a transglycosylase-like domain, have been proposed to act as peptidoglycan hydrolases, altering the mechanical properties of the cell wall and favouring cell division and/or release of anti-dormancy factors [1]. *Mtb* has five genes encoding for Rpf proteins (named RpfA-E). RpfB is the most complex, in terms of structural arrangement, of the five Rpf proteins. In particular, the catalytic domain of RpfB exhibits a fold that is similar to that of c-type lysozyme [2]. The *Mtb* Rpfs appear to be functionally redundant, since deletion of each single gene causes no differences in cell growth or cell morphology in rich medium *in vitro*. The combined deletions of at least three *rpf* genes produce cell-growth defects *in vitro*, uncovering apparent functional specialization of Rpfs in Mtb [3]. To explore the distinguishing characteristics of the five *Mtb* Rpfs, here we report the structural and dynamic characterization by using NMR of the RpfC catalytic domain.

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BIO-P14

Synthesis of cyclic RNAs targeting miRNA-21 as small miRNA sponges

Mercurio M. E., Gaglione M. and Messere A.

Dipartimento Scienze e Tecnologie Ambientali, Biologiche e Farmaceutiche, Seconda Università degli studi di Napoli, Via Vivaldi 43, 81100 – Caserta (Italy)

mariaemilia.mercurio@unina2.it

MicroRNAs (miRNA) are endogenous non-coding small RNA molecules, 19-25 nucleotides in length, that are evolved to concurrently repress multiple mRNA targets through imperfect complementarity. The target recognition is primarily determined by pairing of the miRNA seed sequence (nucleotides 2-8) to complementary match sites in each mRNA target [1]. Recently, it has been highlighted the presence of circular molecules of RNA (circRNA) with many miRNA-binding sites, stably expressed in specific tissues or at particular stages of development in animals. These studies have shown that circRNAs form an important class of post-transcriptional regulators and act as *miRNA sponges* [2]. Therefore, miRNA sponges are cyclic RNA molecules with repeated miRNA antisense sequences that can sequester miRNAs from their endogenous targets and thus serve as a decoy. Here we describe the synthesis of small cyclic RNA "mimics" of miRNA sponges directed against miRNA-21, one of the most prominent miRNAs involved in various aspects of human cancers. In fact, miRNA-21 is overexpressed in solid tumors and his inhibition has been demonstrated to decrease cell growth in many cancer cells [3]. The "mimics" we have synthesized consist of sequences of 2'-OMe RNA complementary to the seed sequence of miRNA-21 (5'-AUAAGCUA-3') repeated in tandem, and spaced by HEG moiety. The cyclic structure of the synthetic sponges has several advantages: greater biostability, high binding affinity and selectivity. The presence of 2'-OMe nucleotides is expected to increase the stability to nucleases and the spacer to improve the delivery and targeting of the "mimic". 5'-phosphate linear precursors were synthesized following the standard protocols of automated solid phase synthesis and the classical phosphoramidite chemistry. Oligo cyclization was attempted in solution by different methods of chemical ligation [4]. Comparative studies have been conducted on linear precursors and cyclic RNAs and their structures have been characterized by MALDI-TOF, HPLC and Circular Dichroism. Cell assays are in progress to study the biological activities of the synthetic small miRNA sponges directed against miRNA-21.

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BIO-P15

Switch on/off of plasmonic CD stemmed by self-assembly of Cysteine on Silver nanoparticles

R. Randazzo[a], *A. Di Mauro*[a], *A. D'Urso*[a], *M. E Fragalà*[a], *G. C. Messina*[a], *G. Compagnini*[a], *V. Villari*[b], *N. Micali*[b], *R. Purrello*[a].

a Dip. di Chimica, Università di Catania., V.le A. Doria 6, 95125, Catania, Italy
b Istituto per i Processi Chimico Fisici IPCF CNR V.le F. Stagno d'Alcontres, 37, 98158 Messina Italy

rrandazzo@unict.it

Nanoparticles (NPs) have raised, to date, great interest of the scientific community, due to a wide range of applications from materials science to medicine.[1] Their peculiar size-dependent chemical-physical properties permit them to exhibit unexpected optical properties, as surface plasmon resonance. This effect is responsible for the signals enhancement of several spectroscopic techniques, allowing for detecting adsorption of molecules (such as polymers, DNA, proteins, etc...) onto NPs surface.[2]

Among noble metals, gold and silver have received most of the attention. In particular, silver nanoparticles (AgNPs) linked to thiol-containing species (such as cysteine (Cys) and glutathione) show quite intense plasmonic CD band. Interestigly, also the enhancement of the CD in the absorption region of the aminoacid is detected. We report here on the versatility of Cys-capped AgNPs to pH changes. In particular, the observation that plasmonic CD signal -induced by attachment of the amino acid onto metal nanoparticles- can be switched by changing the Cys coordination caused by pH variation allowed us for sketching a simple model to rationalize the origin of plasmonic CD.

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BIO-P16

Towards understanding the molecular recognition process in prokaryotic zinc-finger domain.

Russo L., Palmieri M., Malgieri G., D'Abrosca G., Russo F., Baglivo I., Esposito S., Rivellino A., Isernia C., Pedone P.V. and Fattorusso R.

*Dipartimento di Scienze e Tecnologie Ambientali, Biologiche e
Farmaceutiche, Seconda Università di Napoli, via Vivaldi 43, 81100 Caserta,
Italy*

luigi.russo2@unina2.it

Specific DNA recognition by proteins is fundamental to many regulatory process that control the flow of genetic information. Eukaryotic Cys_2His_2 zinc finger is a small domain that typically contains a repeated ~30 aa in which a zinc ion, crucial for its stability, is tetrahedrally coordinated by two cysteines and two histidines. Structural studies on classical zinc-finger protein-DNA complexes have demonstrated that sequence specific recognition is achieved by the interaction of the DNA base with the N-terminus part of the α-helix. Recently, we have characterized the prokaryotic Cys_2His_2 zinc-finger motif [1], included in the DNA binding region (Ros87) of Ros protein from *A. tumefaciens*, demonstrating that, although possessing a similar zinc coordination sphere, this domain present significant differences from its eukaryotic counterpart. Furthermore, basic residues flanking the zinc binding region on either side have been demonstrated to be essential for DNA binding. In spite of this wealth of knowledge, the structural details of the mechanism through which the prokaryotic zinc fingers recognize their target genes are still unclear. Here, to gain insights into the molecular recognition process of prokaryotic zinc finger domains we report molecular docking studies using Nuclear Magnetic Resonance and Molecular Dynamics simulations data.

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BIO-P17

An intein-based strategy for the preparation of isotopically labelled peptides

A. Russomanno,[a] L. De Rosa,[a] D. Diana,[b] A. Romanelli,[c] R. Fattorusso,[b] L. D. D'Andrea [a]

[a]Istituto di Biostrutture e Bioimmagini, CNR, Napoli, Italy;
[b]Dip. di Scienze e Tecnologie Ambientali, Biologiche e Farmaceutiche, Seconda Università di Napoli, Caserta, Italy
[c]Dip. di Farmacia, Università di Napoli "Federico II", Napoli, Italy;

l.dandrea@unina.it

NMR spectroscopy is a powerful method to perform structural studies on peptides. To completely fulfill the potential of NMR, peptides labeled with stable isotopes (^{15}N,^{13}C,^{2}H) are essential [1].

Peptides are usually prepared on solid-phase but chemical synthesis becomes prohibitively expensive when applied to the incorporation of isotopes. An alternative cost-effective strategy is the recombinant expression of peptides in *E. coli* as fusion constructs with carrier proteins[2]. We used the self-cleaving *Mxe*GyrA mini-intein as fusion partner for the preparation by recombinant means of two isotope labeled peptides, HPLW and QK[3,4]. The two peptides have been described to modulate VEGF-dependent angiogenesis.

Our strategy allows to prepare isotope labeled peptides in free or acetylated/amidated form. The availability of isotope labeled HPLW and QK opens the way to further NMR studies aimed to characterize the folding dynamics of the two peptides and their structures in complex with VEGFR.

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BIO-P18

Evolution to carbapenem-hydrolyzing activity in class D β-lactamases by rational protein design

Pozzi Cecilia[a], *Di Pisa Flavio*[a], *De Luca Filomena*[b], *Benvenuti Manuela*[a], *Rossolini Gian Maria*[b], *Docquier Jean-Denis*[b], *Mangani Stefano*[a]

a Dipartimento di Biotecnologie, Chimica e Farmacia, Università di Siena, Via Moro 2, 53100, Siena, Italia

b Dipartimento di Biotecnologie Mediche, Università di Siena, Viale Bracci 16, 53100, Siena, Italia

pozzi4@unisi.it

Class D carbapenemases represent increasingly important bacterial antibiotic resistance determinants which compromise the efficacy of the last-resort carbapenem antibiotics. The 3D structures of *Acinetobacter baumannii* OXA-24 and *Klebsiella penumoniae* OXA-48 were recently obtained [1,2] and revealed significant structural heterogeneity with OXA-10 (a narrow-spectrum enzyme inactive on carbapenems), suggesting the potential role of residues of the β5-β6 loop, showing a typical conformation, in the carbapenemase activity of OXA-24 and OXA-48. To probe this hypothesis, we obtained two hybrid OXA-10 proteins bearing the structurally-equivalent loops of OXA-24 and OXA-48 [3]. Functional analysis revealed that both hybrid OXA-10 proteins acquired significant carbapenem-hydrolyzing activity. Furthermore, we obtained the X-ray crystal structures of the OXA-10 derived hybrids enzymes [3] in both the native form and as acyl intermediates with two carbapenem antibiotics, providing insight into substrate binding and catalysis in class D carbapenemases. In this work, we successfully evolved a narrow-spectrum class D β-lactamase into a carbapenemase using a rational structure-based approach and demonstrated the crucial role of the β5- β6 loop in the acquisition of carbapenemase activity and modulation of substrate specificity among class D β-lactamases.

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Chimica Teorica e Computazionale

Keynote

TEO-K1

Non-empirical exchange-correlation functionals with improved accuracy

Fabio Della Sala

National Nanotechnology Laboratory of CNR-NANO & Istituto Italiano di Tecnologia.

fabio.dellasala@unisalento.it

I will present recent developments for (i) Generalized Gradient Approximation (GGA) and (ii) meta-GGA exchange-correlation (XC) functionals:
(i) Using the semiclassical neutral atom asymptotic expansion we modified the famous Perdew-Burke-Ernzerhof (PBE) XC functional [1]. The resulting non-empirical functional (named APBE[2]) turned out to be the most accurate PBE-like functional for molecules [3], it works still quite well for solid-state systems [2] and it can be also related to a self-interaction-free condition for the hydrogen atom [4].
(ii) Using a novel localization technique for the correlation energy density, we constructed
a meta-GGA dynamical correlation functional [5] which is very accurate for jellium surfaces and the Hooke's atom at all regimes. Then we constructed the full XC meta-GGA functional (named BLOC[6]) with a Balanced Localization of the XC energy density and a more realistic XC hole [7]. This non-empirical functional shows good accuracy for a broad palette of properties and systems outperforming all other non-empirical meta-GGAs [6].

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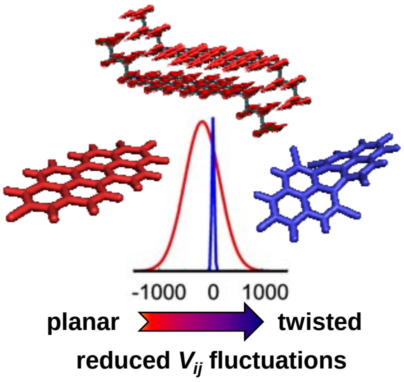
TEO-K2

Interplay of electronic, optical and transport properties in extended core organic semiconductors: rationale from modeling

Fabrizia Negri[a]

a Dipartimento di Chimica "G. Ciamician, Università di Bologna, Via Selmi, 2 ,
40126,Bologna, Italia and INSTM, UdR Bologna, Bologna, Italia

fabrizia.negri@unibo.it



The interplay between intramolecular properties and intermolecular interactions governs, among others, charge conduction mechanisms, energy transfer, optical properties. Core-extended π-systems have been used as building blocks for opto-electronic devices, dye lasers, optical switches, photodetectors, and also for studying photoinduced energy- and electron-transfer processes. Over the past few years we have modelled, with computational tools, structural, electronic, optical and charge transport properties of a number of core-extended conjugated molecules, among which several rylene derivatives which can be regarded to as model compounds for graphene nanoribbons.[1] In this contribution I will summarize our recent simulation results taking into account also the role of thermally induced dynamical effects that have been investigated by means of molecular dynamics simulations coupled to quantum-chemical evaluation of electronic couplings.

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Chimica Teorica e Computazionale

Premi

TEO-R1

Development of an integrated tool to simulate electronic and vibrational spectra

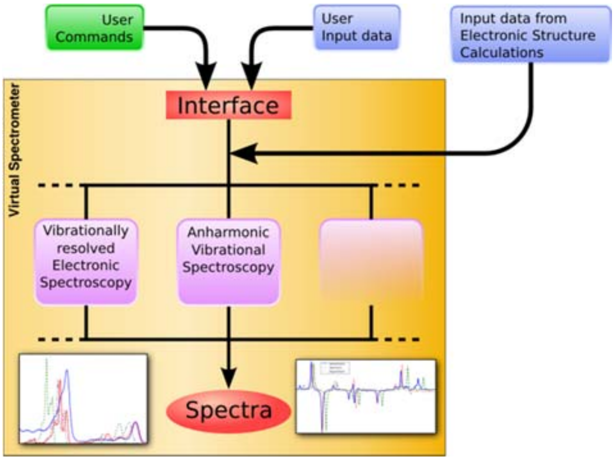
Julien Bloino[a]

[a] *Consiglio Nazionale delle Ricerche, Istituto di Chimica dei Composti*
OrganoMetallici (ICCOM-CNR), UOS di Pisa, Area della Ricerca CNR,
Via G. Moruzzi 1, I-56124 Pisa, Italy

Julien.bloino@pi.iccom.cnr.it

The experimental characterization process of complex molecular systems can be greatly aided by computational spectroscopy. However, accurate simulations of vibrational and electronic spectra, for instance, with inclusion of environment effects (solvent, temperature...) often require an understanding of the underlying theory to be parameterized correctly, in particular to treat efficiently large systems.

In order to define standardized protocols to characterize a wide range of systems, the availability of a versatile and integrated tool is a valuable aid. To this end, a virtual spectrometer[1] has been developed to compute vibrationally averaged properties[2], vibrationally resolved electronic[3,4] and vibrational[2] spectra beyond the harmonic level with the possibility to account for environment effects and to tailor its complexity by applying simplified or reduced-dimensionality schemes. Emphasis has been put on its ease of use by requiring minimal input from the user and on its versatility by adopting a modular approach based on general formulations. Some features of the spectrometer will be illustrated by following a protocol to choose among derivatives of p-phenylene-linked bis-imidazoles those with strong quantum yields and large Stokes shifts for the design of novel solar cells.



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TEO-R2

Investigating Ligand/Protein Binding using Free Energy Calculations

Vittorio Limongelli

Department of Pharmacy, University of Naples "Federico II", via Domenico Montesano 49, Napoli, Italy

vittorio.limongelli@unina.it

Predicting the thermodynamic and kinetic properties of the binding process of a drug to its target is of primary relevance to shed light on its mechanism of action and develop new medications [1,2,3]. Here, I illustrate how this information can be obtained from metadynamics calculations. In particular, we studied the binding of benzamidine to trypsin using a new approach, called Funnel-Metadynamics [4]. This method enhances the exploration of the ligand bound poses and its solvated states leading to an accurate estimation of the protein-ligand binding free energy. Furthermore, we could recover from metadynamics the kinetic rates of the ligand binding process (koff) using a recently developed protocol [5]. In our simulations, the x-ray conformation was found as the lowest energy pose and the computed ligand binding free energy in good agreement with experiments. Our approach allows also to unveil precious details of the docking process, such as the presence of alternative binding modes and the role of the solvent. Albeit very recent, Funnel-Metadynamics has been already successfully used in complex ligand/protein, ligand/DNA and peptide/membrane binding studies, some of them are here discussed.

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Chimica Teorica e Computazionale

Oral

TEO-O1

Slow Manifolds identification as a mean towards dimensionality reduction of chemical kinetics

Alessandro Ceccato, Diego Frezzato

Dipartimento di Scienze Chimiche, Università degli Studi di Padova,
Via Marzolo 1 , I-35131, Padova, Italy

diego.frezzato@unipd.it

Chemical reactions, in laboratory/industrial practice and in natural contexts, often occur via a complex mechanism involving many species and many elementary steps (or "parallel reactions"). Even in the ideal situation of perfectly stirred medium and isothermal conditions, for which the ordinary differential equations yielding the trajectory in the concentrations space are of simple polynomial type, one may encounter severe problems on computational and/or interpretative grounds. For example, the large spread of kinetic constants may originate "stiffness" imposing extremely short propagation time-steps. Thus one wishes to get a "reduced" but enough accurate description of the kinetics, such that only the relevant traits are kept, the dimension of the algebraic problem is lowered, and stiffness is removed. This goal is termed "dimensional reduction" of kinetics description.

Here we exploit an almost ubiquitous trait "observed" in the concentrations space if many trajectories, originating from different initial points, were plotted together: after a fast transient, trajectories seem to "converge" to a hypersurface, named Slow Manifold (SM), and remain close to it up to equilibrium; in the neighbourhood of the SM, the slow evolution takes place. Such a mutual correlation between species concentrations suggests that some degrees of freedom can be eliminated, so achieving the goal. A formal/operative definition of SM has been recently presented [1, 2]. In this communication we outline the theoretical approach and recent algorithmic implementations which prove efficient when applied to some case models.

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TEO-O2

DFT calculations of Xe-129 NMR parameters in weakly interacting systems

Giacomo Saielli[a], Alessandro Bagno[b]

a Istituto per la Tecnologia delle Membrane del CNR, Unità di Padova, Via Marzolo, 1 - 35131 Padova
b Dipartimento di Scienze Chimiche, Università di Padova, Via Marzolo, 1 - 35131, Padova

giacomo.saielli@unipd.it

^{129}Xe NMR has proven to be a very efficient tool for the investigation of various chemical environments, where xenon can be dissolved as a probe, thanks to the extremely high sensitivity of ^{129}Xe chemical shift on intermolecular interactions. These are essentially weak van der Waals interactions whose modeling by means of computational protocols based on Density Functional Theory (DFT) is still challenging. Moreover, relativistic effects are expected to be important when dealing with xenon because of its high atomic number.

Here we will investigate the predictive power of relativistic DFT based protocols in two different cases, both dominated by weak van der Waals interactions. In the first case, the chemical shift change induced in ^{129}Xe encapsulated in a cryptophane upon permetalation will be discussed. The experimental value ($\Delta\delta_{exp}$ = +277 ppm) has been reproduced remarkably well ($\Delta\delta_{exp}$ = +281 ppm) and the various contributions to the deshielding have been rationalized [2].

In the second case we have focused our attention on through-space spin-spin couplings. These are produced by the small overlap of the electronic clouds even in unbound systems. In a cooperation with experimental NMR spectroscopists we have determined, for the first time, the spin-spin coupling $J_{\text{Xe-H}}$ in van der Waals complexes of xenon and pentane in a liquid 50% vol. mixture. The experimental value ($\langle J_{\text{Xe-H}}\rangle_{exp}$ = −2.7 ± 0.6 Hz) is in excellent agreement with the results of relativistic DFT calculations ($J_{\text{Xe-H,calc}}$ −3.2 Hz) averaged over the statistical ensemble obtained from classical MD simulations.

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TEO-O3

Simulating Vibronic Spectra With Internal Coordinates: Achievements And Pitfalls

Javier Cerezo[a] *and Fabrizio Santoro*[a]

a Istituto Chimica Composti OrganoMetallici-CNR, G. Moruzzi 1, I-56124 Pisa, Italy

j.cerezo@pi.iccom.cnr.it (JC); fabrizio.santoro@iccom.cnr.it (FS)

In recent years, computational tools to simulate electronic spectra with vibrational resolution have been vividly developed focusing on a realistic modeling of intramolecular and environmental factors, thus providing an invaluable companion of experimental methods. In this quest, one of the biggest challenges arises in the description of the potential energy surfaces of the initial and final states involved in the electronic transition, with the harmonic approximation still being necessary for full-dimensionality treatments and to provide the suitable framework in subsequent refinements. In this sense, the selection of the coordinate frame reveals a key aspect to ensure the validity of the harmonic picture and to facilitate the separation of the vibrational degrees of freedom. Indeed, the usual Cartesian frame faces remarkable issues to describe the curvilinear nature of some vibrations, deviating from the harmonic curve even at small displacements. In this context, internal coordinates (bonds, angles, dihedrals) have proven useful to overcome these problems[1], showcasing relevant success in cases where the displacements between the initial and final state minima are large[2]. Nonetheless, the internal frame also brings some important concerns[3], as the non-orthogonality of the coordinates or the need of complicated and specific coordinate definition to describe some vibrations (e.g. rings), which have impeded the straightforward generalization of this approach. In this contribution, we present successful applications of internal coordinates which, together with efficient TD formulations, provide a powerful tool to compute spectra at room temperature of relatively large molecules. On the other hand, we also introduce other systems that challenge the use of internal coordinates, proposing strategies to remedy such limitations. All methods are implemented in a development version of our code *FCclasses*[4].

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TEO-O4

Tracking Dynamics of Biological Systems by Ultrafast 2D Electronic Spectroscopy

Ivan Rivalta[a], *Artur Nenov*[b], *Giulio Cerullo*[c], *Marco Garavelli*[b]

a Laboratoire de Chimie, École Normale Supérieure de Lyon, Lyon, France.
b Dipartimento di Chimica "G. Ciamician", Università di Bologna, Bologna, Italy.
c IFN-CNR, Dipartimento di Fisica, Politecnico di Milano, Milano, Italy.

ivan.rivalta@ens-lyon.fr

Two-dimensional electronic spectroscopy (2DES) based on ultrashort laser pulses is a cutting-edge technique to track electronic transitions in complex systems with unprecedented spectral and time resolution.[1-3] 2DES can be used to investigate conformation dynamics in a wide range of systems in physical chemistry, energy sciences and biophysics.[1, 4] By spreading the information content of the nonlinear signal on two frequency axes, 2DES provides a wealth of novel information on molecular structure and dynamics with respect to the linear signal collected in traditional 1D experiments. However, the interpretation of 2D electronic spectra is challenging and computational modeling is required to disentangle the information contained in the nonlinear optical response of the sample. In this talk a computational tool[5] that can be routinely applied to accurately simulate 2DES spectra of multichromophoric systems is introduced. Multiconfigurational and multireference perturbative methods have been used to reliably calculate the electronic properties of multichromophoric systems within a hybrid QM/MM scheme in conjunction with molecular dynamics techniques to assess environmental and conformational effects that shape the 2D electronic spectra. Applications of this methodology for the study of structure and folding dynamics of proteic systems[6] in solution and photochemistry of retinal chromophores embedded in membrane proteins[7] are showed, demonstrating that 2DES holds the promise to become a novel diagnostic tool complementary to well-established multidimensional NMR and 2DIR techniques.

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TEO-O5

Tungsten Oxide: Defects, Dopants and Nanostructures

Gianfranco Pacchioni, *Sergio Tosoni, Cristiana Di Valentin, Fenggong Wang*

a Dipartimento di Scienza dei Materiali, Università di Milano Bicocca, Via R. Cozz, 55 – 20125 Milano, Italy

Gianfranco.pacchioni@unimib.it

We report the results of first principle DFT calculations based on a hybrid functional (CRYSTAL code) that properly reproduce band gap and other fundamental properties of WO_3. We will briefly describe the dependence of the band gap on the crystalline phase of WO_3. Then, we will address the nature of defects and dopants in bulk WO_3. As WO_3 can be easily reduced to WO_{3-x}, we will discuss the nature of isolated O vacancies showing that three different situations arise from the removal of one O atom along each of the three crystallographic directions of monoclinic WO_3. The data provide insight into the origin of electrochromism of this material. Then we will discuss the role doping of WO_3 with substitutional atoms in order to increase the activity for water splitting and we will show that Hf is a promising dopant. The redox properties of WO_3 are discussed also in relation to H_2 adsorption on the $WO_3(001)$ surface. Finally, the role of nanostructuring will be analyzed by studying the properties of $(WO_3)_3$ cyclic clusters deposited on the rutile $TiO_2(110)$ surface. Charge transfers at the $(WO_3)_3/TiO_2$ interface and their role on the activity of this heterogeneous catalyst will be discussed.

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TEO-O6

Energy Transfer in Light Harvesting Systems: a QM/MM-Pol Approach

Sandro Jurinovich[a], *Lucas Viani*[a], *Stefano Caprasecca*[a],
Benedetta Mennucci[a]

a Dipartimento di Chimica, Università di Pisa, Via Risorgimento 35, 56126, Pisa, Italia

sandro.jurinovich@for.unipi.it

Natural light-harvesting (LH) proteins are able to capture the sunlight energy and transfer it efficiently to a reaction center where the photosynthetic processes take place. LH proteins contain many pigment molecules arranged together in antennas with a precise structure which is supplied by the protein scaffold. The excited states properties of LH systems mainly depend on the absorption properties of the single chromophores (site energies) and their interactions (coupling between them). Both are modulated by the environment and also coherence effects seem to be promoted by the environment fluctuations.[1-2]

Here we present a computational strategy to predict the excitonic properties of LH systems combining the classical molecular dynamic simulation (MD) with QM/MM methods.[3] A critical investigation of the role of the environment, in terms of both structural and electrostatic effects, is carried out using a polarizable MM model combined to a TDDFT description of the electronic properties.[4]

This approach allows to shed light on the effect of the environment on energy transfer processes (EET) in natural LH systems and provide useful information for the design of improved nanotechnological devices which make use of EET.

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TEO-O7

Anisotropy of n-type charge mobility and thermal effects in crystals of a fluoro-alkylated naphthalene diimide: a computational investigation

Sofia Canola[a], *Fabrizia Negri*[a,b]

a Dipartimento di Chimica "G. Ciamician, Università di Bologna, Via Selmi, 2 , 40126,Bologna, Italia
b INSTM, UdR Bologna, Bologna, Italia

sofia.canola2@unibo.it

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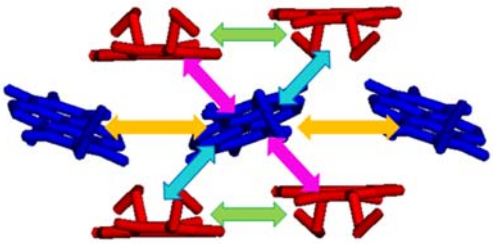

The anisotropy of n-type charge transport of a fluoro-alkylated naphthalene diimide [1] is investigated in the framework of the non-adiabatic hopping mechanism. Charge transfer rate constants are computed within the Marcus-Levich-Jortner formalism including a single effective mode treated quantum-mechanically and are injected in a kinetic Monte Carlo scheme to propagate the charge carrier in the crystal. Charge mobilities are computed at room temperature with and without the influence of an electric field. Thermally induced dynamical effects are investigated by means of an integrated computational approach [2] including molecular dynamics simulations accompanied by quantum-chemical evaluation of electronic couplings.

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TEO-O8

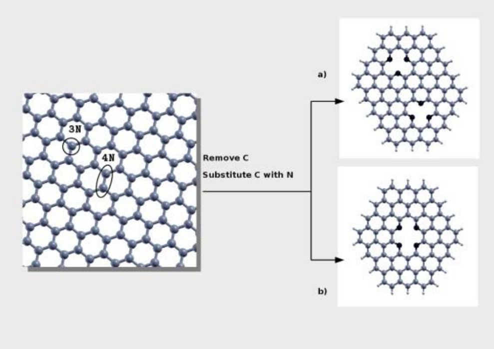
Hydrogen activation on N-doped carbon networks

Remedios Cortese, *Francesco Ferrante, Dario Duca*

Dipartimento di Fisica e Chimica, Università degli Studi di Palermo, Viale delle
Scienze, Parco d'Orleáns II, Ed. 17, 90128, Palermo, Italia

remedios@cccp.unipa.it

The future development and assessment of an industry more environmental friendly will include the use of metal-free catalysts. Recently, N doped nanotubes and graphene sheets were synthesized [1] and it was demonstrated that the incorporation within these carbon structures of nitrogen atoms causes a greater electron mobility and introduces more active sites for catalytic reactions. The aim of this study is to figure out how the mechanism of hydrogen activation could take place without an H2-activating systems containing transition metal atoms. We decided to approach the study of these topics, starting by a set of polyaromatic molecules containing nitrogen and then broadening the analysis to carbon nanotubes, containing nitrogen atoms as dopants. We monitored the effects both of the increase of the size of the aromatic systems and of the curvature of the carbon framework, on the fragmentation energy of the hydrogen molecule. Several models and different theoretical approaches were chosen in order to model defects that combine vacancies and substitutions within carbon frameworks, as showed in Fig. 1. The calculations were carried out within the DFT and depending on the size of the models, employing the g09 suite of codes or the SIESTA code. This investigation allowed us to understand the main elements, which influence hydrogen fragmentation energetics occurring on polycyclic aromatic hydrocarbons containing pyridinic rings, linking the properties of these species to those of periodic extended systems as nitrogen doped carbon nanotubes.



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TEO-O9

Tuning the Stability of $Ca(BH_4)_2$ by the Inclusion of Additives: A Computational Study

E. Albanese[a], B. Civalleri[a] and M. Baricco[a]

a Department of Chemistry and NIS Centre of Excellence, Università di Torino, via P. Giuria 7, I-10125 Torino (Italy)

elisa.albanese@unito.it

Metal borohydrides (MBHs) are considered as promising hydrogen storage materials because of their high weight percent of hydrogen (up to 20.8 wt%). Unfortunately, the MBHs have found limited applicability because of various drawbacks. For instance, alkaline-earth borohydride compounds often show slow kinetics of hydrogen release and are difficult to re-hydride, whereas transition metal borohydrides are either unstable or decompose by releasing impurity gases, such as diborane. Several strategies have been proposed to improve the kinetics and the thermodynamics of the hydrogenation/dehydrogenation reaction, such as the inclusion of additives in the MBHs structure.

In the present work, we studied the inclusion of Ni^{2+} ions at the surface of β-$Ca(BH_4)_2$, which is one of the most interesting systems because of its high H_2 wt% (11.6 wt%), by using quantum-mechanical methods. Calculations were carried out with periodic density functional theory (DFT) calculations employing the PBE-D* (i.e. PBE augmented with the Grimme's DFT-D2 empirical dispersion correction, as modified for solids) functional as implemented in the CRYSTAL code.[1]

As a first stage, we modeled various surfaces of $Ca(BH_4)_2$ and evaluated their relative stability in order to predict the most stable one. To simulate the surfaces, the so-called slab model approach was used. The (001) surface was predicted to be the most stable one. The inclusion of Ni^{2+} as additive was then investigated. Two different molar concentrations were simulated by substituting Ca^{2+} with Ni^{2+} at the top most layer of the (001) surface. The structural deformation and the qualitative information provided by the electrostatic potential maps of the surface have been analyzed. The distortion from the ideal T_d symmetry of $[BH_4]^-$ ion and its destabilization due to the decreasing of the charge transfer from the cation (Ca and Ni) to the anion are likely responsible of the decrease of the activation energy for H_2 release. The effect of other additives (Cu, Co,etc…) is under investigation.

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TEO-O10

A computational approach to study Aqueous Phase Reforming

Schimmenti R.[a], Cortese R.[a], Duca D.[a]

[a] *Dipartimento di Fisica e Chimica, Università degli Studi di Palermo, Viale delle Scienze Ed. 17, I-90128, Palermo*

roberto@cccp.unipa.it

Aqueous Phase Reforming [1] (APR) is recognized as one of the most interesting solution for producing hydrogen from biomass renewable feedstocks; the development of a new generation catalyst with high performances and high hydrothermal stability could provide a great resource for obtaining cheap and environment-friendly fuels.
DFT based methods can be useful for understanding APR catalytic mechanism at atomistic level. In order to gain realistic insights into the polyol/metallic catalyst aqueous system, the computational methods involved have to be selected properly. For his high flexibility the SIESTA[2] method was employed to generate and test pseudopotentials and basis sets specifically designed for the treatment of metallic surfaces; since dispersion forces could have a significant role in the description of the oxygenate species interactions with the metallic catalyst and solvent, the new VdW xc funtionals [3] family has been taken into account.
An extensive calibration of the computational methods used in this study is reported; great attention is paid to the individuation of a suitable xc functional, comparing results from different parametrizations of the VdW-DF xc and the well known PBE GGA xc. Results from the adsorption of different C_1 – C_4 oxygenates onto low miller index platinoids metal surfaces are reported, considering explicitly the coadsorption of a water molecule.

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TEO-O11

Monte Carlo Modeling of Carbon Dioxide Adsorption in Porous Aromatic Frameworks

L.Canti[a], *A.Fraccarollo*[a], *G.Gatti*[a], *M.Errahali*[a], *M.Cossi*[a] *and L.Marchese*[a]

a Dipartimento di Scienze ed Innovazione Tecnologica and Centro Nano-SISTeMI, Università del Piemonte Orientale "A.Avogadro", Via T.Michel 11, 15121, Alessandria, Italy

lorenzo.canti@mfn.unipmn.it

The adsorption isotherms of CO_2 in several porous aromatic frameworks (PAFs) have been simulated with Grand Canonical Monte Carlo technique, to support the synthesis of new materials for efficient carbon dioxide capture and storage. The simulations covered the 0–60 bar pressure range and were repeated at 273, 298 and 323 K. The force field employed in the simulations was optimized to fit the correct behavior of the free gas and to reproduce the CO_2–phenyl interactions computed at high quantum mechanical level. PAFs are based on the diamond structure, with polyaromatic chains inserted in C–C bonds.[1] We examined four PAF-30n (n being the number of phenyl rings in the aromatic linkers), finding that PAF-302 is overall the best performing, although PAF-301 provides higher adsorbed densities at very low pressure. The CO_2 adsorption then was simulated in a number of modified PAF-302, with different functional groups (aminomethane, toluene, pyridine and imidazole) attached to the phenyl chains; different degrees of substitution (25%, 50%, and 100% derivatized rings) were considered. [2]

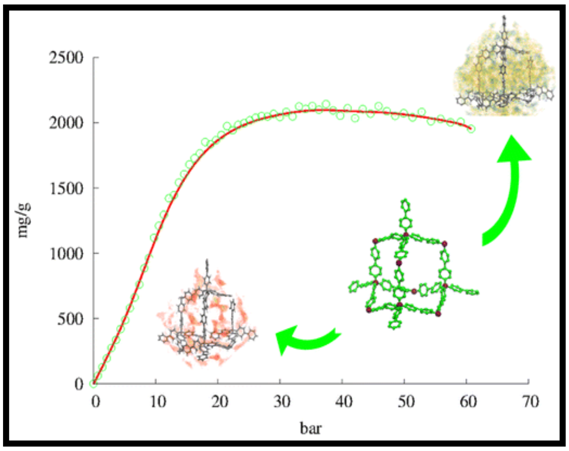

Fig.1. PAF302: The loading density maps change at different pressures.

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TEO-O12

Photo-Induced Charge Separation and Charge Recombination Kinetics in Solution: a Computational Study

Massimiliano Aschi[a], *Giovanni Piacente*[a], *Marco D'Abramo*[b], *Isabella Daidone*[a] *and Andrea Amadei*[c]

a Dipartimento di Scienze Fisiche e Chimiche, Università di l'Aquila, Via Vetotio, 67100, l'Aquila, Italy
b Dipartimento di Chimica, Università di Roma 'La Sapienza', P.le A. Moro 5 , 00185, Roma, Italy
c Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma 'Tor Vergata', Via della Ricerca Scientifica, 00100, Roma, Italy

massimiliano.aschi@univaq.it

The aim of this talk is the outline of the theoretical framework, the computational setup and the results of the modeling of photo-induced Charge Separation (CS) and Charge Recombination (CR) reactions in solution recently carried out in our group. In particular we have addressed the photo-induced CS prototype reaction involving benzene and tetracyanoethylene in CH_2Cl_2. The full understanding of these processes is of great fundamental and practical relecance because of their crucial role in many chemical and biochemical Electron Transfer reactions. At the same time the genuine multi-scale character of these reactions makes their modeling as extremely challenging.

Our approach, based on a combination of Molecular Dynamics simulations and Quantum-Chemical calculations has revealed a rather suitable tools for investigated some of the key aspects of these processes.

TEO-O13

The role of Charge Transfer excited electronic states in the photophysics and photochemistry of DNA.

Roberto Improta[a]

a Istituto Biostrutture e Biommagini-CNR Via Mezzocannone 16, I-80134 Napoli, Italy

robimp@unina.it

The possible involvement of Charge Transfer (CT) excited states in the photoactivated dynamics of DNA is one of the most controversial issues in the photochemistry of nucleic acids. Exploiting Time Dependent DFT calculations using last generation functions (enabling an accurate determination of the CT states stability) and taking solvent effect into account by the Polarizable Continuum Model, we have studied realistic oligonucleotides, including also the phospho-deoxyribose backbone and counter-ions, by combing stati and quantum dynamical calculations. We provide clear indications that states with a noticeable, yet different, degree of CT character are involved in the photophysics and photochemistry of several systems: oligoAdenine,[1,2] d(TpT)[3,4] and d(TpC)[5] and d(Tp5methylC)[5] dinucleotides, Guanine Quadruplex helices[6] Guanine nano-ribbons,[7] and Oxoguanine-Ade dinucleotides.[8] Our predictions are fully consistent with the available experimental results, i.e. Steady State Circular Dichroism,[3,6] Time resolved fluorescence [1-7] and InfraRed spectra, which, for the first time, show a clear spectral signature of CT states.[8] For quadruple helices, our studies also provide a complete assignment of the optical spectra and indications on the factors influencing the excited state dynamics (cation, conformation of the quadruplex…).[6] Finally, it has been possible to explain the role of 5-methylation in the photochemistry of dinucleotides containing Cytosine.[5].

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TEO-O14

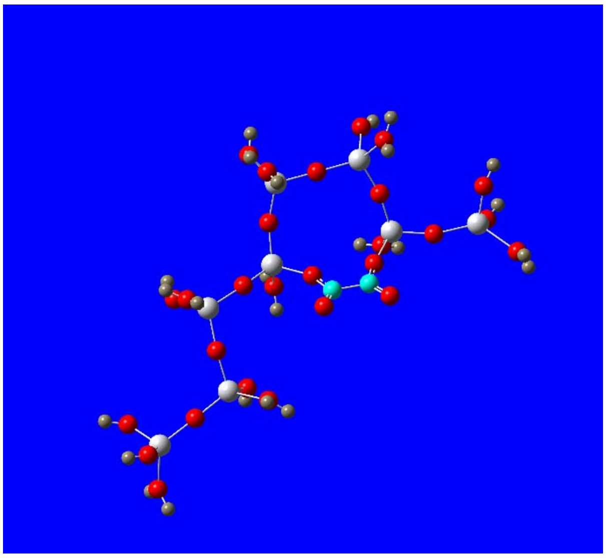
A Computational Approach to Titanium Tanning

Cinzia Chiappe[a], *Christian Silvio Pomelli*[a], *Monica Puccini*[b], *Maurizia Seggiani*[b], *Sandra Vitolo*[b]

a Dipartimento di Farmacia, Università di Pisa, Via Bonanno 33, 56126, Pisa, Italy.
b Dipartimento di Ingegneria Civile ed Industriale, Università di Pisa, Largo Lazzarino, 56126, Pisa, Italy.

pomelli@farm.unipi.it

In mineral tanning process multinuclear a process called olation create chained metal complexes, bridged by oxygen atoms. These complexes coordinate collagen carboxylic groups situated on collagen sidechains [1]. As a result the structure is now crosslinked. Another actor of this process is the masking agent: usually an organic acid that avoids precipitation of metal hydroxides. The pH of the tanning solution is acid. The most used metal ion is Cr(III) but it shows several environmental issues. A possible replacement is the greener Ti(IV) [2] that in aqueous solution exists as titanyl (TiO^{2+}). We have studied with static and dynamic DFT some titanyl oligomers in water solution alone and while interact with model sidechains (acetate ions) and/or common tanning agents. The properties of these systems have been compared with experimental evidences of the tanning process in order to establish a bridge between macroscopic properties and molecular structure.



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TEO-O15

Quantum-mechanical simulations of functionalized silica surfaces for biomedical applications

Marta Corno[a], *Maryline Moreno*[b], *Patrick Choquet*[b], *Piero Ugliengo*[a]

a Dipartimento di Chimica and NIS (Nanostructured Interfaces and Surfaces Centre),
Università degli Studi di Torino, via P. Giuria 7, 10125 Torino, Italia
b Science and Analysis of Materials Department, Centre de Recherche Public – Gabriel
Lippmann, 41 rue du Brill, Belvaux L-4422, Luxembourg

marta.corno@unito.it

Biomaterials are widely studied in material science, due to the increasing life expectancy and the growing senior population. Indeed, a consequent need of biocompatible and bioactive materials for substituting aged or injured tissues of the human body is constantly present, as well as the strong requirement of antiseptic, antimicotic and antibacterial properties of the newly developed materials. Within this scheme, surface functionalization with specific reactive groups has gained strong interest, as a preliminary step to the subsequent immobilization of desired biomolecules. By combining experimental and computational techniques, the aim is to synthesize suitable antibacterial surfaces with properties and reactivity as calculated at atomistic level by periodic surface simulation.

In this contribution, a DFT study of acidic and basic functionalized silica surfaces and their condensation reaction with amino acids will be presented, as possible interesting residues of larger peptides. Indeed, this theoretical investigation is intended to represent the first stage of a wider and more complex simulation work, leading to the interaction of antibacterial peptides with the functionalized surfaces. Hydroxylated surfaces of both a crystalline (101) cristobalite and an amorphous silica, with silanol density of 4.5 OH per nm^2, are considered in the work. The structure of active sites, the hydrogen bonding pattern and the electrostatic potential features will be fully addressed and discussed with reference to the degree and type of functionalization. The added value is given by the simulation of IR spectra of the various models, comparable to those measured on the experimental surfaces, helping in the interpretation of the reaction mechanisms occurred at the functionalized silica surfaces.

TEO-O16

Modeling of the reduction potential of proteins

I. Daidone [a], *C. A. Bortolotti* [b], *M. Aschi*[a] *and A. Amadei* [c]

a Department of Physical and Chemical Sciences, University of L'Aquila, via Vetoio (Coppito 1), 67010 L'Aquila, Italy
b Department of Life Sciences, University of Modena and Reggio Emilia, via Campi 183, 41125 Modena, Italy
c Department of Chemical Sciences and Technologies, University of Rome "Tor Vergata", via della Ricerca Scientifica 1, 00133 Rome, Italy

isabella.daidone@univaq.it

Differences in the reduction potential E^0 among structurally similar metalloproteins cannot always be fully explained on the basis of their 3-D structures. We investigate the molecular determinants to E^0 using the mixed quantum mechanics/molecular mechanics approach named perturbed matrix method (PMM); after comparison with experimental values to assess the reliability of our calculations, we investigate the relationship between the change in free energy upon reduction ΔA^0 and the reorganization energy. We find that the reduction potential of cytochromes can be regarded as the result of the sum of two terms, one being mostly dependent on the energy fluctuations within a limited range around the mean transition energy and the second being mostly dependent linearly on the difference $\Delta\lambda = \lambda_{red} - \lambda_{ox}$ of the reorganization free energies for the ox → red (λ_{red}) and for the red → ox (λ_{ox}) relaxations [1,2].

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TEO-O17

Gas transport in rigid polymers: effect of structural properties

E. Tocci[a], *C. H. Park*[b], *Y. M. Lee*[c], *E. Drioli*[a,c]

a Istituto per la Tecnologia delle Membrane Technology ITM-CNR, c/o Università della Calabria, Via P. Bucci, Cubo 17/C, Rende (CS), 87030, Italy
b Gyeongnam National University of Science and Technology (GNTECH)
33 Dongjin-ro, Jinju-si, Gyeongsangnam-do, 660 - 758, Korea
c WCU Department of Energy Engineering, College of Engineering, Hanyang University, Seoul, 133-791, Korea

e.tocci@itm.cnr.it

Rigid polymer membranes are recently regarded as a state of the art materials for gas separation processes, due to their high permeability and selectivity [1]. However, despite extensive experimental studies, the relationship between structure and transport properties such as diffusivity and solubility is still in dispute. There are some empirically-accepted factors affecting diffusivity such as fractional free volume, interchain spacing, rigidity, etc [2]. Considering that those parameters are various indirect ways to describe a free volume morphology, it is very important to characterize the exact amount, shape and distribution of free volume. In this study, we analyzed the free volume morphology of rigid polymers using molecular dynamics (MD) simulation, where hydroxy-containing polyimides (HPIs) and thermally rearranged polybenzoxazoles (TR-PBOs) were adopted as rigid polymer candidates. Furthermore, mean square displacement calculation for diffusivity and GCMC simulation for solubility were performed with each 3D model. Comparing both results, we will correlate the free volume morphology and diffusivity/solubility, which can suggest the effective polymer structure for high gas transport performance.

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TEO-O18

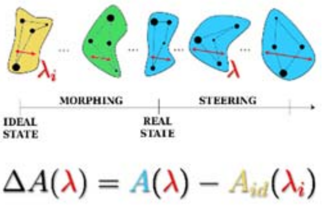
Modeling conformational dynamics of alkyl-thiols tethered to gold surfaces

Mirco Zerbetto, Andrea Piserchia, Federico Rastrelli, Fabrizio Mancin, Diego Frezzato

Dipartimento di Scienze Chimiche, Università degli Studi di Padova,
Via Marzolo 1, I-35131, Padova, Italy

mirco.zerbetto@unipd.it

Interest on coated surfaces is exponentially increasing in the scene of nanotechnology, since by fine-tuning the chemistry of the molecules linked to the surface it is possible to specialize the material to a number of tasks, such as catalysis, recognition, transport. The configurational dynamics of the linkers (such as alkyl-thiols) between the surface and the "reactive" part of the system is expected to play an important role on the function of the material. Here we propose an approach to the modeling of the relevant conformational dynamics of a probe alkyl-thiol in a self assembled monolayer, aimed at rationalizing the effects of the aliphatic environment and the surface on the conformational rigidity of the chain.



To the purpose, we employ the Jarzynski's Equality FREe Energy (JEFREE) software, recently developed in our laboratories. It is an efficient and easy-to-use C++ library targeted to the construction of the Helmholtz free energy profiles of a general molecular/supra-molecular system. The approach fits in the framework of the non-equilibrium steered transformations as introduced by Jarzynski.[1] JEFREE implements the novel idea of making first the "morphing" of the real energy landscape from an ideal "flat" state, followed by a steering along the controlled coordinate. Such a protocol revealed to outperform standard sampling routes based on Metropolis-Monte Carlo or equilibrium molecular dynamics.[2]

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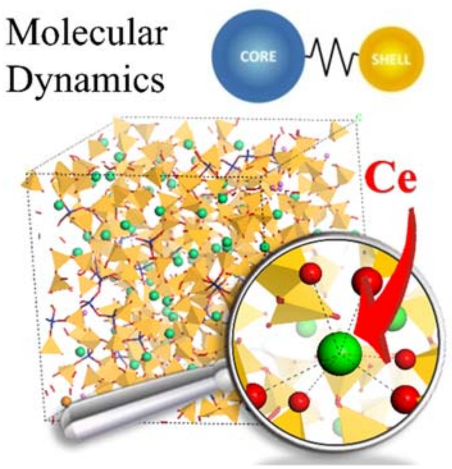
TEO-O19

Modelling of Ce-containing glasses: insight and improvement of design ability.

Elisa Gambuzzi[a] *Valentina Nicolini*[a], *Gianluca Malavasi*[a] and *Alfonso Pedone*[a]

a Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia,
Via G. Campi, 41125, Modena, Italy

elisa.gambuzzi@unimore.it



Cerium-containing glasses are widely used in optical and photonic devices such as optical windows, laser, and optical amplifiers because of their enhanced UV absorption and radiation damage resistance properties. [1-2].
Moreover, in the last decade the antioxidant properties of Ce^{3+} ions has been also exploited in the field of biomaterials by including it in bioactive glasses.[3]
Understanding the structure of Ce-doped silicophosphate glasses and the relation between the glass composition, the Ce environment and clustering has thus become fundamental to design new glasses with desired optical and antioxidant properties.
In this communication we will thus present a new core-shell force field parameterization for Ce^{3+}–O and Ce^{4+}–O atom pairs developed to simulate phosphosilicate glasses.
We will show the accurate performances achievable in reproducing the structure of silicophosphate glasses for photonics applications and bioactive glasses for biomedical applications.[4]

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TEO-O20

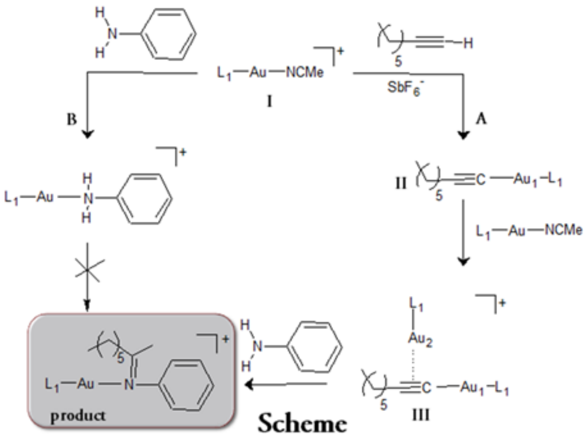
Theoretical insights on the role of digold(I)-alkynide complexes in catalysis.

Gloria Mazzone, *Emilia Sicilia*, *Nino Russo*

Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Via P. Bucci, 87936, Arcavacata di Rende, Italy

gloria.mazzone@unical.it

Gold homogeneous catalyst to act as soft carbophilic Lewis acid toward C−C multiple bonds has emerged in the last 15 years. It is well accepted that the coordination of a C-C multiple bond molecule to a cationic Au(I) complex represents the starting point for Au(I)-catalyzed reactions. Moreover, a second mode of interaction between terminal alkynes and Au(I) complexes has been found, due to the acidity of the terminal proton, which, in presence of a base, can be replaced by the gold(I) center, forming Au(I)-alkynil complexes (**II**).



Scheme

Very recently, the formation of dinuclear gold alkynide complexes, which exhibit both π coordination and gold-alkynyl-σ-bond structural motifs (**III**) has been evidenced.[1] The authors have studied the hydroamination of 1-octyne with aniline by using the complex **I** (with L_1= dialkylbiarylphosphine ligand) as precatalyst, performing two independent experiments, pathway A and pathway B as shown in Scheme.

To gain more information about the role played by digold(I)-alkynide complexes in catalysis, the detailed mechanism of the whole hydroamination of 1-octyne with aniline has been explored by means of Density Functional Theory calculations. Furthermore, to probe whether the performance of cationic digold complex **III** can be superior than that of mononuclear complexes, the reaction of aniline with both monogold(I) complexes formed by π- and σ-coordination, respectively of 1-octyne to the precatalyst has been investigated.

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TEO-O21

Force Field for ZIF-8 via Force Matching

A. Gabrieli[a], *M. Sant*[a], *P. Demontis*[a], *G. B. Suffritti*[a]

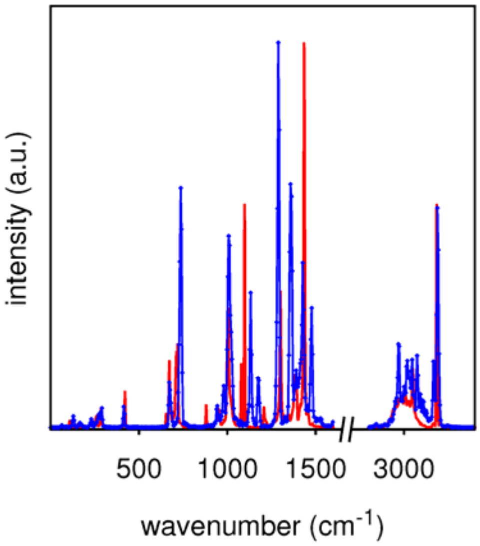
a Dipartimento di Chimica e Farmacia, Università degli Studi di Sassari, Via Vienna 2, 07100, Sassari, Italia

pino@uniss.it

Classical Molecular Dynamics is one of the most widespread tools to study the evolution of microporous materials and their sorbates up to the microsecond scale. To perform such simulations, thought, one must provide a force field ruling the system interactions: the accuracy of the simulation ultimately depends on the quality of such force field. Various database of generic force fields are available, but these are not so accurate when applied to complex systems they were not developed for.

One option to obtain reliable force fields, tailored to the specific system under investigation, is to reproduce the forces obtained by accurate but computationally expensive simulation techniques (such as ab-initio molecular dynamics) taken as a reference via the *force matching* method [1].

A fast and efficient implementation of this technique has been developed and applied to ZIF-8 crystal obtaining a reliable parameterization of its bonded interactions. The quality of the model has been assessed comparing its IR spectrum with the reference system one (see Figure). The overall agreement is excellent: note that the parameters to be optimized are 46. The full parameterization is accom- plished in less than 10 minutes on a common desktop pc [2].



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TEO-O22

Ab Initio Assessment of Ring Current Models

Guglielmo Monaco[a], Paolo Della Porta[a], Riccardo Zanasi[a], Stefano Pelloni[b], Paolo Lazzeretti[b]

a Dipartimento di Chimica e Biologia, Università degli Studi di Salerno, Via Giovanni Paolo II, 132, Fisciano 84084 SA Italy
b Dipartimento di Scienze Chimiche e Geologiche, Universitá degli Studi di Modena, via G. Campi 183, 41100 Modena, Italy

gmonaco@unisa.it

Interpretation of both measured and computed values of chemical shift in (poly)cyclic molecules is widely based on ring current models (RCMs), which are also a basic tenet in the discussion of (magnetic) aromaticity. Few improvements have been considered to date for the reference RCM, consisting in an infinitely-thin circular loop of current (ICLOC). Five improved analytical RCMs have been recently discussed, and they have been graded by comparing their ability to reproduce the π and σ contributions to the ab initio ring current strengths and the scans of to the parallel component of the magnetic shielding ($\sigma\| = -\mathrm{NICS}\|$) in a large set of monocycles.[1]

The introduction of a second ICLOC is almost always needed to achieve good agreement with the ab initio values. The best two-ICLOCs models allow understanding why the assumption that the magnetic aromaticity can be clearly assessed from the shape of the NICS scan[2] is not generally valid.

At a more basic level, the straightforward identification of magnetic aromaticity with an ICLOC-like NICS scan is challenged by the recent report of strong delocalized currents occurring in noncyclic molecules.[3]

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TEO-O23

Nonelectrostatic contributions to spectroscopic properties of solvated systems

Lorenzo Cupellini[a], *Claudio Amovilli*[a], *Benedetta Mennucci*[a]

[a] *Dipartimento di Chimica, Università di Pisa, Via Risorgimento 35, 56126, Pisa, Italia*

lorenzo.cupellini@for.unipi.it

Dispersion and repulsion forces are important contributions to solvation, but their treatment in QM/classical method is often reduced to a simplified classical expression, which cannot describe the influence of such interactions on the wavefunction and the properties of molecular solutes. Here we present a new parameterization of the quantum dispersion and repulsion extension to the Polarizable Continuum Model [1], in order to compute the nonelectrostatic effect on spectroscopic properties. We validated and parameterized the model, within the time-dependent Density Functional Theory, against a set of several valence excitations of organic chromophores.

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TEO-O24

A General Purpose Implementations of Semiclassical Molecular Dynamics for CPU and GPU hardware

Michele Ceotto[a], *Dario Tamascelli*[b], *Francesco Saverio Dambrosio*[c]

a Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133, Milano, Italia
b Dipartimento di Fisica, Università degli Studi di Milano, Via Golgi 19, 20133, Milano, Italia

michele.ceotto@unimi.it

The calculation of the semiclassical propagator is a Monte Carlo integration over classical trajectories. This can be accelerated either by importance sampling or by phase space integration parallelization. First, a multiple coherent states time-averaging semiclassical initial value representation method for spectra calculations is presented[1]. This is implemented for *ab initio* semiclassical simulations, i.e. a direct dynamics approach, and it is shown to faithfully reproduce all kind of quantum effects, including ZPEs, anharmonicities, tunneling splitting[2], resonances[3] and vibrational eigenfunctions.[4] This on-the-fly approach is useful in particular for complex systems[5], where the elaboration of a pre-computed potential energy surface can turn into a formidable task. In the second case, SC-IVR is implemented for GPUs hardware shown in figure[6]. With respect to the CPU code, GPU code provides an average 100x computational speed-up and an order of magnitude of power saving. GPU limitations will be discussed.

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TEO-O25

Organic Frameworks from large scale DFT calculations

B. Civalleri[a], M. D'Amore[a], M. Ferrabone[a], E. Albanese[a], R. Orlando[a]

a Dipartimento di Chimica, Università di Torino, Via P. Giuria 7, 10125, Torino, Italia

bartolomeo.civalleri@unito.it

Metal-Organic Frameworks (MOFs) are a new class of materials that are expected to play a huge impact in the development of next-generation technologies. They consist of inorganic nodes connected through organic linkers to form a porous three-dimensional framework. The combination of different nodes and linkers makes MOFs very versatile materials with promising applications in many fields, including [1]: gas adsorption, catalysis, photo-catalysis, drug delivery, sensing and nonlinear optics.

We will show results on the ab-initio modeling of the adsorptive capacity of the so-called *giant* MOFs. They possess pores with a very large size and, in turn, a huge surface area. Among giant MOFs, the most representative one is probably MIL-100 [2]. It ideally crystallizes in a non-primitive cubic lattice with 2788 atoms in the primitive cell. MIL-100 is characterized by the presence of a large number of coordinatively unsaturated metal atoms (e.g. Al, Sc, V, Mn, Cr, Fe) exposed at the inner surface of the pores that are crucial in determining its adsorption capacity. In particular, we are investigating MIL-100 for its ability of capture carbon dioxide, which is one of the hottest topic in MOFs research [3], and the adsorption of large molecules such as drugs, for drug delivery purposes [4]. The project is ongoing and available results will be shown.

Giant MOFs, with thousands of atoms in the unit cell, represent a tremendous challenge for current ab-initio calculations. The use of Tier-0 computer resources provided by PRACE is essential to tackle this challenging problem. All calculations have been carried out with the B3LYP-D method by using the massively parallel (MPP) version of the ab-initio code CRYSTAL (http://www.crystal.unito.it/) [5,6].

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TEO-O26

Effects of Organic Ligands on the Optical Properties of Undecagold Nanoclusters

Alfonso Pedone[a], *Francesco Muniz-Miranda*[a], *Maria Cristina Menziani*[a],

a Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia,
Via G. Campi 183, 41125, Modena, Italia

alfonso.pedone@unimore.it

Organic protected gold nanoclusters (NC) exhibit unique optoelectronic properties that make them very promising nanodevices for a wide range of electronic and biomedical applications.

Besides the size and shape of Au-based nanoparticles, the interaction between organic ligands and gold surfaces is also believed to affect the optoelectronic properties of such nanodevices [1].

In fact, very recently the conjugation between aromatic ligands and metal electrons has been advocated to explain the shape of UV-Vis spectra of thiolate-protected Au_{25} [1] and phosphine-protected Au_{11} NCs [2].

In this communication we will present a detailed time-dependent density-functional investigation aimed at systematically dissecting the electronic spectra of two thiolate and phosphine protected undecagold nanoclusters.

Calculations performed on the experimental structures of $Au_{11}(PPh_3)_7Cl_3$ and $Au_{11}(PPh_3)_7(SPyr)_3$ show that ligands give negligible contributions in the visible region. Metal→ligand charge transfer transitions appear at energies well above the visible threshold, while transitions with some small ligand→metal and ligand→ligand character occur sporadically at even higher energies. Thus, the conjugation effect between π-electrons of the ligand and gold electrons, recently hypothesized to interpret the spectra of phosphine and thiolate-protected nanoclusters, is not confirmed by our calculations.[3,4]

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TEO-O27

Binuclear Co^{2+} Organophosphate Degrading Enzyme working mechanism. A theoretical prediction

Marta E. Alberto[a], *Gaspar Pinto*[a], *Nino Russo*[a], *Marirosa Toscano*[a]

a Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria,
Via P.Bucci ,87036, Arcavacata di Rende (CS), Italy

marta.alberto@unical.it

Organophosphate degrading enzyme from Agrobacterium radiobacter (OpdA), is a promiscuous binuclear metalloenzyme able to hydrolyze a large number of phosphotriesters, including highly toxic pesticides and nerve agents, with a modest disterase activity. Despite its promiscuous nature make it possible for OpdA to have different metals in the active site, in vitro studies showed that the binuclear di-Co^{2+} derivative possesses a catalytic activity higher than the native Fe^{2+}-Zn^{2+} form.
Herein, the diesterase and triesterase activities of di-Co(II) OpdA have been compared investigating the hydrolysis of trimethylphosphate and dimethylphosphate at density functional level of theory in the framework of the cluster model approach. The reaction mechanisms have been fully elucidated also confirming the crucial role played by a water molecule and some residues in the outer coordination sphere. Similarities with the working mechanism of other bimetallic phosphatases have been found. Two exchange-correlation functionals have been used to derive the potential energy profiles, in gas phase and protein environments. Moreover, to correctly describe the electronic configuration of the d shell of the binuclear center, high- and low- spin arrangement jointly with the occurrence of antiferromagnetic (AFM) coupling, have been herein considered.

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Chimica Teorica e Computazionale

Poster

TEO-P1

Methane Adsorption in Porous Aromatic Frameworks (PAFs)

L. Canti[a]*, A. Fraccarollo*[a]*, M. Errahali*[a]*, G. Gatti*[a]*, L. Tei*[a]*, M. Cossi*[a] *and M.Marchese*[a]

a Dipartimento di Scienze ed Innovazione Tecnologica and Centro Nano-SISTeMI, Università del Piemonte Orientale "A.Avogadro", Via T.Michel 11, 15121, Alessandria, Italy

lorenzo.canti@mfn.unipmn.it

PAFs are microporous polyphenylic networks obtained by the replacement of the C-C tetrahedral covalent bonds of diamond-like structure with phenyl rings. PAF-302 has shown very interesting properties for methane storage suitable for automotive applications.[1] For this reason, FT-IR and Raman spectroscopies are employed in this contribution, along with ab initio calculations, to describe the vibrational features of PAF-302 material and investigate the interactions of methane with the porous framework. A comparative investigation of the physico-chemical properties of the material was carried out by a multidisciplinary approach using FTIR, Raman, SS-NMR, TGA, N_2 physisorption at 77K. FTIR and SS-NMR spectra of PAF-302 show that a complete polymerization occurred leading to a material with the expected structural units. PAF-302 shows a high thermal stability (up to 450 °C) and high specific surface area (BET up to 4500 m^2/g) with a predominant microporosity. We also collected the infrared spectra for the adsorption of CH_4 on PAF-302 at low temperature: the vibrational spectra of PAF-302 and its adduct with methane have been recorded and resolved (Fig.1) to investigate the interactions with the adsorbed gas. [2]

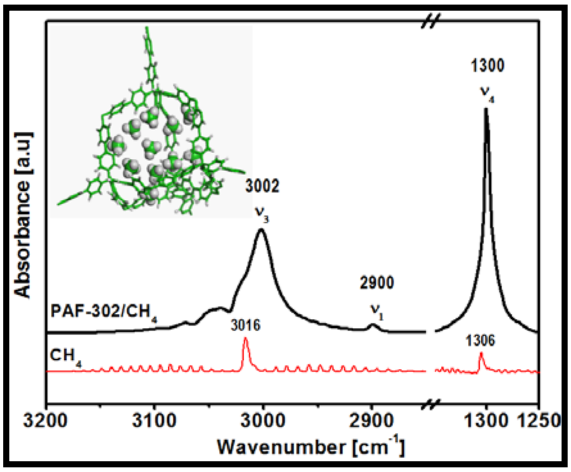

Fig.1. FTIR spectra of CH_4 gas and difference spectrum of PAF-302 at equilibrium pressure of 10 mbar CH_4

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TEO-P2

Contributo Ritirato

TEO-P3

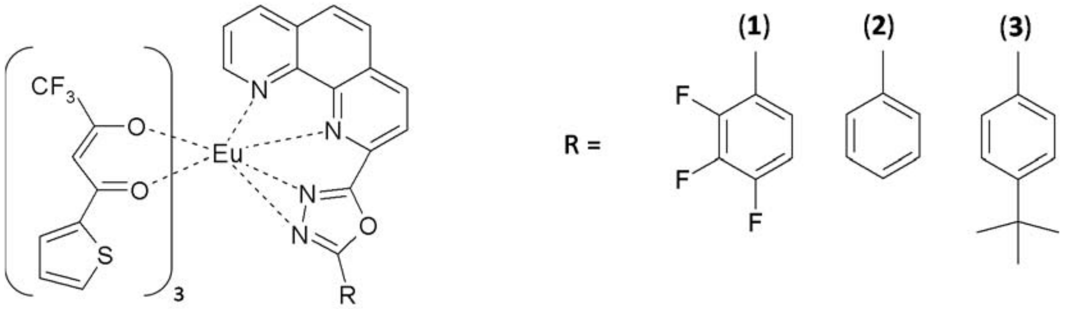
Theoretical investigation on Spectroscopic properties of Europium complexes

Ugo Cosentino,[a] *Claudio Greco,*[a] *Damiano Gerosa,*[a] *Giorgio Moro*[b]

a Dipartimento di Scienze dell'Ambiente e del Territorio e di Scienze della Terra, Università degli Studi di Milano-Bicocca; Piazza della Scienza 1, 20126 Milano, Italy
b Dipartimento di Biotecnologie e Bioscienze Università degli Studi di Milano-Bicocca; Piazza della Scienza 2, 20126 Milano, Italy

ugo.cosentino@unimib.it

Due to their photophysical properties, Lanthanide complexes with β-diketonate (β-DK) ligands find applications in several technological fields. [1] In particular, europium β-DK complexes have attracted more interest in optoelectronic applications because of their strong and narrow red emission. Previously, we set up a computational protocol [2] able to reproduce key spectrophotophysical properties of a series of β-diketonate Europium complexes.



Here we present the results of our theoretical investigation on the spectroscopic properties of complexes (**1**)-(**3**) of Europium ion, the photophysical characterization of which has been recently reported in literature. [3]

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TEO-P4

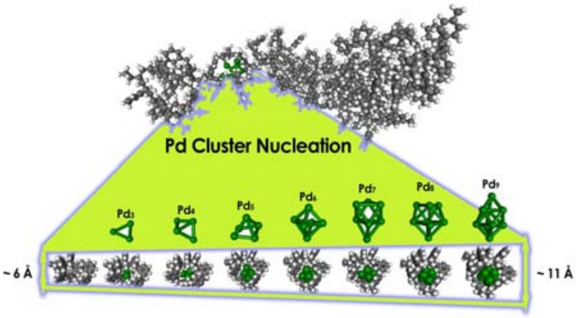
Studio computazionale sulla nucleazione e l'accrescimento di cluster di palladio su polistirene hypercrosslinked

Francesco Ferrante, *Antonio Prestianni*, *Dario Duca*

Dipartimento di Fisica e Chimica, Università degli Studi di Palermo, Viale delle Scienze,
Parco d'Orleáns II, Ed. 17, 90128, Palermo, Italia

francesco.ferrante@unipa.it

Presentiamo i risultati di uno studio di nucleazione e accrescimento di piccoli cluster di palladio Pd_n (n=1-9) su una specifica cavità di una matrice di polistirene hypercrosslinked (HPS). L'indagine è stata condotta a livello DFT:MM su una cavità facente parte di una porzione di HPS estratta dal polimero già costruito e rilassato con un apposito algoritmo di dinamica molecolare[1]. L'energetica della nucleazione e dell'accrescimento, così come la geometria del cluster assorbito, sono governate da un sottile bilancio tra le interazioni Pd-benzene e quelle Pd-Pd. La nucleazione sembra essere regolata dalla particolarmente forte interazione tra il palladio e l'anello benzenico [2] mentre, in quella che si ritiene essere l'inizio della fase di accrescimento, le seconde prevalgono sulle prime. Il cluster di palladio assorbito induce forti distorsioni sulla cavità che lo ospita, in accordo con l'esistenza di proprietà elastiche della matrice di HPS.



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TEO-P5

Combined DFT and experimental Study on N1s NEXAFS Spectra of 1,4 Diaminobenzene on Au (111) Surface

G. Fronzoni[a], G. Balducci[a], M. Romeo[a], M. Stener[a]
G. Kladnik[b], D. Cvetko[b] , A. Cossaro[c] , A. Morgante [c] , L.Venkataraman [d]

[a] Dipartimento di Scienze Chimiche e Farmaceutiche, Universita' di Trieste, Trieste,
[b] University of Ljubljana, Ljubljana, Slovenia, [c] CNR-IOM, Trieste, [d] Columbia University, New York, NY 10027, USA

fronzoni@units.it

The Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy is a powerful technique to investigate the orientation and geometry of molecules adsorbed on surfaces. The computational simulation of NEXAFS spectra of such systems represents a significant challenge both for a proper modelling of the adsorbate structure as well as for the size of the system which need theoretical methods capable to fulfill requirements of accuracy and computational economy. The not easy task of an accurate modeling of the systems is tackled by a preliminary optimization of the surface and of the molecules adsorbed on it through a periodic slab methodology in the frame of DFT. The Quantum-Espresso suite of codes has been used as the practical implementation of this methodology[1]. From the optimized periodic structures, suitable finite clusters can be cut out and used for the calculation of NEXAFS spectra employing molecular DFT techniques[2] to fully exploit their accuracy for the electronic spectra simulations. Here we present the simulations of the angle resolved NEXAFS of 1,4-diaminobenzene adsorbed on Au (111) surface to support the interpretation of the experimental spectra. Two main adsorption configurations have been considered, namely a tilted binding mode, in which the diaminobenzene binds through only one nitrogen atom to an Au of the surface, and a flat binding mode, in which the diaminobenzene molecule binds parallel to the surface with both nitrogen atoms. Possible influence of H−bond formation between adsorbed molecules has been also explored. The comparison with the experimental spectra provides information on specific details of the adsorbtion geometries and shows that the methodology employed is reliable to describe the K-shell spectra of this kind of systems.

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TEO-P6

Effect of Nanoparticles Size on the Formation of Ubiquitin Corona

Francesco Tavanti, Alfonso Pedone, Maria Cristina Menziani

Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di
Modena e Reggio Emilia, Via Campi 183, 41125, Modena, Italy.

francesco.tavanti@unimore.it

The use of nanoparticles (NPs) of various size and shape is increasing due to their unique chemical, physical, optical and magnetic properties. When NPs are exposed to the biological medium, biomolecules absorb on their surface creating a bio-corona that determines the subsequent cellular response. Absorbed proteins undergo to structural changes depending on the NP curvature and on NP charge density. These structural modifications are responsible of changing in proteins function and of health risks [1,2].

In this work, we computationally investigated the bio-corona formation by Ubiquitin proteins as a function of the NPs size. Ubiqutin represents a good test because it is ubiquitous in eukariotic organisms, it is small in size and has a well characterized three dimensional structure[3]. In order to maintain acceptable computational costs and to reach timescales in the order of hundreds of ns, a multi-scale coarse grained representation has been adopted, where gold NPs (AuNPs) with different diameter surrounded by 50 ubiquitin proteins have been simulated. Results show that ubiquitins conformational changes are related to NP curvature.

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TEO-P7

Contributo Ritirato

TEO-P8

A New Valence Photoabsorption TDDFT Algorithm for Large Systems

Oscar Baseggio, Giovanna Fronzoni and Mauro Stener

Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Trieste, Via Giorgieri 1,
34127 Trieste, Italy

stener@units.it

The calculation of optical spectra for large molecules has become a routine task thanks to efficient implementations of the TDDFT method. The most common procedure in quantum chemistry is to diagonalize the Ω matrix according to the formulation of Casida. Such method is efficiently implemented in the ADF code. However, when very large molecules are considered, it is very difficult to calculate valence photoabsorption spectra over a wide excitation energy range. In fact the Davidson algorithm is very efficient on very large Ω matrices, but is limited to extract a relatively small number of lowest eigenvalues and eigenvectors. The characteristic of the present new algorithm is to avoid the diagonalization of the Ω matrix. This can be formally obtained if the photoabsorption spectrum $\sigma(\omega)$ is calculated point by point, from the imaginary part of the dynamical polarizability $\alpha(\omega)$: $\sigma(\omega) = (4\pi\omega/c)$ $Im[\alpha(\omega)]$. This expression should be of practical interest when the polarizability is calculated for complex frequency, i.e. $\omega = \omega_R + i\omega_i$, where the real part ω_R is the scanned photon frequency (energy) and ω_i is the imaginary part which corresponds to a broadening of the discrete lines and can be interpreted as a pragmatic inclusion of the excited states finite lifetime. It will be shown that it is possible to calculate efficiently the complex polarizability $\alpha(\omega)$ introducing some approximations. The method should be suitable for applications on large systems, for example to investigate plasmon resonances in metal clusters which can be properly described at TDDFT level[1] but start to appear only when the system size is above 2 nm.

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TEO-P9

Peptides at gold/water interface

Luca Bellucci[a], *Giovanni Bussi*[b], *Rosa Di Felice*[c], *Stefano Corni*[a]

a Centro S3, CNR-NANO,via G. Campi 213/A, 41125, Modena, Italia
b SISSA, via Bonomea 265, 34136 Trieste, Italia
c University of Southern California, Los Angeles, CA, USA

E-mail luca.bellucci_s3@unimore.it

Understanding adsorption processes of bio-molecules at inorganic surfaces is crucial to rationalize the behavior of a new generation of nanoscale-based systems, which are of great importance in emerging disciplines spanning from nanotechnology to nanomedicine. In particular, recent experimental works tackled the effect, in vitro, of nanoparticles (NPs) on protein fibrillation. Protein fibrillation is involved in many human diseases, including Alzheimer's, Parkinson's, Creutzfeld-Jacob's and dialysis-related amyloidosis. Molecular adsorption on solid surfaces or NPs is a complex process that involves many dynamical steps from the initial recognition of the molecule by the surface, to the equilibrium conformational rearrangement of the adsorbed molecule. The rationalization of such aspects represents one of the major challenges for experimental and theoretical investigation methods. Specific dynamical aspects can be investigated by using advanced molecular dynamics (MD) simulations [1], exploiting the availability of classical force-fields (FF) that describe the interaction of proteins with gold surfaces in water, e.g. GolP [2]. With these tools, we simulated the interaction between a gold surface and prototypical peptides in solution. In particular, the peptides studied by us are (i) the alanine dipeptide [3], (ii) the KLVFFAE (KE7) peptide and (iii) the amyloid β-peptide (Aβ).

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[2] F. Iori, R. Di Felice, E. Molinari, S. Corni, *J. Comput. Chem.*, 2009, **30** 1465-1476.
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TEO-P10

Computational investigation of CO_2 activation with a non-symmetrical aluminium salen complex

Valeria Butera[a], *Ugo Cosentino*[a], *Claudio Greco*[a], *Giorgio Moro*[b], *Nino Russo*[c], *Emilia Sicilia*[c]

a Dipartimento di Scienze dell'Ambiente e del Territorio e di Scienze della Terra, Piazza della Scienza 1, 20126,Milano, Italy.
b Dipartimento di Biotecnologie e Bioscienze, Piazza della Scienza 2, 20126 Milano, Italy.
c Dipartimento di Chimica e Tecnologie Chimiche, Universita` della Calabria, Via P. Bucci 87036 Arcavacata di Rende (CS), Italy.

valeria.butera@unimib.it

The use of carbon dioxide (CO_2) as a C1 building block for chemical synthesis has recently attracted much interest because of its abundance, low cost, nontoxicity, and high potential as a renewable source. However, due to the high thermodynamic stability and low reactivity of CO_2catalysts are needed to reduce the activation energy of any reaction in which it is involved. In this regard, synthesis of cyclic carbonates via cycloaddition of CO_2 to epoxides is one of the most attractive processes (Scheme 1). Cyclic carbonates are valuable products widely used as green solvents, electrolytes, fuel additives and intermediates for polycarbonates. In the past decade, several catalysts have been reported to catalyze cyclic carbonates formation by homogeneous cycloaddition of carbon dioxide to epoxides. Among the homogeneous catalysts, salen complexes of cobalt and aluminium show high catalytic activities under mild conditions. In particular, salen complexes of aluminium have received considerable interest in the synthesis of cyclic carbonates, mainly due to the low environmental impact of aluminium, its high Earth abundance and its high catalytic activity. Styring and coworkers[1] reported the synthesis of styrene carbonate using the novel non-symmetrical aluminium(III) salenac complex that displayed a better catalytic activity than a symmetrical aluminium salen complex previously reported at low CO_2 pressure. They found also that the presence of Tetrabutylammoniumbromide (TBAB) enhances the catalytic activity increasing the conversion from 70%, using the catalyst alone, to 90% when TBAB is added as a co-catalyst. However, a high temperature was required in order to achieve high yields. In this context, a rigorous quantum-mechanical investigation of the cyclic carbonates formation has been performed in order to gain useful information about the mechanistic aspects of the overall catalytic process.

[1] S. Supasitmomgkol, P. Styring, A, *Catal. Sci. Techol.*, 2014, **4**, 1622-1630.

TEO-P11

Interaction of oxaliplatin with carnosine and its derivatives. A computational study of the fragmentation process

Ida Ritacco[a], *Nino Russo*[a], *Emilia Sicilia*[a], *Tamer Shoeib*[b]

a Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Via Pietro Bucci , 87036, Arcavacata di Rende (CS), Italia
b Department of Chemistry, The American University in Cairo, New Cairo 11835,Egypt

ida.ritacco@unical.it

Oxaliplatin (OxPt) is a chemotherapeutic drug developed for the treatment of colorectal and cisplatin resistant cancers. OxPt interacts with DNA causing the death of cancer cells, but as other Pt-based anticancer drugs it can form complexes with particular dipeptides abundantly present in the cytoplasm, such as carnosine and its derivatives anserine and N-acetylcarnosine. In vitro studies on hepatocellular carcinoma HepG2 cells suggest that carnosine may inhibit the cytotoxic action of OxPt most likely through the formation of complexes that are less cytotoxic than OxPt alone. Various mass spectrometry techniques have been, recently, employed to study the interaction of oxaliplatin with carnosine and its anserine and N-acetylcarnosine derivatives and evidences of the complexation have been presented. In this paper the theoretical investigation of the potential energy surfaces calculated in the framework of DFT, at B3LYP/LANL2DZ level, for the fragmentation pathways resulting from the interaction of the drug with the three dipeptides ($[M+OxPt+H]^+$, M = carnosine, anserine or N-acetylcarnosine) is presented. Calculated fragmentation mechanisms and energetics are in very good agreement with information coming from experiments.

TEO-P12

Contributo Ritirato

Didattica Chimica

Keynote

DID-K1

Una nuova formazione bidisciplinare degli insegnanti di Scienze Sperimentali

Michele A. Floriano[a],

[a] *Dipartimento di Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche, Università di Palermo, Viale delle Scienze, ed. 17, 90128, Palermo, Italia*

michele.floriano@unipa.it

La proposta[1] riguarda una strategia mirata a superare le difficoltà sia di competenze, sia organizzative, derivanti dall'attuale distribuzione delle specificità disciplinari nell'insegnamento scientifico della scuola secondaria di secondo grado.

La proposta si articola in due punti:

- Le discipline interessate sono: biologia, chimica, fisica e scienze della terra. Con la laurea magistrale per l'insegnamento si consegue una abilitazione primaria nella disciplina della laurea triennale di provenienza. Si consegue inoltre una abilitazione secondaria in una delle altre discipline.
- Vengono superate le graduatorie relative alle attuali abilitazioni. Gli aggregati disciplinari vengono scomposti in insegnamenti singoli, ed eliminando le attuali classi di concorso. Ai docenti in servizio viene attribuita una abilitazione primaria (o "maior") coerente con la laurea di provenienza, nel caso si tratti di docenti con un'abilitazione in una classe di concorso che preveda insegnamenti pluridisciplinari; o nella disciplina in cui sono abilitati all'insegnamento, nel caso si tratti di classe di concorso monodisciplinare. A scelta del docente può anche essere attribuita una sola abilitazione secondaria (o "minor"), dopo verifica dei necessari requisiti e/o riqualificazione. Nei licei, ciascun docente insegna le due discipline corrispondenti alle due abilitazioni così conseguite. Negli istituti tecnici e in quelli professionali, per le intrinseche caratteristiche, le discipline di insegnamento sono attribuite ai soli docenti in possesso di abilitazione primaria coerente con i contenuti del corso. Negli istituti che abbinano insegnamenti tecnici e liceali, gli organici vengono riorganizzati secondo quanto sopra.

[1] Documento redatto dal gruppo di lavoro della DD-SCI, realizzato con il contributo di: A. Andracchio, M. A. Floriano, E. Ghibaudi, S. Palazzi, G. Passarelli, A. Regis e approvato dal C.D. DD-SCI (https://www.soc.chim.it/sites/default/files/users/div_didattica/PDF/Bidisciplinarieta.pdf)

DID-K2

Il contributo della chimica allo sviluppo delle competenze scientifiche nella scuola di base

Antonio Testoni

IIS “Copernico Carpeggiani” via Pontegradella, 25 44123 Ferrara
ajteston@tin.it

“Una riflessione sul curricolo di scienze non può prescindere da un dato ampiamente condiviso dalla comunità scientifica nazionale e internazionale: i risultati conseguiti nell’insegnamento in tale area sono molto deludenti e sprecano, nella maggior parte dei casi, il patrimonio di intelligenza dei giovani. Molte ricerche convergono nell’individuare la principale criticità nel modo in cui le scienze vengono proposte in ambito scolastico. Tra gli aspetti di maggiore criticità vengono indicati i seguenti: prevale un insegnamento nozionistico, manualistico anziché per problemi; la priorità è assegnata alla trasmissione di contenuti anziché ad un processo di costruzione della conoscenza; nel passaggio da un livello scolastico all’altro si riparte sempre da zero in quanto manca qualsiasi idea di curricolo verticale; le attività di laboratorio (quando ci sono) servono a confermare conoscenze già possedute; lo studente apprende in modo passivo”[1]. I nodi che vengono evidenziati riguardano innanzitutto la prevalenza di un insegnamento tradizionale, enciclopedico-nozionistico, nonostante che, da molti decenni, i programmi prima e le indicazioni poi, avessero prospettato in modo chiaro un’impostazione dell’insegnamento scientifico di tipo laboratoriale. L’alternativa non è tra insegnare poco o tanto, ma tra insegnare tante nozioni superficiali e insignificanti, seguendo la logica enciclopedica del programma, oppure una quantità di conoscenze compatibili con il tempo che si ha disposizione, che consentano uno scandaglio in profondità sì da renderle significative e trasformarle in *competenze*. La significatività delle conoscenze, in particolare nella scuola del primo ciclo, è connessa al contatto diretto con le cose. Le esperienze sono indispensabili per realizzare il processo di concettualizzazione, ma esse diventano rilevanti solo se “inserite in processi di conoscenza”, se sono cioè connesse ad altre esperienze. Per essere significativi i saperi, oltre che essenziali (fondamentali e generativi), dovrebbero essere adeguati alle strutture cognitive e motivazionali degli studenti. Pensiamo che sia impossibile, pur in presenza di una didattica laboratoriale, far diventare significative, e trasformare in competenze, conoscenze troppo lontane dalla possibilità di essere comprese. Anche gli esperimenti di per sé non sono concettualmente evidenti; come tutta la riflessione epistemologica degli ultimi cinquant’anni ha messo in evidenza, gli esperimenti sono infatti carichi di teoria. Per costruire quindi ipotesi di curricolo verticale delle scienze, ed in particolare della C*himica*, basate sugli esperimenti, è indispensabile una analisi, fondata sul piano epistemologico e psicologico, dei concetti scientifici per individuare, in via ipotetica, quei concetti e quegli esperimenti più adatti alle varie età. Il rischio altrimenti è quello di confondere un insegnamento significativo con forme di magia. Ma magia è soprattutto l’antitesi della scienza, è l’opposto della razionalità, della costruzione lenta, problematica, critica, progressiva, democratica del sapere. In questo senso l’educazione scientifica non può che essere l’opposto della magia: non tutto e subito, ma lentezza, lentezza nella costruzione problematica e graduale della conoscenza.

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[1] Provincia di Trento, *Piani di studio Provinciali Primo Ciclo di Istruzione, Linee guida per l’elaborazione dei piani di studio di istituto*, Trento, 2009.

DID-K3

CLIL: a pragmatic guide for Renovating Chemistry Education

Y.L. Teresa Ting
Dipartimento di Chimica e Tecnologie Chimiche, Università di Calabria, Via P. Bucci, 87010, Rende (CS), Italia
teresa.ting@unical.it

Sebbene il CLIL –Content and Language Integrated Learning–sia nato negli anni 90 nell'ambito dell' "insegnamento di lingua straniera", da qualche anno si sta rivelando come qualcosa che è molto di più che un semplice metodo per "imparare un po' più di Inglese"[1]. Se ben messo in pratica, il CLIL fornisce agli insegnanti di contenuto una guida pragmatica per rinnovare e migliorare l'insegnamento della loro materia. Per gli insegnanti di chimica delle scuole secondarie di secondo grado, dove il contenuto è spesso considerato "difficile" ma dove gli studenti, contrariamente agli studenti universitari, non hanno "optato" di studiare la chimica[2], i DD.PP.RR. nn. 88/2010 e 89/2010 costituiscono una opportunità per rinnovare le "aule di chimica". Nella prima parte di questo workshop sarà presentato un set di materiali[3] per dimostrare come il CLIL possa facilitare l'apprendimento di contenuti a livello di secondaria superiore[4]. La seconda parte sarà invece centrata sull'analisi del perché il CLIL renda più accessibile un contenuto "difficile". Tale analisi sarà condotta anche guardando il CLIL alla luce di ciò che le neuroscienze ci indicano a proposito di "information processing", "attenzione" e "processi di apprendimento"[5]: quando apprendiamo, apprendiamo con il cervello – qualsiasi nuovo metodo / approccio deve considerare questo fatto. Il Workshop si concluderà con dei suggerimenti su come programmare una formazione docenti che utilizzi il CLIL per rinnovare la didattica della Chimica: questo è importante non solo per preparare i chimici di domani, ma anche per "alfabetizzare chimicamente" la società e quindi far apprezzare la Chimica come scienza presente in vari aspetti della vita quotidiana, sia visibili che "invisibili".

[1] Ting, Y.L.T. (2011) CLIL…not only not immersion but also much more than the sum of its parts. *English Language Teaching Journal*, 65/3: 314-317.
[2] See British Council Signature Panel on *English as a Medium of Instruction* (EMI). IATEFL 2014, Harrogate, UK. http://iatefl.britishcouncil.org/2014/sessions/2014-04-02/british-council-signature-event-english-medium-instruction-cure-or-curse
[3] I materiali hanno ricevuto il premio internazionale ELTons dal British Council: *The Macmillan Education Award for Innovative Writing*. http://englishagenda.britishcouncil.org/eltons
[4] Ting Y.L.T. (with Grandinetti, M. and Langellotti, M.). (2013). How CLIL can provide a pragmatic means to renovate science-education - even in a sub-optimally bilingual context. *International Journal of Bilingual Education and Bilingualism* 16/3: 354-374.
[5] Ting, Y.L.T. (2010) CLIL appeals to how the brain likes its information: examples from CLIL-(Neuro)Science. *International CLIL Research Journal*, 1/3:1-18, (In Focus Article). http://www.icrj.eu/13-73

DID-K4

Progetti locali, nazionali ed europei: sono realmente un aiuto nella comprensione della chimica?

Maria Maddalena Carnasciali

Dipartimento di Chimica e Chimica Industriale, Università di Genova,

Via Dodecaneso 31, 16146 Genova, Italia

marilena@chimica.unige.it

L'Università degli Studi di Genova ha iniziato a preoccuparsi delle scarse conoscenze scientifico-tecnologiche delle sue matricole prima ancora che nascesse il Piano Lauree Scientifiche, ormai noto come PLS. Un gruppo di colleghi, uniti dalle più disparate motivazioni, sollecitati da Giunio Luzzatto, ha costituito il Gruppo di Lavoro Università E Scuola, GLUES, nel tentativo di fare da "collante" tra scuola e università. Il progetto è servito per allacciare i primi contatti con le scuole del territorio ligure, preparando di fatto il terreno per il PLS, che da subito ha riscosso un grande successo. Il desiderio di comprendere se le motivazioni della carenza di vocazioni scientifiche nei corsi universitari italiani fossero le stesse riscontrate in altri paesi dell'Europa, ha portato ad affrontare le difficoltà e le gratificazioni di due progetti europei che avevano come principale obiettivo quello di stimolare la motivazione all'apprendimento della chimica dalla scuola all'università, sia da parte degli studenti, sia da parte degli insegnanti.

Sono ormai passati quasi dieci anni dai primi incontri tra il mondo universitario e quello scolastico: possiamo dire che tanto lavoro è stato davvero utile? Come si inserisce in tutto ciò l’orientamento? Chi ha più bisogno di essere orientato, gli studenti che devono cercare di comprendere le loro reali attitudini o gli insegnanti, non sempre consapevoli del ruolo determinante che svolgono nel delicato passaggio tra scuola e università?

E gli universitari, quanto sono disposti a entrare in questo meccanismo complesso?

Didattica Chimica

Oral

DID-O1

Global Competences and Philosophical Implications in Chemical Education

Teresa Celestino[a,b], *Fabio Marchetti*[a]

a School of Science and Technology, Chemistry Section, University of Camerino, Via S. Agostino 1, 62032, Camerino (MC), Italy
b Technical High School "Galilei-Sani", Via Ponchielli s.n.c., 04100, Latina, Italy

teresa.celestino@unicam.it

In Italy, chemistry teaching does not focus enough on the interplay of science, technology and society. A "socio-critical and problem-oriented approach"[1] fitting the Italian school context can promote the essential skills of well-developed scientific literacy, with regard to local issues, public policy-making and global problems. The presented work is related to the study of some daily life products offering different starting points for a critical examination, highlighting ethical issues involved. First year secondary school students deal with these issues by different activities. The learning outcomes show that educating future citizens is more effective if they are helped in relating what they learn in school to their daily lives and global issues.

The foundation of global competences is a disciplinary and interdisciplinary understanding of the world. Students do not develop global competence after they gain fundamental disciplinary knowledge and skills, but rather while they are gaining such knowledge and skills [2]. Teaching chemistry in a so wide context must not deprive this discipline of its intrinsic peculiarity. Chemistry is the first true systemic science, capable of explaining the inanimate and living world in a non-reductionist and pluralist way [3]. Particular aspects of the Systems Theory can contribute in developing a correct vision of chemistry in an interdisciplinary perspective. It follows that students' global competences come out from meeting between science education theories and philosophical tools, properly highlighting the central role of chemistry and its systemic character.

[1] R. Marks, I. Eilks *International Journal of Environmental & Science Education - Special issue on scientific literacy*, 2009, **4**, 231-245.
[2] V. Boix Mansilla, A. Jackson *Educating for Global Competence: Preparing Our Youth to Engage the World*, Council of Chief State School Officers' EdSteps Initiative & Asia Society Partnership for Global Learning, 2011.
http://www.edsteps.org/CCSSO/SampleWorks/EducatingforGlobalCompetence.pdf
[3] Villani *G. Found. Chem.*, Jan 2013, doi: 10.1007/s10698-013-9178-0

DID-O2

Nuovi docenti. Il laboratorio di organica

Patrizia Dall'Antonia[a], *Patrizia Nitti*[b]

[a] *I.T.I. "A. Volta", Via Monte Grappa 1, 34100, Trieste, Italia*
[b]*Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Trieste, Via Licio Giorgieri 1 , 34127, Trieste, Italia*

patriziadallantonia@libero.it

La Chimica Organica è spesso un punto debole per chi insegna nella scuola superiore. Le ragioni sono molteplici e una tra queste è l'idea che la Chimica Organica sia *un capitolo a parte*, *e non abbia alcun legame* con la Chimica Generale.

Lo scorso anno, all'interno dei percorsi di TFA, ci si è reso conto che manca totalmente nell'insegnamento della chimica un'integrazione tra la Chimica Generale e la Chimica Organica, dato che quest'ultima viene spesso insegnata come corollario della prima e in poche ore. Il problema dell'insegnamento della Chimica Organica è stato allora ripreso da un piccolo *team* di docenti di varia formazione che hanno rivisto insieme alcune attività di laboratorio e rimeditata la loro organizzazione. L'idea di base è stata che nel momento in cui i concetti base di Chimica Generale vengono presentati agli studenti, si possa creare un immediato collegamento con i concetti di Chimica Organica, in modo che sia visibile la necessaria integrazione tra questi due aspetti della stessa disciplina. Sarebbe bene quindi che questo lavoro di consolidamento delle conoscenza venisse affrontato nei laboratori, con esperimenti opportuni, in modo da rendere evidente allo studente come la disciplina Chimica sia un *unicum*. Tutto questo in linea con le nuove direttive date dal Ministero sul riordino degli insegnamenti nelle scuole secondarie di secondo grado: esse puntano proprio alla programmazione per competenze e alla realizzazione di significative unità di apprendimento come occasioni favorevoli per la rimeditazione di alcuni percorsi di apprendimento.

Il lavoro che viene presentato vuole suggerire alcuni percorsi sperimentali in grado di fornire allo studente una visione integrata, anche se limitata, delle conoscenze nell'ambito della chimica alla luce delle problematiche sopra esposte.

DID-O3

PLS Piano di Formazione Docenti in Didattica della Chimica in Puglia

Paola Fini[a], Pinalysa Cosma[b], Mario Forenza[c] e Maria Veronico[d]

a Istituto per i Processi Chimico Fisici - CNR UOS di Bari, c/o Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro", Via Orabona 4, Cap 70126, Bari, Italia
b Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro", Via Orabona 4, Cap 70126, Bari, Italia
c Liceo Scientifico Fermi, via R.Bovio 19/A, Cap 70125, Bari, Italia
d Ufficio Scolastico Regionale –Puglia, Via Castromediano 123/B, Cap 70126, Bari, Italia
p.fini@ba.ipcf.cnr.it

Il Piano Nazionale Lauree scientifiche si articola su due livelli strettamente interdipendenti, ovvero quello della formazione/orientamento degli studenti e quello dell'aggiornamento dei docenti sulle tematiche disciplinari che lo connotano, ovvero matematica, fisica e chimica.

In questo contributo viene presentato il risultato di un'azione di formazione *blended*, rivolta ai docenti delle classi A060, A012, A013 e A057 per l'ambito chimico, organizzata dal prof. Forenza, dirigente scolastico della Scuola Polo PLS per la Puglia, il Liceo Scientifico Fermi, di concerto con la referente PLS della Direzione Regionale del USR Puglia, prof.ssa Veronico. Tale azione è stata sviluppata in collaborazione dalla dott.ssa Paola Fini e dalla prof.ssa Pinalysa Cosma, responsabile del PLS-Chimica per la Puglia, nella sede di Bari e nella sede di Brindisi, presso l'IISS Marconi-Flacco- Belluzzi.

Il corso ha affrontato il ruolo svolto dalla chimica in quattro ambiti importanti ed attuali: l'energia, la salute, l'alimentazione ed i nuovi materiali. La scelta di queste tematiche oltre ad avere una valenza motivazionale, permette all'insegnante di partire dal contesto di senso dei ragazzi, elemento dal quale non si può e non si deve prescindere se si vuole avere una valenza formativa autentica. I ragazzi non devono sentire le tematiche trattate a scuola come avulse dalla loro vita e devono avere ben chiaro in che modo tali tematiche li riguardano.La modalità blended è stata organizzata in modo che ogni incontro in presenza sia preceduto da una parte teorica introduttiva ad ogni tematica on line e seguito da una riflessione e rielaborazione di quanto fatto in laboratorio, anch'esso on line.

DID-O4

Esperienze di formazione degli insegnanti: verso un futuro possibile?

Alberto Regis

Gruppo SENDS, Storia ed Epistemologia per una Nuova Didattica delle Scienze

reg.al@alice.it

Questo intervento proporrà una riflessione suscitata dall'esperienza di docente di Didattica della Chimica per la classe A059 nella SIS dell'Università di Torino e nei PAS dell'Università Milano-Bicocca.

Saranno presentati alcuni esempi di concezioni difformi evidenziate dai corsisti in merito ai concetti fondanti della chimica e alcuni interrogativi a proposito della futura strutturazione dei corsi di formazione primaria degli insegnanti.

DID-O5

La calce…un legante per la chimica a scuola

Eleonora Aquilini[a],

a Liceo Artistico "F.Russoli" Via San Frediano 13, 56126 Pisa, Italia

ele.aquilini@tin.it

Nella biennio della scuola secondaria di secondo grado incontriamo il calcare quando, nell'ambito della chimica delle arie, lo decomponiamo ottenendo la calce viva. E' necessario qui il riferimento a Black che decomponendo la *magnesia alba* (carbonato di magnesio), ottenne una nuova sostanza la *magnesia usta* (l'ossido di magnesio) e raccolse un'aria diversa dall'aria atmosferica, l'aria fissa (l'anidride carbonica). Tale aria si produceva anche nelle trasformazioni che coinvolgono la produzione della calce viva dal calcare. Si fa reagire il calcare con un acido, l' "aria" che fuoriesce viene raccolta in un bagno pneumatico, la calce viva viene spenta con quantità precise di acqua; il calcare viene poi ricostituito nuovamente facendo reagire calce, acqua e aria fissa. In questo ciclo si parte dal calcare e si ritorna al calcare dopo una serie di reazioni che hanno senso chimico di per sé e che assumono significato particolare nella fase in cui si spiega la nascita della chimica ad alunni che devono costruire i concetti di sostanza semplice e composta [1]. *Le terre* e l'*aria* si scompongono in sostanze diverse, anche in "arie" [2]. La scoperta della chimicità dell'aria, e di un'aria diversa da quella atmosferica, infatti porta successivamente a considerare l'aria come *reattivo* fondamentale nella combustione e nella calcinazione. Il ruolo che Lavoisier attribuisce all'aria in queste due trasformazioni si contrappone alla teoria del flogisto che spiegava la combustione e la calcinazione mettendo in gioco questo "fluido magico". La scoperta fondamentale del 1772 definisce il ruolo chimico dell'aria nella calcinazione e nella combustione, contro la teoria del flogisto.[3]

Dopo l'individuazione dell'ossigeno come il componente dell'aria responsabile della combustione, Lavoisier giunge a comprendere quale sia la composizione dell'aria fissa. Il carbone e l'ossigeno compongono l'aria fissa. Ciò contribuisce a costruire i concetti di composto ed elemento. L'aria fissa (l'anidride carbonica) è quindi un composto e il carbone (il carbonio) e l'ossigeno sono elementi.

[1] C. Fiorentini, E. Roletto, *Ipotesi per il curricolo di chimica,* La Chimica nella Scuola, 2000, n. 5, pp. 158-168;
[2] F. Abbri, *Le terre, l'acqua, le arie,* Bologna, Il Mulino, 1984.
[3] C. Fiorentini, E. Aquilini, D. Colombi, A. Testoni, *Leggere il mondo oltre le apparenze,* Roma, Armando, 2007.

DID-O6

Attività didattica sul DNA al Museo: Esperienze con gli alunni, dalle Scuole Elementari al Liceo.

Valentina Domenici, *Chiara Gerardi*, *Erica Parri*

Dipartimento di Chimica e Chimica Industriale, Università di Pisa,
Via Risorgimento 35, 56126, Pisa, Italia

chiaragerardi89@gmail.com

In questa relazione presenteremo una serie di attività didattiche legate al tema del DNA, sviluppate nell'ambito del corso di Didattica della Chimica presso l'Università di Pisa in collaborazione con il Museo di Storia Naturale di Rosignano Solvay e alcune Scuole del Comune di Rosignano Marittimo e del Comune di Cecina, nel periodo che va da Ottobre 2013 ad Aprile 2014 [1]. Insieme agli studenti del corso abbiamo progettato una serie di attività didattiche diversificate per il tipo di target, competenze e obiettivi, in continuità con i lavori svolti precedentemente [2][3]. Le attività didattiche saranno discusse tenendo conto delle fasi della progettazione, degli aspetti pratici legati alla realizzazione e del feed-back avuto da alunni e insegnanti.

[1] V. Domenici, C. Gerardi, A. Lenzi, E. Parri, *La Chimica nella Scuola*, 2014, in revisione.
[2] E. Parri, L. Cetti, M. Macelloni, L. Rossetti, E. Magazzini, A. Lenzi e V. Domenici, *La Chimica nella Scuola*, 2013, Anno XXXV, n.**1**, 15-37.
[3] V. Domenici, in "I Musei della Chimica e la Chimica nei Musei della Scienza" (Ed. L. Campanella e V. Domenici), Sapienza Editrice Roma: 2014.

DID-O7

Progetto uniscuola

Daniela Romanazzo[ab]*, Vanessa Biagiotti*[b]*, Giovanni Fares*[b]*, Gianluca Adornetto*[ab]*, Alessia Amodio*[ab]*, Andrea Idili*[ab]*, Mario Naitana*[ab]*, Daniela Roversi*[ab]*, Martina Tiravia*[ab]*, Andrea Vecchi*[ab]*, Giuseppe Palleschi*[a]

a Dipartimento di Chimica, Università di Roma Tor Vergata, Via della Ricerca Scientifica 1, 00133, Roma, Italia
b L.U.D.I.S. srl Via Opita Oppio, 00174, Roma, Italia

daniela.romanazzo@uniroma2.it

Il progetto UniScuola svoltosi nel corso dell'A.S. 2013/2014 presso l'Università degli studi di Roma Tor Vergata, ha visto la realizzazione di più di trenta eventi di didattica e divulgazione della chimica che hanno coinvolto quaranta istituti scolastici e più di duemila studenti. UniScuola è un progetto finanziato e premiato con il massimo del punteggio a livello nazionale dal MIUR - bando legge 6/2000 per la diffusione della cultura scientifica. Ogni evento è stato riservato ad un massimo di 70 studenti del medesimo livello scolastico, al fine di garantire un coinvolgimento diretto, capillare e specifico. Gli Istituti scolastici coinvolti, di ogni grado e livello, hanno potuto selezionare un percorso a scelta tra: *AccadueO* (esperimenti divertenti relativi alle proprietà dell'acqua: polarità, capacità termica, passaggi di stato e legame idrogeno); *Chimica e Provette* (lezione di chimica divertente ricca di esperimenti riguardo reazioni di ossidoriduzione, miscibilità, polimerizzazione, passaggi di stato).

Al termine di ogni incontro gli studenti partecipanti sono stati sottoposti ad un test utile alla valutazione dell'apprendimento a breve termine degli studenti. Le migliori classi partecipanti al progetto Uniscuola saranno invitate ad ottobre 2014 per un evento finale in cui gli studenti saranno suddivisi in due squadre e si contenderanno la vittoria finale tra esperimenti,quesiti e sfide scientifiche.

Troppo spesso nelle scuole lo studio della scienza è ridotto alla pura teoria a causa dell'assenza di laboratori didattici. Il rischio legato a tale deficienza è che gli studenti considerino le discipline scientifiche non soltanto poco affascinanti e tediose ma soprattutto ostiche lontane dalla loro realtà; il progetto Uniscuola si è rivelato un utile mezzo per i docenti delle scuole che hanno avuto la possibilità di integrare il lavoro svolto in classe con un'attività che inducesse nei loro allievi curiosità, stupore e quindi interesse.

DID-O8

Apprendimento basato sull’indagine dei fenomeni termici di dissoluzione

Anna Caronia[a], *Roberta Maniaci*[b], *Michele A. Floriano*[c]

a Ist. Superiore di Istruzione Ettore Majorana, via G. Astorino 56, 90146 Palermo, Italia b Liceo Artistico Damiani Almeyda, via Vivaldi 58, 90145 Palermo, Italia
c Dipt. STeBiCeF, Università di Palermo, Viale delle Scienze, ed. 17, Palermo, Italia;

anna.caronia@tin.it

Fra le attività previste nell’ambito del Master di II livello Formatore Docenti di Scienze dell’Università di Udine sull’“Energia”, uno dei principali nuclei fondanti in tutti gli ambiti scientifici, è stata realizzata una microsperimentazione didattica sugli aspetti energetici dei processi di dissoluzione. Quest’attività, della durata di sei ore, è stata realizzata in una classe di secondo anno di un Istituto Tecnino in compresenza con il docente di Scienze Integrate: Fisica, inserendola nella parte di Termologia della sua normale programmazione dittatica. L’attività è stata realizzata con il fine di acquisire competenze didattiche utilizzando un approccio di tipo induttivo basato sull’indagine e verificandone l’efficacia, d’altronde già ampiamente documentata in letteratura[1], [2]. Prima e dopo la realizzazione del percorso è stato somministrato uno stesso questionario, con l’obiettivo di verificare le conoscenze pregresse e i risultati di apprendimento. La reazione degli studenti nello svolgimento del questionario in ingresso è stata sicuramente di grande sorpresa, in quanto si sono trovati ad affrontare argomenti sconosciuti. L’attività in classe è stata avviata con opportune domande stimolo, basate sull’osservazione dei fenomeni termici che accompagnano il processo di dissoluzione di sostanze diverse. Successivamente gli studenti sono stati invitati a proporre individualmente una procedura sperimentale idonea alla misura del calore di dissoluzione del cloruro di sodio e dell’idrossido di sodio e dopo una discussione collettiva si è pervenuti a una procedura condivisa, che è stata realizzata sperimentalmente. Dal confronto dei risultati del questionario è emerso che gli alunni hanno acquisito un linguaggio specifico utilizzato in risposte articolate e capacità logiche di collegamento tra gli aspetti macroscopici e microscopici.

[1] NCR *National Science Education Standards J*, 1996.
[2] Europen Commission, *Science education NOW: A renewed Pegagogy for the Future of Europe*, Luxembourg, Office for Official Pubblications of the E. C.2007

DID-O9

Redox reactions: a conceptual mess?

Elena Ghibaudi[a, b], *Alberto Regis*[b], *Ezio Roletto*[b]

a Dipartimento di Chimica, Università di Torino, Via Giuria 7, 10125, Torino, Italy
b Gruppo SENDS, Storia ed epistemologia per una nuova didattica delle scienze

elena.ghibaudi@unito.it

Redox reactions are fundamental chemical processes that include an heterogeneous range of phenomena (from photosynthetic and respiratory processes to combustion, corrosion and a number of organic reactions). Indeed redox processes are a central topic of any introductive chemistry course, at the level of secondary school as well as at the University. Learning such an intrinsically complex subject implies dealing with conceptual obstacles that are often magnified, rather than overcome, by the teacher's choices. Two most frequent mistakes in teaching redox are: i) the implicit reference to distinct models (e.g. oxidation numbers and electron transfer) without pointing them out or highlighting their different nature and realm of validity; ii) to mix up the formal level of explanation with the level of physical evidence.
Four models are usually employed to interpret and classify redox phenomena. They refer to the transfer of oxygen, hydrogen and electrons, respectively, or to a change in oxidation numbers. The first three models are empirical, they overlap only partially and have limited validity. The fourth is a purely formal model and it has wider applicability. Reactions that are not recognized as redox by the first three models may be included in the redox family based on the change of oxidation numbers. The coexistence of distinct models is often overlooked in redox teaching: this may result in considerable learning problems. A critical discussion of these educational implications will be proposed.

[1] H. Sisler and C. Vanderwerf, *J. Chem. Educ.*, 1980, **57**, 42-44
[2] T.P. Silverstein *J.Chem. Educ.*, 2011, **88**, 279-281
[3] E.Ghibaudi and E.Roletto, 2014, *Progress Sci.Educ.*, submitted

DID-O10

Un percorso didattico sul legame chimico in un contesto autentico

Roberta Maniaci[a,c] *Anna Caronia*[b], *Delia Chillura Martino*[c],

Michele A. Floriano[c]

a Liceo Artistico Damiani Almeyda, via Vivaldi 58, Palermo, Italia
b Ist. Superiore di Istruzione Ettore Majorana, via G. Astorino 56 Palermo, Italia
c Dipt. SteBiCef, Università di Palermo, Viale delle Scienze, ed. 17, Palermo, Italia

roberta.maniaci@unipa.it

Ispirandosi a esempi tratti dai risultati nel campo dell'elettronica molecolare e delle nanomacchine, è stato progettato congiuntamente con i docenti curriculari di due classi prime di due Istituti Tecnici e di due classi quarte di un Liceo Scientifico, un percorso didattico riguardante il legame chimico e le interazioni intermolecolari. Il percorso, della durata di 12 ore, è stato sperimentato in ciascuna delle classi, coinvolgendo circa 80 studenti. Il percorso è stato aperto con un questionario, con l'obiettivo di verificare l'esistenza di conoscenze pregresse e/o misconcezioni, che è stato ripetuto a chiusura. Dopo una introduzione sulla rilevanza scientifica delle ricerche nel settore, il concetto di legame chimico è stato introdotto rivolgendo agli studenti opportune domande stimolo, con l'ausilio di apposite schede e guidando la conseguente discussione verso conclusioni condivise e corrette. Il progresso del lavoro è stato osservato e registrato mediante la compilazione di un diario di bordo. Per quanto riguarda la valutazione dei risultati di apprendimento, è stato deciso di confrontare i risultati ottenuti con i dati di letteratura riguardanti la frequenza e il tipo di misconcezioni sul concetto di legame[1], [2]. Un'analisi preliminare di questi risultati e un confronto tra i risultati ottenuti dal questionario somministrato prima e dopo il percorso, dimostrano complessivamente che l'approccio didattico proposto ha condotto al miglioramento dell'apprendimento. Sono comunque necessari ulteriori approfondimenti e, dopo avere messo a punto alcuni aspetti risultati critici, una sperimentazione su scala più ampia.

[1] H. Ozmen, *Some student misconceptions in chemistry: a literature review of chemical bonding*, J. of Science Education and Technology, vol 13, No. 2, June 2004.
[2] C. J. Luxford and S. Lowery Bretz, *Development of the bonding representations inventory to identify student misconceptions about covalent and ionic bonding representations*, J. of Chem. Educ., 2014, 91, 312-320.

DID-O11

Chimica e Istituto Alberghiero: una questione (di) pratica

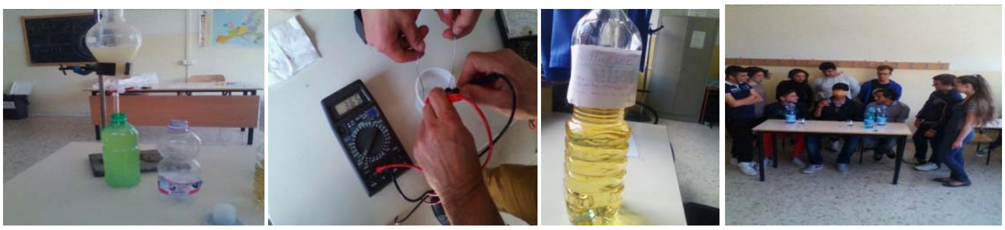
P. Aurilia, A.M. Colonescu, R. Restivo, M. Gobbo, S. Gobbo, M. Daiu, T. Lauretti, A. Ruggeri, S. Tiberia, I. Tammetta, C. Ciotoli, M. C. Salvatori, F. Ferraro, A. Romanazzi, L. Carnevale, E. Pastore, G. Micheli, D. Verro, R. Nhila, A. De Stefano, V. Quaranta, R. Klay, M. Marzella, R. Bove, M. Azoitei, A. Mattone, K. Andreoli, R. Pasarica, M. Rossi, E. Mansueti[a] ; F. Macale, V. Frioni 2[b]; A. Pizzing [c]

***a** I.I.S. Ceccano, via Gaeta 105, 03023, Ceccano, Italia*
***b** I.I.S. A. G. Bragaglia, via Casale Ricci 2, 03100, Frosinone, Italia*
***c** Dipartimento di Chimica e Tecnologia del Farmaco, Università La Sapienza di Roma, P.le Aldo Moro 5, 00183, Roma, Italia*

enrico.man@libero.it

La chimica nel piano di studi dell'istituto alberghiero rappresenta una novità troppo recente. Le indicazioni ministeriali sembrano non cogliere appieno le opportunità offerte dai cambiamenti in atto. Il congresso della divisione didattica offre l'opportunità di discutere sui problemi e sui punti di forza della situazione; questo lavoro vuole portare un piccolo contributo di riflessione.

In servizio su due scuole (IPSSEOA e IPSIA), ho strutturato un progetto di esercitazioni pratiche pomeridiane, partendo da domande legate prevalentemente a materie professionalizzanti (l'enogastronomia), come il problema dell'abbassamento della salinità in una soluzione di NaCl contenente patate; il concetto di residuo fisso di acque diverse attraverso prove in cieco; la rilevazione degli enzimi dell'ananas; l'azione della ptialina sull'amido; una pila al ketchup; i materiali di conservazione degli alimenti; una reazione di trans-esterificazione trasformando l'olio di girasole (un prodotto alimentare) in biodiesel; la formazione dei cristalli di solfato rameico. L'osservazione della realtà con i suoi problemi ha funzionato da catalizzatore per lo studio dei fatti e la formulazione delle leggi: alla base della disciplina deve esserci la pratica. Manca un esperimento per capire perché alunni poco brillanti in classe si siano rivelati tra i più attivi in questi progetti. Ho fortemente voluto nel gruppo anche ragazzi con problemi relazionali e comportamentali, riuscendo a motivarli attraverso un carico di responsabilità che all'inizio io stesso ho dubitato eccessivo, quando ho temuto di alterare troppo i confini delle zone di sviluppo prossimale di Vigotsky.



La terra sembrava poco profonda, ma è bello ora per il seminatore contemplare il colore dei frutti. Enrico Mansueti

DID-O12

La spirale delle competenze. Esperienze di didattica chimica ricorsiva negli Istituti Tecnici

Sergio Palazzi,

ISIS di Setificio "Paolo Carcano", via Castelnuovo, 22100, Como

sergio@kemia.it

La riforma della scuola superiore, con il reorientamento di molti indirizzi specie tra gli istituti tecnici, può essere un'utile occasione per rivedere criteri didattici di cui da tempo sono noti i limiti. La didattica lineare, sequenziale, che informava il binomio "programma ministeriale - libro di testo", ha forse aspetti di economicità funzionale se rivolta a discenti già esperti, ma pare poco adeguata agli studenti della scuola attuale: bisognosi di riferimenti e di motivazioni, disorientati dal rumore di fondo di informazioni non vagliate, disabituati ad un apprendimento autonomo e critico che si consolidi progressivamente. Per definire le modalità di forme di insegnamento/apprendimento alternative, a livello sia neurologico sia didattico, sono in uso una serie di metafore, da quella della *rete* a quella dell'*albero ramificato*. La didattica ricorsiva si richiama alla *spirale*: un argomento viene progressivamente ripreso con successivi ampliamenti, rivedendo ed approfondendo le varie aree tematiche che concorrono a definirlo, incontrando via via momenti in cui vengono consolidati gli aspetti fin lì sviluppati. Essa contempera, senza forzature artificiose, il ruolo di guida esperta dell'insegnante con quello attivo e di scoperta dei discenti. L'elasticità di tale approccio permette di articolare gli spazi di didattica frontale o partecipata, in aula o in laboratorio, in base alle esigenze riscontrate nel dialogo educativo, ed anche a superare la rigidità di libri di testo ed altri sussidi standardizzati.

Il primo contatto da cui partire ed a cui progressivamente ritornare può essere un dato esperienziale, come l'esame di specifici processi tecnologici: ai quali la didattica lineare tende ad arrivare solo in una fase molto più avanzata, lasciando a lungo lo studente incerto sul quadro teorico e l'utilità pratica di quanto gli viene sequenzialmente spiegato. Sulla base di esperienze consolidate in vari corsi ad indirizzo chimico, specie (ma non solo) su materie di ambito tecnologico-applicativo, si ritiene che tale metodo sia particolarmente adatto alle nuove linee guida per gli ITI a indirizzo chimico, in particolare per "Tecnologie chimiche industriali". Esse richiedono infatti di declinare la didattica sulle competenze, superano le vecchie elencazioni di "argomenti da fare" e chiedono alle singole scuole di contestualizzare l'insegnamento/apprendimento nelle specificità delle tradizioni e delle prospettive di sviluppo del proprio territorio.

[1] S. Palazzi: The colours of chemistry: There's a new scent in the air, or old perchance?, ICCE-ECRICE 2012, *CnS – La Chimica nella Scuola*, 2012, **XXXIV/3**, 284-289

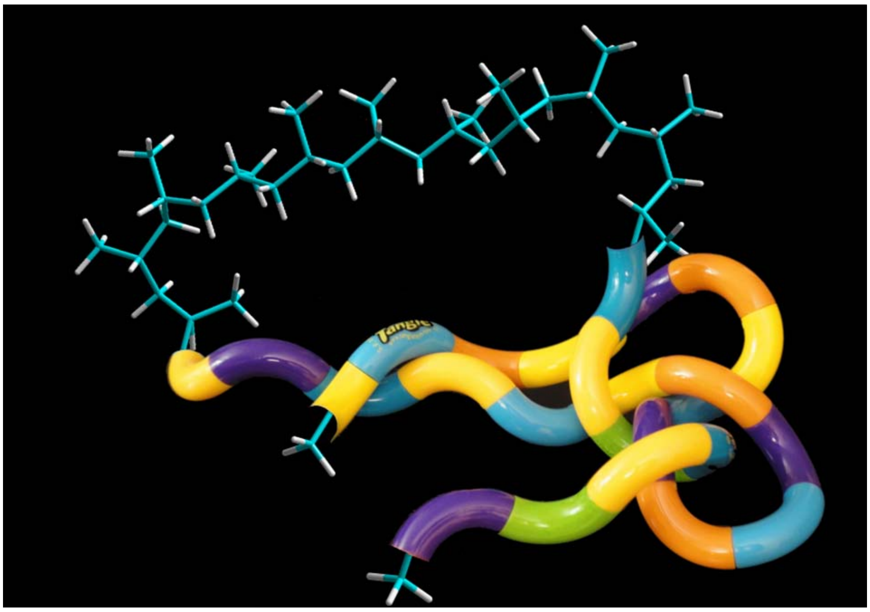
[2] S. Palazzi: L'istituto tecnico e la cultura dell'innovazione, *Notiziario Tecnico Tessile*, 1998, **XLVIII/4**, 21-24

DID-O13

Storie di macromolecole che hanno fatto la Storia

Vincenzo Villani

Negli anni trenta del secolo scorso eminenti scienziati come Staudinger e Carothers introdussero in chimica il concetto di macromolecola. Il lavoro completamente empirico che fino ad allora era stato svolto con lo sviluppo della gomma naturale, della celluloide e della bachelite, ricevette un impulso straordinario con la messa a punto dei primi moderni materiali polimerici. Nylon, poliesteri, teflon, poliolefine contribuirono all'esito del secondo conflitto mondiale e al successivo sviluppo della società. Se è vero, come è vero, che le epoche della storia umana sono state segnate dal materiale strutturale di volta in volta predominante…età della pietra, del rame, del bronzo, del ferro, l'epoca in cui viviamo è certamente da considerare l'età dei polimeri, a indicare il ruolo prioritario svolto in ogni campo dai materiali macromolecolari. L'Italia con la scuola di Giulio Natta che produsse oltre 1200 pubblicazioni e 500 brevetti ha svolto un ruolo da protagonista. Oggi che gli Airbus vengono realizzati in materiale composito a base di resina epossidica, il Mater-Bi biodegradabile si è affermato con successo e i nanocompositi polimerici sono al di qua dell'orizzonte, resta da vincere la sfida di uno sviluppo sostenibile con il rilancio di una chimica consapevole dei propri limiti ecologici.



Didattica Chimica

Poster

DID-P1

Explosion of colored hydrogen balloons for everybody

Francesco Caruso, Giulia Gelardi, Bernhard Elsener, Robert J. Flatt

Physical Chemistry of Building Materials, Institut für Baustoffe, ETH Zürich, HIF B60.2,
Stefano-Franscini-Platz 3, 8093 Zurich, Switzerland

fcaruso@ethz.ch

A variation of the demonstration on the explosion of hydrogen balloons is presented in this paper. Such a demonstration can be employed as an experimental aid to teach combustion reactions, gas laws, corrosion resistance of aluminum and its alloys, emission spectra of the elements, and their electronic energy levels. The new method here presented makes this demonstration accessible to almost every school. The in-class use and the hazards are also illustrated. [1]

Figure 1 – Explosion of a hydrogen balloon containing a copper chloride alcoholic suspension.

[1] F. Caruso, G. Gelardi, B. Elsener, and R.J. Flatt *J. Chem. Educ*, 2013, **90**, 1406-1408.

DID-P2

Valutazione del potere antiossidante di varie sostanze con una mela

Paola Fini[a], Pinalysa Cosma[b]

a Istituto per i Processi Chimico Fisici - CNR UOS di Bari, c/o Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro", Via Orabona 4, Cap 70126, Bari, Italia
b Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro", Via Orabona 4, Cap 70126, Bari, Italia

p.fini@ba.ipcf.cnr.it

Un'alimentazione ricca di antiossidanti è oggi fortemente raccomandata per prevenire le patologie associate allo stress ossidativo. E' sempre più diffusa la pratica di indicare l'indice ORAC (Oxygen radical absorbance capacity) di ogni alimento. Le metodiche utilizzate per tale determinazione si basano sull'utilizzo di strumentazione e reagenti quasi mai presenti nelle scuole.

La ricerca in ambito didattico si è occupata di questa tematica ed ha proposto l'utilizzo della reazione oscillante di di Briggs-Rauscher per comparare il potere antiossidante di alcune bevande. Tale reazione richiede però l'utilizzo di alcuni reagenti non sempre facilmente reperibili e di alcune accortezze nella realizzazione e nello smaltimento dei rifiuti.

In questo lavoro viene presentata una semplicissima metodica per valutare il potere antiossidante di vari alimenti, basata sull'utilizzo di una mela.

Quando tagliamo una mela vediamo, nel giro di un po' di tempo, la formazione di uno strato scuro sulla superficie dove è avvenuto il taglio.

Questo imbrunimento è dovuto ad un processo di ossidazione, promosso da un enzima, la polifenilossidasi, presente nelle mele.

In sostanza questo enzima in presenza dell'ossigeno dell'aria promuove la ossidazione dei polifenoli, anch'essi presenti nella mela, dando luogo alla formazione di sostanze incolori. Queste sostanze a loro volta reagiscono con gli aminoacidi dando luogo a composti scuri.

Trattandosi di un processo di ossidazione, è possibile ridurre tale fenomeno di imbrunimento utilizzando un antiossidante quale ad esempio la vitamina C o qualche miscela di antiossidanti come ad esempio quelli presenti nel tè verde o nella curcuma.

DID-P3

L'insegnamento per gli adulti quali strategie. Esperienze nella casa circondariale

Patrizia Mazzei

Doc. di Chimica, ITI e IPSAR Casa Circondariale, 87012, Castrovillari , Italia

patrizia.mazzei@istruzione.it

Le strategie di insegnamento per studenti adulti necessitano di una didattica laboratoriale a tutto tondo inserita in contesti del quotidiano cosi "imparando si impara ad imparare"[1]. Le classi, infatti, si presentano molto eterogenee perché costituite da adulti di età diversa, spesso di diversa etnia e quindi con esperienza di vita e di studio molto differenti e con un bagaglio linguistico non sempre adeguato alla comprensione della disciplina. La motivazione allo studio, inoltre, è data da esigenze differenti e differenti sono gli obiettivi per il quale essi richiedono il conseguimento del titolo di studio. La frequenza, l'impegno e le modalità di apprendimento sono altresì disomogenee e non semplice risulta la valutazione in particolare per la non facile possibilità di verifiche di classe. Si rende, allora, necessario impostare percorsi individualizzati. A tale scopo sono state predisposte schede tematiche[2][3] le più frequenti contenenti essenzialmente tre parti: Presentazione semplice del contenuto; Esempio di applicazione; Esercitazione per verificare la comprensione.

Durante l'attività in aula ogni studente può così lavorare su schede anche differenti dagli altri o uguali per gruppo di studio e il docente può intervenire nella guida in modo personalizzato. La consegna delle schede, utilizzabili anche per più lezioni, permette di poter verificare e valutare l'apprendimento di ciascuno. Esse possono essere riutilizzate in bianco per un apprendimento efficace.

L'apprendimento risulta così motivato, contestualizzato e proficuo perché permette di formalizzare le conoscenze acquisite con il proprio vissuto dando fiducia in sé stessi ad adulti, in particolare quelli della Casa Circondariale, in cerca di un reinserimento positivo nella società.

Nello stesso tempo il docente ha la possibilità di lavorare e valutare con serenità.

[1] R. Conserva "*Imparando s'impara ad imparare*" in Il sapere della scuola – proposte e contributi Quaderno 1, 1999

[2] A. Borsese *Insegnamento della chimica, immagine della chimica, ruolo dei contenuti nella comunicazione didattica*" in Fondamenti Metodologici ed Epistemologici Storia e Didattica della Chimica Vol 1 pag. 155 SEChimica 2000

[3] E. Niccoli, F. Olmi, P. Riani "*La chimica nei curricoli di formazione scientifica*" in Fondamenti Metodologici ed Epistemologici Storia e Didattica della Chimica Vol 2 pag 415 SEChimica 2000

DID-P4

Setaioli, alla carica!

Arianna Boehm, Massimiliano Gatti, Annamaria Rampoldi, Sara Scarso, Sergio Palazzi,

ISIS di Setificio "Paolo Carcano", via Castelnuovo, 22100, Como

sergio@kemia.it

La città di Como si è caratterizzata, a partire dalla metà del XIX secolo, come centro di un distretto tessile imperniato sulla tessitura e nobilitazione della seta e sulle lavorazioni da esse derivate.
Una delle aziende che meglio hanno caratterizzato tale periodo è stata la Ambrogio Pessina, attiva per quasi un secolo sulle rive del Cosia, di fronte al sito che ospita oggi il nostro Istituto. Nell'ambito dell'iniziativa "Adotta una fabbrica", promossa sul nostro territorio per la riscoperta e valorizzazione delle realtà imprenditoriali e del lavoro che hanno caratterizzato la vita delle generazioni precedenti, la nostra classe partecipa ad un progetto su base triennale per la riscoperta di tale azienda.

A margine di tale lavoro, che permette tra l'altro di riscoprire esperienze organizzative che precorrevano di alcuni decenni quelle che sarebbero state celebri nel lavoro di Olivetti, abbiamo ritenuto di replicare alcune delle lavorazioni seriche sviluppate e perfezionate proprio in tale azienda.
Tra esse, un ruolo importante era la carica della seta con ricette minerali, vegetali e miste; tale operazione permetteva da un lato di ridare alla fibra quanto viene perso con la *sgommatura*, cioè l'eliminazione della sericina, e dall'altro di fornire alle bave di fibroina caratteristiche di mano e di aspetto idonee per tessuti di prestigio, eventualmente combinando la carica con la tintura a base di tannini ed altri estratti vegetali.

Le procedure studiate sono abbandonate da decenni per ragioni ambientali e di costo.

Per una classe come la nostra, che fa parte non dell'indirizzo chimico ma di quello *Sistema Moda,* e che eredita le secolari esperienze dell'indirizzo tessile, approfondire tali aspetti ricercandole sui testi originali ha portato ad una migliore ed anche più piacevole comprensione delle basi chimiche dei processi di nobilitazione, insieme ad una migliore comprensione del percorso storico che stiamo scoprendo grazie alle testimonianze scritte ed iconografiche ed ai ricordi di chi ha vissuto quella realtà.

L'occasione di questo Congresso ci permette di ricordare che proprio a Cosenza si era evoluta una forte tradizione nella produzione serica.

DID-P5

Valutiamo il rischio chimico: REACH e CLP

Maria Turano[a,b], *Patrizia Mazzei*[a]

a Dipartimento di Chimica, Università degli Studi della Calabria, Via Pietro Bucci, 87036, Arcavacata di Rende (Cs), Italia.
b Scuola Secondaria di Primo grado "Via Pascoli", Via G. Pascoli 256, 47521 Cesena (FC), Italia

maria.turano1@istruzione.it

Il progetto di tirocinio a conclusione del percorso del TFA 1° ciclo è stato svolto in una I classe dell' IIS "Garibaldi" di Cesena, ed è stato inserito come approfondimento del primo modulo della programmazione didattica "La sicurezza in laboratorio ", facendo riferimento alle linee guida per il passaggio al nuovo ordinamento degli Istituti Tecnici [1], e per essere in linea con l'impegno profuso dal MIUR nella divulgazione di regolamenti europei REACH e CLP [2], [3]: "*In tutti i percorsi dell'istruzione tecnica, infatti, la sicurezza è un valore da perseguire attivamente*"**.** Il progetto è stato strutturato con l'obiettivo di dare consapevolezza dell'utilità delle etichette di pericolo, in maniera da stimolare una lettura critica e sollecitare cambiamenti positivi nelle proprie abitudini, al fine di ridurre i rischi per la propria e altrui salute e per l'ambiente. Esso è stato svolto in momenti diversi scanditi da discussioni guidate, lezioni frontali, esperienze di laboratorio, attività di verifica e si è concluso con una riflessione metacognitiva con tutta la classe, sul percorso didattico svolto insieme.

Da un esame critico sull'esperienza personale di tirocinio si evince chiaramente che la scuola oggi ha la necessità di fornire strumenti di base per la comprensione adeguata dei fenomeni e delle strutture sociali ed economiche: deve essere "formativa" cioè deve elaborare un progetto culturale ma soprattutto "orientativa", nel senso che deve creare le condizioni ottimali per fornire gli abiti comportamentali e gli strumenti culturali per decodificare, la realtà circostante.

[1] Linee guida per il passaggio al nuovo ordinamento (d.P.R. 15 marzo 2010, articolo 8, comma 3) e Allegato A
[2] Regolamento 1907/2006 REACH: Registrazione, Valutazione e Autorizzazione delle sostanze chimiche.
[3] Regolamento 1272/2008/CE CLP:Classificazione, Etichettatura e Imballaggio delle sostanze e delle miscele

DID-P6

Il benzene: rischi e reattività.

Paolo Vangone[(a)], *Patrizia Mazzei*[(a)]

(a)Dipartimento di Chimica, Università degli Studi della Calabria, Via Pietro Bucci, 87036,
Arcavacata di Rende (Cs), Italia.

paolovangone@gmail.com

Il progetto di tirocinio a conclusione del percorso del TFA (I ciclo) per la classe di abilitazione A013 è stato svolto in una terza classe dell'I.I.S. "F. Todaro" di Rende (Cs) ad indirizzo Industria e Artigianato - articolazione Industria - all'interno della disciplina "*Tecnologie applicate ai materiali e ai processi produttivi e tecniche di produzione e di organizzazione*". Esso ha avuto l'intento di far comprendere la stabilità dei composti aromatici e far prevedere la reattività del benzene con alcuni esempi di reazioni di sostituzione elettrofila aromatica.

È nato così nella classe un interesse particolare su questa molecola aromatica e sul suo utilizzo come solvente organico; da qui l'esigenza di una successiva lezione di laboratorio (progetto *spin-off*) nella quale si è discusso dei rischi legati all'uso del benzene. Parallelamente è stata distribuita la scheda tecnica aggiornata della *Carlo Erba Reagents*[1] discutendo i pittogrammi e le indicazioni riguardo la gestione delle situazioni di rischio quando si manipolano sostanze tossiche [2].

Dal percorso di tirocinio si sono dunque tratte le seguenti considerazioni:

- Il compito principale del docente è quello di formare ogni singolo individuo, di renderlo autonomo e in grado di confrontarsi con le difficoltà della vita e di affrontarle con le proprie capacità.
- La Scuola è il luogo privilegiato dove l'individuo acquisisce la consapevolezza di sé e la dignità individuale, per partecipare attivamente alla vita sociale, politica e lavorativa del Paese e dunque per essere Uomo e Cittadino. Essa è in definitiva una valida occasione di crescita umana oltre a quella di acquisizione di competenze e di strategie utili nei contesti extra-scolastici.

[1] CARLO ERBA REAGENTS *Scheda dati di sicurezza ai sensi del regolamento 1907/2006/CE, Articolo 31Vers. N°76. Revisione: 12.03.2013.*
[2] Benzene - Toxicological overview, *Health Protection Agency,* Prepared by R. P. Chilcott, CHAPD HQ, HPA 2007, page 1-14.

DID-P7

Percorsi abilitanti alternativi

Paolo Vangone

Dipartimento di Chimica, Università degli Studi della Calabria, Via Pietro Bucci, 87036, Arcavacata di Rende (Cs), Italia.

paolovangone@gmail.com

L'esperienza di abilitazione tramite TFA[1] in Chimica e Tecnologie Chimiche suggerisce di porre l'accento su modalità più significative di formazione della classe docente. La tipologia del percorso prende spunto dalle precedenti SSIS[2] ed ha pressappoco la medesima procedura concorsuale e didattica.

Il progetto è di promuovere un percorso abilitante per gli insegnanti che sia scevro dalle didattiche disciplinari di indirizzo poiché si presuppone che un laureato abbia già le conoscenze e le competenze professionali per quell'area del sapere. La sostituzione delle didattiche disciplinari di indirizzo, che diventano inevitabilmente formali lezioni accademiche, con casi pratici di unità di apprendimento da trasmettere alla platea scolastica è la strada migliore per raggiungere l'obiettivo di formazione degli insegnanti. Ancor più interessante sarebbe l'istituzione di corsi basati sulla simulazione, vale a dire percorsi nei quali gli abilitanti come in un'esercitazione e sotto la guida del tutor riproducano sperimentalmente un'azione di insegnamento.

Il lavoro di tirocinio abilitante per gli insegnanti di Chimica presupporrebbe un internato di almeno 12/18 mesi a Scuola in modo che le "dinamiche didattiche" che si apprendano in classe si discutano poi in aula con i docenti delle aree *pedagogiche*. Verificare in oltre le abilità di condurre autonomamente un'esperienza di laboratorio da parte dello studente sarebbe la prova del nove sulla bontà delle competenze didattiche del docente e sulla riuscita dell'obiettivo vale a dire "aver imparato ad insegnare".

Riguardo poi le modalità di reclutamento, il *test* d'accesso ai corsi dovrebbe essere basato su prove psicoattitudinali che garantiscano ed assicurino la disponibilità mentale e morale ad affrontare un lavoro di dedizione, pazienza e controllo, ricordando che il compito principale del docente è quello di formare ogni singolo individuo, di renderlo autonomo e in grado di confrontarsi con le difficoltà della vita e di affrontarle con le proprie capacità.

[1] GU 12.12.2011 n. 288**.** Decreto 11 novembre 2011.

[2] Scuole di abilitazioni all'insegnamento secondaria. Decreto MURST del 26 maggio 1998.

DID-P8

Un esperimento PLS: Studio della denaturazione dell'albumina bovina attraverso misure di fluorescenza

R. Berdini,[a] *M. Della Rocca,*[b] *A. Di Genova,*[b] *F. Ventresca,*[b] *and M. Paci,*[c] *D. Roversi,*[c] *L. Stella,*[c] *M. Venanzi*[c]

a ITIS E. Fermi, Frascati, Italia
b Liceo Scientifico E. Maiorana, Via Sezze, 04100, Latina, Italia
c Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Via della Ricerca Scientifica 1, 00133, Roma, Italia

venanzi@uniroma2.it

Questo attività si inserisce all'interno di una collaborazione pluriennale tra il Laboratorio di Spettroscopia Molecolare della Università di Roma Tor Vergata e alcune scuole del Lazio (ITIS Enrico Fermi di Frascati (RM), Liceo Scientifico Ettore Majorana di Latina). La collaborazione è stata resa possibile dal Piano Lauree Scientifiche, inteso a favorire la collaborazione tra Università e Scuole di istruzione secondaria nel campo delle scienze 'dure' (chimica, fisica e matematica).

In questi anni sono state messe a punto diverse esperienze di laboratorio allo scopo di approfondire processi e proprietà a livello molecolare attraverso tecniche di spettroscopia ottica (assorbimento UV-Vis, Dicroismo circolare, fluorescenza, Infrarosso).

Il lavoro oggetto di questa comunicazione si riferisce allo studio mediante fluorescenza della denaturazione della albumina bovina per aggiunte di cloruro di guanidinio. In particolare, si è seguita la variazione degli spettri di emissione della tirosina e del triptofano a seguito del processo di denaturazione, monitorando la diversa intensità e posizione del segnale per effetto della differente esposizione al solvente e della efficienza del trasferimento energetico tirosina → triptofano.

Inoltre, sempre attraverso misure di fluorescenza, è stata studiata l'associazione tra un probe estrinseco, il dye naftalensulfonato (ANS), e la albumina bovina.

Questo ha permesso di illustrare la dipendenza dei processi di rilassamento fotofisico dall'intorno chimico, mettendone in luce gli aspetti molecolari.

L'attività si è dimostrata molto interessante e utile per un appproccio interdisciplinare, coinvolgendo aspetti chimici fondamentali (interazioni intermolecolari), fisici (rilassamento energetico) e biologici (conformazioni biologicamente attive, processi di denaturazione).

DID-P9

Attività in laboratorio con studenti della Casa Circondariale

Clementina Iannuzzi[a], *Patrizia Mazzei*[b], *Giuseppe Scornavacca*[c]

a Dirigente Scolastico b Doc. di Chimica, c Docente Lab. di Chimica
ITI "Fermi" Via P. della Francesca, 87012, Castrovillari , Italia

clementina.iannuzzi@istruzione.it

Nell'a.s. 2011-12 e nel corrente a.s. sono state realizzate attività nei laboratori scientifici dell'istituto scolastico per un piccolo gruppo di studenti della sezione della Casa Circondariale dello stesso comune.
La difficoltà tipica di queste realtà non consente un percorso tradizionale soprattutto per l'assenza di laboratori didattici, da qui l'esigenza di poter ottenere il permesso studio dal Magistrato di Sorveglianza per poter accede ai locali del vicino Istituto Scolastico con un'organizzazione non semplice per le attività di laboratorio di Chimica, Fisica e Meccanica.
In particolare il laboratorio di Chimica è stato progettato per la sezione femminile per una terza classe nell'a.s. 2011-12 a completamento e approfondimento del percorso biennale e per una prima classe per l'a.s. in corso con l'obiettivo di poter avviare un proficuo percorso di studi.
La principale finalità è stata quella di far prendere coscienza della funzionalità del laboratorio di chimica con gli obiettivi di**:** Conoscere e comprendere l'organizzazione di un laboratorio scientifico; Conoscere e saper mettere in atto le norme di sicurezza per un comportamento adeguato al luogo; Avere consapevolezza delle peculiarità della materia; Comprendere i fenomeni chimici.

L'approccio è stato di tipo laboratoriale: le esperienze sono state svolte in modo interattivo con l'utilizzo di schede operative atte a stimolare l'osservazione e il ragionamento. I fenomeni e le tecniche sono stati scelti in modo da essere riscontrabili nel quotidiano per un apprendimento motivato. Le schede operative sono state utili, inoltre, per verificare le attività in itinere.

Le attività nel laboratorio scientifico risultano essere sempre essenziali per un apprendimento motivato, contestualizzato e proficuo anche per studenti adulti che hanno modo di formalizzare conoscenze acquisite con il loro vissuto ed in particolare con studenti della Casa Circondariale in cerca di un reinserimento positivo nella società.

[1] P. Mazzei *Gli studenti come risorsa in un processo di ricerca/azione: il laboratorio sperimentale nella didattica* in Didattica e didattiche disciplinari Quaderni per la nuova secondaria Parte A vol. 2 pag. 35 Pellegrini Editore

DID-P10

Attività Laboratoriali in sinergia di competenze

Gianni Tornello[a], *Patrizia Mazzei*[b] , *Donatella Barca*[c]

a Doc. Sperimentatore Scuola Secondaria di I grado Paludi (CS), Italia

b Doc. Formatore UNICAL CS, Doc Scuola Secondaria di II grado Dotazione Organica (CS) Italia

c DiBEST UNICAL CS, Italia

patrizia.mazzei@istruzione.it

All'interno del progetto LIBERA LE IDEE (Laboratorio, Interdisciplinarità e introduzione di "BEst pRActice" Largamente consolidatE per Innovare la Didattica e migliorarE l'apprendimento sciEntifico) dell'Università della Calabria sono state sperimentate in orario extracurriculare delle attività laboratoriali di scienze lavorando in sinergia Gianni Tornello docente in servizio della scuola secondaria di primo grado Bennardo di Cropalati sede di Paludi (CS) – docente sperimentatore – Patrizia Mazzei docente esperto selezionato dall'università – docente formatore - e Donatella Barca ricercatrice del Dipartimento di Biologia, Ecologia e Scienze della Terra dell'Università della Calabria come coordinatore delle attività.

La tematica multidisciplinare "Le fonti energetiche non rinnovabili: I combustibili fossili" è stata svolta affrontando i diversi contenuti:

- i fossili e il processo di fossilizzazione attraverso la realizzazione di cartelloni e la riproduzione di fossili tramite calchi con argilla;
- la permeabilità dei terreni verificata costruendo semplici strumenti rudimentali quali setacci e clessidre, i primi utilizzati per confrontare le caratteristiche della permeabilità in funzione della granulometria, le seconde per misurare il tempo di passaggio dell'acqua nei diversi terreni;
- l'energia tra passato e presente con visita al vicino sito archeologico di Castiglione di Paludi con riflessione sulle condizioni di vita tra ieri e oggi con particolare riferimento alle fonti energetiche;
- Costruzione di un glossario al fine di focalizzare l'attenzione sulle nuove parole incontrate.

L'esperienza ha visto in campo competenze diverse che hanno reso possibile un'attività didattica che seppur attenta al rigore dei contenuti, ha coinvolto in modo divertente studenti appartenenti ad una fascia di età in cui l'attenzione al gioco è ancora alta.

[1] Barca D., Bonanno A., Canino A.M., D'Aprile M., Mantovano F., Mazzuca S., Y.I.T. Ting a cura di G.M. Crisci Libera le Idee nella scuola Calabrese Risultati e prospettive per la didattica delle discipline scientifiche pp. 225 Luigi Pellegrini Editore Cosenza

Elettrohimica

Oral

ELE-O1

Hybrid organic – inorganic membranes for low temperature H_2-O_2 fuel cell

P. Bocchetta[a], *M. Santamaria*[b], *C. M. Pecoraro*[b], *F. Di Quarto*[b]

a Dipartimento di Ingegneria dell'Innovazione, Università del Salento, via Monteroni, 73100 Lecce, Italy
b Electrochemical Materials Science Laboratory, Facoltà di Ingegneria, Università di Palermo, Viale delle Scienze, Ed.6, 90128 Palermo, Italy

monica.santamaria@unipa.it

Chitosan (CS) is the *N*-deacetylated derivative of chitin and due to its excellent properties, such as biocompatibility, biodegradability, non-toxicity, low-cost has found many applications in industrial areas. As cationic polyelectrolyte, CS can react with various natural and synthetic anionic species or anionic polyelectrolytes to form polyelectrolyte complexes (PECs). These complexes are generally water insoluble and make hydrogel. The gelation process is related to the formation of intramolecular hydrophobic interactions between chitosan polymer chains, hydrogen bonding between hydroxyl and amino groups of CS and/or intermolecular bonding with the polyanion counterparts. Heteropolyacids (HPAs) are strong Bronsted acid as well as solid electrolytes and are considered promising materials in the fabrication of organic–inorganic nanocomposite membranes for fuel cell thanks to their high proton conductivity. To overcome the problems relating to their solubility in water and low mechanical strength, it has been proposed to prepare insoluble CS and HPAs polyelectrolyte (PECs) films to be employed as proton exchange membrane in low temperature fuel cell.

In this work we propose a novel procedure to fabricate homogeneous CS-HPA polyelectrolyte films using phosphotungstatic acid (PTA) or phosphomolybdic acid (PMA) as cross-linking agent. The reaction between CS chains and PTA or PMA is controlled in order to allow fabricating PEC thin films, that can be easily peeled off from the support, cut to any size and shape. The obtained membranes were tested in a H_2/O_2 fuel cell working at low temperature (25°C), low humidity (T_{gas} = 25°C) and fixed Pt loading (1 mg cm^{-2}). The open circuit voltage was ~ 0.95 V and peak power up to 0.5 W cm^{-2} was measured. Impedance Spectroscopy was used to get information of the conductivity of the membrane and to model the cell electrical behaviour.

ELE-O2

Pd/Ti_nO_{2n-1} Bifunctional Catalyst for Air Electrode of Iron-Air Batteries

V. Baglio, C. Alegre, E. Modica, C. Lo Vecchio, A. Stassi, A.S. Aricò

CNR-ITAE, Messina (Italy)

vincenzo.baglio@itae.cnr.it

Lithium ion batteries are currently considered the best option for transportation batteries to be used in plug-in hybrid and full EVs. However, to cope with the proposed battery challenges for this application, a new generation of battery system will be required providing higher energy density, lower cost and use of abundant safe materials. One of the main areas researchers are exploring to achieve that breakthrough is metal-air batteries. Iron-air batteries belong to the category of metal-air batteries, in which the anode or negative electrode is formed by a metal and the cathode or positive electrode is a porous air breathing composite material. Having only one reactant contained inside the cell, metal-air batteries permit much more compact and lighter designs and therefore, they are capable of very high energy densities.

Air electrode is a key component of metal/air batteries, where molecular oxygen takes electrons from the counter metal electrode to complete the electrochemical reaction generating electrical energy, being necessary not only a good performance but a proper stability. In the present work several Pd-based catalysts have been studied for both the Oxygen Reduction Reaction (ORR), taking place in the discharge process of the battery, and the Oxygen Evolution Reaction, taking place during charging. Pd-nanoparticles (3-7 nm) were supported on several supports by means of a sulphite complex route: (i) carbonaceous supports such as Vulcan-XC-72-R (from Cabot) and Ketjenblack (from Azkonobel), and (ii) non-carbonaceous supports, Ti-suboxides. The electrochemical behavior of these catalysts for both ORR and OER was investigated in half-cell configuration in an alkaline solution (6M KOH) at room temperature. Stability tests were carried out in order to properly select the most appropriate catalyst to be used in a complete cell.

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2012-2015) under the call GC.NMP.2012-1; NECOBAUT Project n° 314159.

ELE-O3

Electrochemical preparation and characterization of Rh-Fecralloy foam catalysts for catalytic partial oxidation of methane

Enrico Verlato[a], *Stefano Cimino*[b], *Marco Musiani*[a], *Lourdes Vázquez-Gómez*[a]

a IENI-CNR, Corso Stati Uniti 4, 35127 Padova, Italy
b IRC-CNR, P.le V. Tecchio 80, 80125 Napoli, Italy

l.vazquez@ieni.cnr.it

Rh-based catalyst are the most active and selective for the catalytic partial oxidation (CPO) of hydrocarbons [1]. Being Rh a scarce and expensive noble metal, its effective usage is of crucial importance. We have explored the spontaneous deposition and electrodeposition of Rh onto Fecralloy foams as alternative routes for the preparation of structured catalysts.

Electrodeposition was found to be an effective method for supporting Rh nanoparticles onto Fecralloy foams, with an accurate control of the Rh loading in a wide range, compared with standard washcoating methods. The as-prepared catalysts were characterized by SEM-EDS, XRD and electrochemical methods; then they were tested in the CPO of CH_4 to syngas and characterized again. Cyclic voltammetry, over a potential range where the H adsorption/desorption charge could be measured [2], was employed to determine the real surface area of the noble metal, both before and after their use in the catalytic partial oxidation tests, so as to asses to what extent the sintering of Rh nanoparticles affected the catalysts performance in CPO.

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[2] E. Verlato, S. Cattarin, N. Comisso, L. Mattarozzi, M. Musiani, L. Vázquez-Gómez, *Electrocatalysis*, 2013, **4**, 203-211.

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ELE-O4

An EIS study on the preparation of electrocatalysts through galvanic displacement reactions

Enrico Verlato, Sandro Cattarin, Nicola Comisso, Luca Mattarozzi,
Marco Musiani, Lourdes Vázquez-Gómez

IENI CNR, Corso Stati Uniti 4, 35127 Padova, Italy

m.musiani@ieni.cnr.it

Our group has prepared a variety of electrocatalysts and catalysts for gas-phase processes (e.g. CPO of CH_4) by using galvanic displacement reactions in which a noble metal, displaces a non-noble substrate, often in the form of a metal foam [1-3]. Nanometric Pd, Pt and Rh particles can be deposited in a homogeneous way onto substrates with a complex shape, e.g. porous electrodes and foams.

Since galvanic displacement is a corrosion process, when noble metal deposition is the exclusive (or largely prevailing) cathodic partial reaction, monitoring its rate is possible through the measurement of the corrosion current, e.g. using electrochemical impedance spectroscopy (EIS).

To explore the potential of EIS, the Ni/Rh galvanic displacement has been investigated, using both Ni disc and Ni foam electrodes. The Rh deposition rate has been evaluated from EIS data and compared with values obtained by ion chromatography, obtaining a good agreement. Furthermore, the Rh surface area has been estimated from double layer capacity and the results have been compared with those achieved by cyclic voltammetry, finding in both cases similar linear variations with the duration of the galvanic displacement reaction.

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The authors acknowledge the financial support of the Italian Ministry for Economic Development (MSE) – MSE-CNR Agreement on National Electrical System.

ELE-O5

Solid State NMR investigations of polymer nanocomposite membranes for Fuel Cells

Alice Silvia Cattaneo[a], *Chiara Ferrara*[a], *Simone Angioni*[a], *Davide Carlo Villa*[a],
Eliana Quartarone[a], *Piercarlo Mustarelli*[a]

a Dipartimento di Chimica, Università degli Studi di Pavia, Via Taramelli,16 27100, Pavia, Italy

piercarlo.mustarelli@unipv.it

Proton Exchange Membrane Fuel Cells (PEMFCs) are of growing interest as energy sources for portable, stationary and transportation applications. The polymer electrolyte membrane, a proton conductor, plays a key role in determining the functional properties of the fuel cell. Polybenzimidazole (PBI), a heterocyclic-based thermoplastic polymer, is one of the most promising candidates for cells working at high temperature (120-200°C), but it needs to be activated with H_3PO_4, to assure high proton conductivity.

A possible strategy for improving the transport properties, is the design of polymer nanocomposite membranes, i.e. including an inorganic or hybrid filler in the PBI matrix. Clays and mesoporous silicas have already demonstrated to be suitable filler for polymer nanocomposite, especially for improving thermal and mechanical properties of the matrix. SBA-15 mesoporous silica possesses an hexagonal arrays of pores, i.e. an high surface area, which can be easily functionalized with organic chains having different terminal units ($-SO_3H$, -SH, $-NH_2$, imidazole). This peculiarity allows a further fine tuning of both the active role of the filler in the proton transport, and the filler-matrix interactions.

Here we present a multinuclear solid state NMR characterization of H_3PO_4-doped PBI membranes, having pure or SO_3H-functionalized SBA-15 as filler. The change in the matrix structure induced by the acid doping is followed by ^{13}C NMR, while ^{31}P and ^{1}H T_1 and T_2 relaxation times are used for monitoring the proton and acid mobility. Further insights in the role of the fillers in changing the transport properties are given by $^{31}P(^{1}H)$ HETCOR experiments. The role of the filler functionalization in modulating the acid-filler interactions is also explored.

ELE-O6

Effect of Temperature and pH of the electrolyte on charge/discharge phenomena related to IrO_x-SnO_x films

Sergio Ferro[a], *Davide Rosestolato*[a], *Achille De Battisti*[a]

[a] *Dipartimento di Scienze Chimiche e Farmaceutiche, Università degli Studi di Ferrara, Via Fossato di Mortara, 17, 44121, Ferrara, Italy*

rssdvd@unife.it

The electrochemical properties of oxide electrodes depend on preparation method, as well as on composition of the chosen oxide mixtures. Typically, the catalytic noble-metal-based oxide material is mixed with one or more oxides, which have the double role of increasing the stability of the catalyst while diluting it, in order to improve the accessibility to active sites and to decrease the noble-metal content. The catalytic activity is necessarily bound to the accessibility to active sites; the former is the result of a specific ability of the catalyst to stabilize the reaction intermediate(s), and the interaction generally requires modifications of the active site surroundings, which result from a change of its oxidation state. This work proposes a study of the effect of both pH and temperature on the kinetics of redox processes that involve the electrocatalytic sites. At first, electrodes based on iridium and tin oxides, having different molar compositions, were studied by WAXS, in order to characterize the system under investigation, and with the four-probe method, to evaluate how the film resistivity varies with the oxide composition. Then, cyclic voltammetric experiments have been accomplished, at different temperatures, to estimate the activation energy to the charging/discharging process of active sites. Obtained data showed that the activation energy is extremely low (less than 0.1 kcal/mol) and realistically not attributable to any chemical reaction: the "double injection / double ejection" process is plausibly due to a mechanism of proton hopping, which takes advantage from the fact that iridium sites have different chemical surroundings, and thus different energy content.

ELE-O7

Electrochemical fabrication of high k Al-Ta mixed oxides

F. Di Franco[a], *A. Zaffora*[a], *M. Santamaria*[a], *F. Di Quarto*[a], *E. Tsuji*[b], *H. Habazaki*[b]

a Electrochemical Materials Science Laboratory, Faculty of Engineering, University of Palermo, Viale delle Scienze, 90128 Palermo, Italy

b Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan

francesco.difranco@unipa.it

Anodic oxides on tantalum and aluminium have been studied in the last decades for their possible application in electrolytic capacitors [1-2]. Mixed aluminium-tantalum oxides appear very promising dielectrics for electrolytic capacitors or integrated circuit, owing to the expected higher values of dielectric permittivity with respect to pure Al_2O_3, provided that an improving in leakage current with respect to tantalum oxide can be obtained [1-2].

In this frame we have started an extensive investigation on the characterization of anodic oxides grown on magnetron sputtered Al-Ta alloys covering all the range of composition. More specifically, in this work we have prepared Al-Ta mixed oxides of different thickness by anodizing the alloys to different formation voltages in slightly alkaline solutions, where both Al_2O_3 and Ta_2O_5 are thermodynamically stable. A photoelectrochemical investigation was performed in order to estimate the band gap, E_g, and flat band potential, U_{FB}, of the oxide as a function of the growing conditions. The dependence of E_g on the oxide composition has been rationalized in the frame of the semi-empirical correlation between the electronegativity of the oxides' constituents and the band gap previously proposed in ref. [3]. Differential admittance and electrochemical impedance measurements were also carried out for some selected composition (including pure Al_2O_3 and Ta_2O_5) to get information on their dielectric properties. The dielectric constant resulted to increase monotonically from the value estimated for Al_2O_3 to that estimated for Ta_2O_5.

[1] R.C. Frunză et al., Materials Research Bulletin, 2014, **50**, 323-328.
[2] G. Alcalà et al., Corrosion Science, 2003, **45**, 1803-1813.
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ELE-O8

How to approach a Grätzel solar cell in a multivariate way

Federico Bella[a,b], *Diego Pugliese*[b], *Andrea Lamberti*[b], *Adriano Sacco*[a], *Simone Galliano*[c], *Valentina Cauda*[a], *Stefano Bianco*[a], *Claudio Gerbaldi*[b], *Claudia Barolo*[c]

a Center for Space Human Robotics @Polito, Istituto Italiano di Tecnologia, Corso Trento 21, 10129 Torino, Italia
b Dipartimento di Scienza Applicata e Tecnologia - DISAT, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italia
c Dipartimento di Chimica e Centro Interdipartimentale NIS, Università degli Studi di Torino, Via Giuria 7, 10125 Torino, Italia

federico.bella@polito.it

Nowadays, modern science proposes and optimizes new materials and technologies, whose characteristics and performances are governed by many factors. However, the scientific community rarely adopts multivariate strategies for the comprehension of what is proposed. As a striking example, a standard dye-sensitized solar cell (DSSC) is a typical complex system assembled with different and heterogeneous layers (FTO/nanocrystalline semiconductor/sensitizer/electrolyte/Pt-FTO), each one affected by intrinsic variability; moreover the layers influence each other and this increases the number of variables involved at the same time in the photoconversion process.

Thousands of articles have been published to study a single parameter or component of DSSCs, but a comprehensive approach which considers all the experimental factors simultaneously has never adopted.

In this work, we show how chemometric design of experiments (DoE) can be used for the formulation of UV-cured polymer electrolyte membranes [1], for the preparation of a cellulose-based gel-polymer electrolyte [2], for the proper sensitization of a ZnO photoanode [3] and for the photostability optimization of a series of NIR dyes under different dipping conditions.

[1] F. Bella et al., *Phys. Chem. Chem. Phys.*, 2013, **15**, 3706-3711.
[2] F. Bella et al., *RSC Adv.*, 2013, **3**, 15993-16001.
[3] D. Pugliese et al., *ACS Appl. Mater. Interfaces*, 2013, **5**, 11288-10295.

ELE-O9

Electrocatalytic reduction of organic halides in the ionic liquid [BMIM]BF_4

Abdirisak A. Isse, Christian Durante, Ludovico Scarpa, Armando Gennaro

Dipartimento di Scienze Chimiche, Università degli studi di Padova
Via Marzolo 1, 35131 Padova, Italia

abdirisak.ahmedisse@unipd.it

Activation of C-X bonds, especially in alkyl halides, requires electrocatalysis and indeed electrocatalytic reduction of RX has been a central topic in organic electrochemistry for the last few decades. The process has been mainly investigated in organic solvents such as CH_3CN and DMF, showing that a few metals such as Ag, Cu and Pd possess remarkable electrocatalytic properties.

Room temperature ionic liquids (RTILs) are widely used as green solvents in many electrochemical processes. Strikingly, however, there are only very few studies regarding RX reduction. Here, we report the results of a general survey on the electrochemical behavior of a wide variety of organic halides in 1-butyl-3-methylimidazolium tetrafluoroborate. GC, Cu and Ag were used as cathodes.

The most relevant findings of the study are (i) the mechanism of the dissociative electron transfer (DET) in the RTIL remains the same as in molecular solvents, and (ii) the catalytic effect strongly depends on halogen type, molecular structure and mechanism of DET. For example, while there is no catalysis for aromatic chlorides, Ag shows significant catalytic activities for the reduction of aromatic bromides (Fig. 1). Comparing [BMIM]BF_4 with molecular solvents, in general the electrocatalytic activity of the metals is lower in the ionic liquid than in CH_3CN.

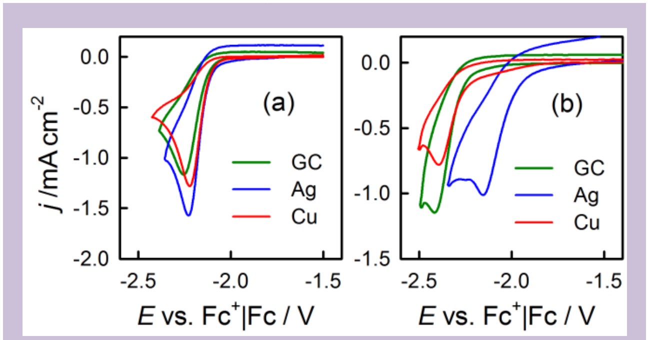

Fig.1. Cyclic voltammetry of 10 mM (a) 4-chlorobenzonitrile and (b) 4-bromobiphenyl in [BMIM]BF_4 at $\upsilon = 0.2$ Vs^{-1}.

This work was financially supported by Fondazione Cariplo, project 2011-1851.

ELE-O10

Premio di dottorato "Fondazione De Nora"

Electrochemical fabrication of metal/oxide/conducting polymer junctions for electronic devices

F. Di Franco,

Electrochemical Materials Science Laboratory, Faculty of Engineering, University of Palermo, Viale delle Scienze, 90128 Palermo, Italy

francesco.difranco@unipa.it

The metal/oxide/conducting polymer junctions are hybrid inorganic/organic structures usually employed in several electronic devices such as electrolytic capacitor, inorganic-organic thin field effect transistors, organic light emitting diode, sensors and solid state photovoltaic or photo-electrochemical cells. These widespread fields of application are mainly due to the possibility to simply modify the electronic properties of conducting polymer, that can show a semiconducting or metallic behaviour depending on the degree of doping. For instance, in solid state electrolytic capacitors, which are passive components in electronic circuits, conducting polymers are used in their metallic state to form a so called Metal/Insulator/Organic Metal junction (MIM_{org}), while they work in their semiconducting state in Metal/Oxide/Organic Semiconductor junction (MOS_{org}), to be integrated in Field Effect Transistors (FET), active components of electronic circuits. This work is focused on the electrochemical fabrication of metal/oxide/conducting polymer junctions to be integrated in electronic devices. Thus, the first part of the research activity was devoted to the preparation and physico-chemical characterization of high k oxides with good dielectric properties. In the second part of this work, the deep knowledge of the solid state properties of the investigated oxides was used to design a photoelectrochemical process able to allow the electro-polymerization of Edot (3,4-Ethylenedioxythiophene) on a not conducting substrate. This step was followed by a de-doping process to bring the polymer from its metallic to its p-type semiconducting state to test the performance of the prepared metal/oxide/polymer junction in thin film transistor.

ELE-O11

Premio di dottorato "Fondazione De Nora"

Chimiche avanzate di batteria al litio per un trasporto sostenibile

Simone Monaco[a],

*a Dipartimento di Chimica "Giacomo Ciamician", Università di Bologna, Via Selmi 2 ,
40126, Bologna, Italia*

simone.monaco2@unibo.it

L'energia specifica massima delle batterie Li-ione è oggi di 200 Wh/kg, un valore non sufficiente per alimentare veicoli completamente elettrici con autonomie di percorso di 400 km. Questo lavoro di dottorato si è focalizzato su due principali strategie per aumentare l'energia delle batterie al litio ricaricabili. La prima prevedeva lo sviluppo di catodi che lavorano a potenziali di intercalazione/de-intercalazione medio-alti per batterie ricaricabili Li-ione; la seconda si è focalizzata sullo studio di fattibilità di una batteria litio/ossigeno (Li/O_2) operante in liquidi ionici. Come materiali catodici per batterie Li-ione sono stati sintetizzati e caratterizzati tre diversi fosfati di Mn e Fe ($LiMn_{1-x}Fe_xPO_4$). I risultati ottenuti hanno dimostrato la possibilità di sintetizzare un'olivina a base di Mn ($LiMnPO_4$) con buone prestazioni elettrochimiche [1]. Relativamente alle batterie Li/O_2 sono stati indagati tre aspetti: lo studio di base del processo redox dell'O_2 [2], la sintesi e la caratterizzazione di carboni porosi come materiali per l'elettrodo positivo [3] e lo studio dei fattori che limitano la capacità dell'elettrodo e la vita di ciclo della batteria. Questo lavoro ha evidenziato che il trasporto di massa dell'O_2 limita la capacità della batteria ad alte correnti e ha proposto l'utilizzo di una cella a flusso per superare tale limitazione [4]. È inoltre emerso che il principale ostacolo da superare prima che la batteria Li/O_2 operante in liquidi ionici diventi la soluzione tecnologica per un trasporto sostenibile, è la non sufficientemente alta efficienza di ricarica e la conseguente bassa vita di ciclo della batteria.

[1] L. Damen, F. De Giorgio, S. Monaco, et.al. *J. Power Sources*, 2012, **218**, 250–253.
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[3] F. Soavi, S. Monaco, M. Mastragostino *J. Power Sources,* 2013, **224**, 115–119.
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ELE-O12

Premio di dottorato "Metrohm Italiana Srl"

Advanced materials for electrode modification in trace electroanalysis

Valentina Pifferi

Università degli Studi di Milano, Dipartimento di Chimica, via Golgi 19, 20133, Milano, Italia

valentina.pifferi@unimi.it

Trace analysis has shown in the last years a tremendous growth, prompted by the urgent need of many International Organizations looking for new analytical techniques for the detection of different molecules in different and increasingly more complex matrixes. The determination of trace analytes requires reliable and robust analytical methods. Among different analytical techniques, electroanalytical ones and particularly those based on pulsed voltammetry, seem to be promising independent alternatives in terms of very high precision, accuracy and sensitivity, simplicity of use, portability, easy automation and possibility of on-line and on-site monitoring, without sample pre-treatments and low costs.

In this context, recent technological developments have enhanced the chances of progress and growth of electroanalytical methodologies for trace analysis. In particular, with the aim of increasing the affinity for the analyte, increasing sensitivity, lowering the limits of detection and minimizing or completely avoiding interferences, research has focused its attention on the possibility of producing electrodes by the use of the screen-printing microfabrication technology and the use of nanosized and/or nanostructured materials, sometimes combined with the use of polymeric materials.

This PhD thesis has sought to provide a contribution in this framework, trying to enhance the technological potentialities of electroanalytical methodologies in the field of inorganic and organic trace analysis, with the use of screen-printed electrodes and electrodes modified by nanomaterials and/or polymeric membranes.

After an attentive physico-chemical characterization of the advanced materials, the modified electrode performances were studied and optimized and the resulting sensors and biosensors applied to the detection of some contaminants of emerging concern: benzidines, furan, arsenic, chromium, H_2O_2, ethanol, glucose, glycerol, organic chlorides.

ELE-O13

Premio di laurea “Photo Analytical Srl”

Fundamental aspects of aqueous Atom Transfer Radical Polymerization

Marco Fantin

Dipartimento di Scienze Chimiche, Università degli Studi di Padova
Via Marzolo 1, 35131 Padova, Italia

marco.fantin.1@studenti.unipd.it

Aqueous controlled radical polymerization is a powerful technique for the development of water-soluble polymers, for potential biomedical and pharmaceutical applications. Unfortunately, however, full application of atom transfer radical polymerization (ATRP) in water has so far been limited by a poor level of control on polymer growth.

The mechanism of ATRP in aprotic solvents is well known (Fig. 1). Conversely, in aqueous environments, catalysts have a highly different reactivity and are involved in a series of competitive reactions that can undermine their efficiency. Moreover, pH is a new fundamental variable that has to be considered.

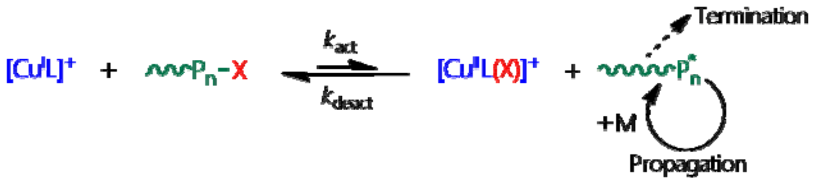

Fig. 1: General ATRP mechanism.

Three copper catalysts with polyamine ligands have been studied in water, with particular attention to the stability of activator and deactivator complexes, reactivity of Cu(I) and ATRP equilibrium constant, K_{ATRP}. It is found that Cu(I) is always extremely active with high K_{ATRP}, resulting in high radical concentrations and consequently a loss of control. Also disproportionation is quite important, especially at low pH, and the deactivator $[Cu^{II}L(X)]^+$ is unstable.

Careful analysis of the system suggests that gaining full control and capacity of prediction on polymer growth requires considering the following points: control on pH and halide ions concentration, use of ligands that stabilize Cu(I) and careful choice of monomers and polymerization initiators.

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ELE-O14

Premio di laurea "Materials Mates Italia Srl"

Low temperature proton conductivity in porous TiO_2

Alessandro Senocrate [a], *Truls Norby* [b], *Umberto Anselmi-Tamburini* [a]

a Dipartimento di Chimica, Università di Pavia, V.le Taramelli 16, 27100, Pavia, Italia
b Dipartimento di Chimica, Università di Oslo, Gaustadallèen 21, 0349, Oslo, Norvegia

alessandro.senocrate01@ateneopv.it

A number of studies have shown relatively high conductivities in nanograined ceramics such as yttria-stabilised zirconia (YSZ) and gadolinia-doped ceria (GDC) at ambient temperatures.[1-2] The conductivity contribution increases with decreasing temperature and with increasing water activity. From transport number measurements it was attributed to protonic transport and, after initial uncertainty, it now seems clear that the source of this contribution is ionic transport in water condensed in the open porosity (or relatively open grain boundaries) of the samples.[1-3] The water condenses at higher temperatures and lower water activities than the ambient dew point because of the curvatures of the porosity. Aim of this work was to investigate this peculiar conductivity increase, as a function of several parameters such as doping, grains and pores sizes and porosity of a sample. Pure samples, along with 1 mol. % Fe-doped and 1 mol.% Nb-doped samples were analysed, finding no immediate correlation between doping type and conductivity increase. To better relate microstructural parameters to the final increase in conductivity at ambient temperature, we also developed a simple mathematical model to calculate the amount of condensed water (and thus the protonic conductivity) as a function of temperature, water activity, sample relative density, and grain/pore size. A good correlation was found between the model and the experimental data, but further work is still required in order to reach a useful tool for parameterisation of conductivity in condensed water in porous media at near ambient conditions. At last, using both the model and experimental data, it was possible to make some consideration on the nature of the mechanism involved in low temperature proton conductivity.

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ELE-O15

Premio di laurea “Claind Srl”: Roberta Verrelli

Studio dell’elettrolita solido $Li_{10}GeP_2S_{12}$

Roberta Verrelli[a], *Jusef Hassoun*[a], *Stefania Panero*[a], *Bruno Scrosati*[b]

a Dip. di Chimica, Università di Roma “Sapienza”, P.le A. Moro 5, 00185, Roma, Italia
b Italian Institute of Technology, Genova, Italia

roberta.verrelli@uniroma1.it

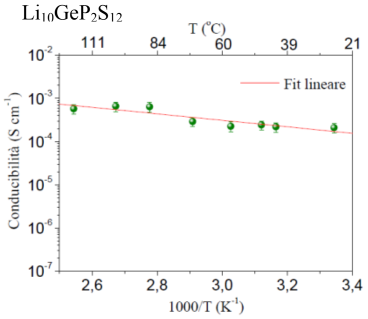
Le batterie al litio convenzionali non sono ancora idonee a soddisfare gli stringenti requisiti di efficienza e sicurezza imposti dalle tecnologie emergenti dell’autotrazione elettrica ed ibrida e dei sistemi stazionari di accumulo integrati con fonti di energia rinnovabile, di cui si prevede la diffusione su larga scala nei prossimi anni.

In particolare, uno dei maggiori limiti delle attuali batterie risiede nella loro infiammabilità, legata alla co-presenza di agenti ossidanti e materiali combustibili. La sostituzione dei convenzionali elettroliti liquidi organici con elettroliti solidi non infiammabili potrebbe essere la chiave per superare tali problemi di sicurezza ed affidabilità.

In questo lavoro è stato approfondito lo studio del super-conduttore ionico $Li_{10}GeP_2S_{12}$, presentato in letteratura nel 2011 come uno dei più promettenti elettroliti solidi finora sintetizzati[1].

E’ stato effettuato uno studio strutturale della fase $Li_{10}GeP_2S_{12}$ mediante diffrazione a raggi X e spettroscopia Raman. La caratterizzazione elettrochimica dell’elettrolita ha evidenziato valori elevati di conducibilità ionica ($\sigma \sim 10^{-3}$ S/cm – Figura 1) in un ampio intervallo di temperature, un numero di trasporto degli ioni Li^+ di circa 0.92 e un intervallo di stabilità esteso fino a 5.5 V vs Li^+/Li. E’ stata, inoltre, valutata l’applicabilità dell’elettrolita in batterie a stato solido, con catodi convenzionali di $LiFePO_4$ e $LiNi_{0.5}Mn_{1.5}O_4$ finora mai realizzate.

Figura 1: Arrhenius plot dell’elettrolita $Li_{10}GeP_2S_{12}$



I risultati ottenuti in questo studio[2] confermano che l’elettrolita $Li_{10}GeP_2S_{12}$ è il candidato ideale per la realizzazione di batterie a stato solido più sicure.

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[2] J. Hassoun, R. Verrelli, P. Reale, S. Panero, G. Mariotto, B. Scrosati, *J. of Power Sources* 2013, **229**, 117.

ELE-O16

Polybenzimidazole-based membranes for HT-PEMFCs

Eliana Quartarone[a], *Simone Angioni*[a], *Davide C. Villa*[a], *Piercarlo Mustarelli*[a] *and Aldo Magistris*[a]

a Department of Chemistry, University of Pavia, Via Taramelli 12 , 27100, Pavia, Italy

eliana.quartarone@unipv.it

Polymer electrolyte fuel cells (PEMFC) are leading-edge targets for what concerns the key technology of the next generation hydrogen-powered vehicles. However, the scale-up of PEMFCs is still limited by their incompatibility with the operating conditions of the automotive applications, namely working temperatures around 130°C and low humidification. Acid-doped Polybenzimidazoles are actually considered as promising electrolytes to replace Nafion in HT-PEMFCs [1]. Nevertheless, some relevant questions are still open: under which operating conditions (chiefly temperature) are the acid-doped PBI systems a real alternative to Nafion? What is the real durability of the PBI cells/stacks?

Here we will report the state of the art and our most recent developments, which could make polybenzimidazole systems the market choice for high temperature (HT)-PEMFCs. Particular emphasis is given to problems such as acid leaching, membrane degradation and stack durability, as well as to the strategies adopted in our laboratory to properly address these issues [1-7].

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[7] D.C. Villa et al., *Adv. En. Mat.*, 2014, DOI: 10.1002/aenm.201301949.

ELE-O17

Layered nanostructures for composites hybrid membranes in fuel cell application: investigation of water and methanol transport properties

Isabella Nicotera [a], *Kristina Angjeli*[a], *Cataldo Simari* [a], *Vassiliki Kosma* [a], *Luigi Coppola* [a], *Vincenzo Baglio* [b]

a Department of Chemistry, University of Calabria, 87036 Rende, Cosenza, Italy
b CNR-ITAE, Via Salita S. Lucia sopra Contesse 5 - 98126 Messina, Italy

isabella.nicotera@unical.it

A class of layered fillers, belong to cationic smectite clays (Laponite and Montmorillonite) family, were investigated in Nafion composite membranes. The presence of 2D platelike silicate layers in the matrix of a polymer was of major interest due to the significant gains in thermal stability, mechanical and barrier properties of the resulting nanocomposites Smectite clays were suitably functionalized with organo-surfactants having hydrophilic terminal groups such as sulfonilic groups, in order to improve the water retention (at high temperature), affinity for polymer and reinforcement of the polymeric network, reducing the swelling and lowering the methanol permeability.

Water and methanol transport behavior, solvents adsorption and electrochemical properties were investigated using DMFC tests and NMR methods, including spin-lattice relaxation and pulsed-gradient spin-echo (PGSE) diffusion under variable temperature conditions. Transport mechanism of water and methanol appears to be influenced from the dimensions of the dispersed platelike silicate layers as well as from their cation exchange capacity (CEC). Clays particles, and in particular Swy-2, demonstrate to be a potential physical barrier for methanol cross-over, reducing the methanol diffusion with an evident blocking effect and nevertheless ensuring a high water mobility up to 130 °C and for several hours, proving the exceptional water retention property of these materials extending in this way the operating range of a direct methanol fuel cell.

ELE-O18

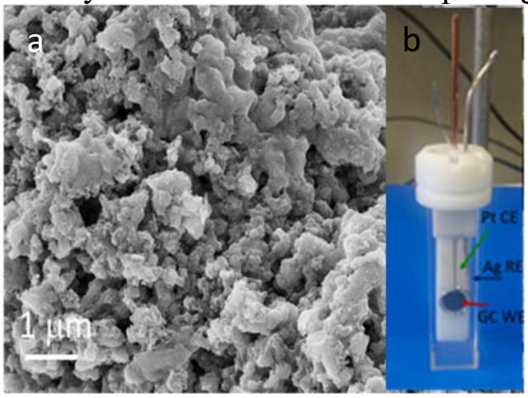
Nitrogen-Doped Mesoporous Carbons: Activity Towards Oxygen Reduction

Valentina Perazzolo,[a] *Christian Durante,*[a] *Roberto Pilot,*[b] *Zheng Jian*[a]
Renato Bozio,[a] *Gaetano Granozzi,*[a] *Armando Gennaro*[a]

a Dept. of Chemical Sciences, University of Padova, Via Marzolo 1, 35131 Padova
b Consorzio INSTM and Dept. of Chemical Sciences, University of Padova, Via Marzolo 1, 35131 Padova - Italy

perazzolo.valentina@gmail.com

Nitrogen-doped mesoporous carbons (N-MCs) are highly porous materials of particular interest in the field of fuel cell and battery technology due to their possible employment as catalyst supports or metal free catalysts.[1] In this work a hard template approach was used to prepare N-MCs from different organic precursors, namely EDTA, phenanthroline, phenothiazine and carbazole. Depending on the synthesis conditions and on the starting precursor it was possible to tune the MC chemistry in terms of nitrogen content and nitrogen functional groups. The catalytic performances of the different N-MCs were investigated by cyclic voltammetry and by rotating disk electrode, allowing a careful analysis of the chemical aspects governing the catalytic activity towards ORR. The morphology of the N-MCs was investigated by SEM (Fig. a) and TEM, whereas the surface area was evaluated by BET. The chemical stability of the N-MCs was tested in-situ by RAMAN spectroscopy in a home-made spectroelectrochemical cell (Fig. b). Any changes observed in the D-band/G-band intensity ratio were taken to be indicative of a degradation of the N-MCs.



We acknowledge financial support from Joint Undertaking (FCH-JU) within the CathCat project under contract No. 303492.

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ELE-O19

Dissymmetric Modification of Micro- and Nanoparticles for Energy Conversion

Michael Ongaro[a], *Jérome Roche*[b], *Alexander Kuhn*[b], *Paolo Ugo*[a]

a Department of Molecular Sciences and Nanosystems, University Ca' Foscari,
Santa Marta 2137, 30123, Venice, Italy
b Université de Bordeaux, ISM, UMR 5255, ENSCBP, 33607 Pessac, France.

michael.ongaro@unive.it

In this communication we present two simple and efficient methods for the asymmetrical functionalization of micro-and nanoparticles by bipolar electrochemistry (BPE) for obtaining anisotropic materials suitable for water splitting and photocatalysis. Bipolar electrochemistry (BPE) occurs when faradaic reactions are driven on electronic conductor not directly connected to an electrical power source, but in contact with a dielectric (typically a solution) which is polarized under the influence of an applied electric field.

At first, we present here the asymmetrical modification of the two tips of carbon microfibers with a donor and an acceptor characterized by a difference in redox potential as high as 3 V. To this aim, gold and polythiophene are deposited by BPE at the cathodic and anodic tips of the microfibers, respectively [1]. As a second case study, we examine the role that irradiation with light plays on the electronic conduction features of semiconductor nanowires and, consequently, on BPE. When BPE is performed in the dark on a dispersion of TiO_2 nanowires (TiO_2-NWs) in Au(III) solutions, no gold deposit is formed. When the NWs suspension is irradiated with UV light in the absence of an electric field, small metallic gold deposits, randomly located all over the nanowires are formed. Finally, when both UV light and electric field are applied, a metallic deposit is formed, but in a precise position of the NW, that is at its cathodic tip. These results indicate that the application of the external electric field allows one to drive locally the action of the light thus achieving the localized asymmetrical modification with gold of the TiO_2-NWs.

Application prospects of these topologically modified nanowires for the photoconversion of energy will be finally discussed.

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ELE-O20

Mathematical modeling and simulation of Li-ion battery

Italo Doberdò, A. Maheshwari, M. Santarelli, S. Bodoardo, N. Penazzi

Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129, Torino, Italia

italo.doberdo@polito.it

Lithium-ion batteries (LIB), with their high energy and power density, are becoming increasingly popular for various applications in portable electronic devices and electric vehicles. Multi-physicochemical models, able to estimate the battery behavior in adequate details under different conditions, are fundamental for the design and the optimization of LIBs. Another useful aspect of computer simulations is that they allow us deeper and more detailed understanding of the cell limiting factors during operation [1].

There are substantially five driving forces that influence the lithium-ion transfer within a battery, namely the electric field of the solid-porous electrode and of the liquid electrolyte, the lithium-ion concentration in the solid electrode and in the electrolyte phase, and the reaction rate occurring at the electrode/electrolyte boundary [2]. Fig.1 shows how the model can predict the discharging behavior by varying the C-rate (top); the concentration of Li-ion in the electrolyte is evaluated during operation (bottom), showing an increase of concentration at the anode side upon time and vice versa at the cathode side.

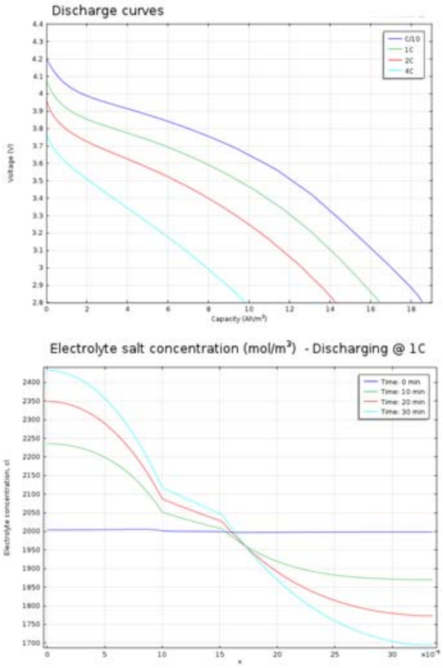

Fig.1: Simulated discharge profile at different C-rate (top); Li-ion concentration in the electrolyte across the cella t diffrent times during 1C discharge (bottom).

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ELE-O21

Carbon nanotubes modified electrodes for the detection of benzidines.

Valentina Pifferi, Luigi Falciola, Elena Ferrari, Paolo Ferruti, Amedea Manfredi, Elisabetta Ranucci

Università degli Studi di Milano, Dipartimento di Chimica, via Golgi 19, 20133, Milano

valentina.pifferi@unimi.it

Carbon nanotubes modified electrodes have been prepared, completely characterized (by cyclic voltammetry, electrochemical impedance spectroscopy, BET, SEM, TEM) and employed for the electroanalytical detection of some contaminants of emerging concern: benzidine, o-toluidine, o-tolidine and tetramethylbenzidine, organic carcinogenic synthetic pollutants mainly used as intermediate in production of azo-dyes.

The developed electroanalytical methodologies are based on voltammetric techniques, which allow to achieve excellent results in terms of large dynamic concentration ranges, high accuracy and precision and low limits of detection and quantification, with respect to conventional HPLC technique. The use of nanomaterials further enhances the potentialities of the methods [1].

The optimized sensors allows to monitor the disappearance of toxic compounds and to compare the resins efficiencies during sorption experiments with α-, β-, γ-cyclodextrine-polyamidoamine nanosponges.

[1] J.J. Gooding *Electrochimica Acta,* 2005, **50**, 3049.

ELE-O22

A comparison between Cu and Cu-Ni porous electrodes for the detection of nitrates in water

Nicola Comisso, Sandro Cattarin, Luca Mattarozzi, Marco Musiani, Lourdes Vázquez-Gómez, Enrico Verlato
IENI CNR, Corso Stati Uniti 4, 35127 Padova, Italy

nicola.comisso@ieni.cnr.it

Porous electrodes are interesting for a wide range of applications. Electrodeposition at high current density, in a regime of vigorous hydrogen bubbles evolution, is a convenient method to obtain a bimodal porosity: macropores (size of tens of microns) for enhanced mass transport and a microporous structure able to ensure large surface area, both useful properties for applications in electrocatalysis. In recent years we have studied the electrochemical reduction of nitrates on both compact [1] and porous [2] electrodeposited Cu-Ni electrodes, and assessed the potential of these materials in the environmental remediation of alkaline, nitrate-rich waters. The use of porous Cu-Ni electrodes is potentially interesting in the detection and analysis of nitrate in aqueous media, for which the results obtained by Compton on Cu [3] and Cu-Ni [4] are still a reference. In the present work we report on the preparation of Cu and Cu-Ni porous electrodes, obtained using hydrogen bubbles as a template agent, and their application to the analysis of nitrate ions in aqueous media of different pH, comparing our results with previous ones. The porous Cu-Ni electrodes have lower sensitivity but better stability in prolonged experiments and lower noise than those previously obtained.

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ELE-O23

Effect of porosity on the electroanalytical performances of modified electrodes.

Luigi Falciola, *Valentina Pifferi*

Università degli Studi di Milano, Dipartimento di Chimica, via Golgi 19, 20133, Milano

luigi.falciola@unimi.it

In the last years, the use of polymer films and/or the employment of layers of carbon nanotubes (CNTs) to build "chemically modified electrodes" to be used in the electroanalytical field are spreading. The reason is that the final devices present better performances, particularly in terms of peak current increments and of voltammetric peak separation narrowing, useful features for increasing selectivity and sensitivity and lowering detection limits.

Recently, it has been proposed that the better performances are not only due to a change in electrode kinetics (*e.g.* catalytic effects brought by nanomaterials or their functionalization, decrease in charge transfer resistance) or to an increment of surface area or porosity distribution, but also by a change in the diffusion mechanism, from linear to thin-layer or convergent [1-2].

In this presentation, we would like to contribute to this debated topic, with some experimental results obtained working with electrodes modified with appropriately functionalized CNTs and with electrodes modified with Sulphonated Poly (Aryl Ether Sulphones), a new class of polymers, ad hoc tailored for our electroanalytical applications. These modifications have led to an increase in the mesoporosity which, according to us, is the responsible of the transition from the linear diffusion regime to the thin layer behavior, causing the enhancement of the peak currents.

Applications of the optimized devices to the detection of some contaminants of emerging concern (*e.g.* benzidines) will be also presented.

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ELE-O24

The effect of chemico-structural features of molecules of biological interest on their electrochemical response @ AuNps modified electrodes

Antonella Curulli[a], *Gabriella Di Carlo*[a], *Alessandro Trani*[a], *Daniela Zane*[a], *Rita Petrucci*[b], *Giancarlo Marrosu*[b]

a Istituto per lo Studio dei Materiali Nanostrutturati (ISMN), UOS Sapienza, Via del Castro Laurenziano 7, 00161 Roma, Italia
b Dipartimento di Scienze di Base Applicate all'Ingegneria (SBAI), Università di Roma Sapienza, Via del Castro Laurenziano 7, 00161, Roma, Italia

antonella.curulli@cnr.it

In the last decades, gold nanoparticles (AuNPs) have received an increasing attention due to their unique physical and chemical properties, which make them of considerable interest for applications in many fields, such as biotechnology, optics, electronics and catalysis. In this communication, we present study on the design of differently functionalized AuNPs, with tailored morphological properties as sensing platform able to interact directly and specifically with molecules of biological interest.

We have investigated chitosan-stabilized and cysteamine-stabilized AuNps. The synthesis of AuNps was carried out by using a route, according to our recently published procedures, from a $HAuCl_4$ aqueous solution and were characterized by UV-vis spectroscopy, as previously reported [1,2].

The redox behaviour of molecules of biological interest, such as caffeine (CAF) and serotonin (5-HT), has been investigated at electrode surfaces modified with different gold nanoparticles (AuNPs). Our findings demonstrate that the chemical structural features of the molecules play a key role in the interaction with modified electrodes that strongly affect the electrochemical response.

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ELE-O25

Inherent Chirality in Electrochemistry: a Versatile Concept

F. Sannicolò[a], *S. Arnaboldi*[a], *P. R. Mussini*[a], *E. Lo Bello*[a], *S. Riva*[a], *V. Marino*[a], *T. Benincori*[b], *S. Rizzo*[c], *V. Mihali*[a], *A. Gennaro*[d], *A. A. Isse*[d]

a Dip. di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milano
b Dip. di Scienza e Alta Tecnologia, Univ. dell'Insubria, Via Valleggio 11, 22100 Como
c CNR ISTM, Via Golgi 19, 20133 Milano
d Dip. di Scienze Chimiche, Univ. degli Studi di Padova, Via Marzolo 1, 35131 Padova

serena.arnaboldi@unimi.it

The typical design of chiral electroactive materials involves attaching chiral pendants to an electroactive polyconjugated backbone and generally results in modest chirality manifestations. We have designed "inherently chiral" thiophene-based electroactive monomers, where chirality is not external to the electroactive backbone but inherent to it, and results from a torsion generated by the presence of an atropisomeric, conjugatively active biheteroaromatic scaffold. Through the electrooligomerization of the starting monomer with these intriguing properties we obtained enantiopure electrode surfaces with impressive chiroptical activity and outstanding enantiorecognition ability towards specular redox probes [1].
Recently we exploited the "inherent chirality" concept for the development of chiral ionic liquids (CILs), hopefully endowed with high enantioselectivity. The new molecules are based on cations including different atropisomeric bis-benzimidazolium groups acting as stereogenic element, responsible for both molecular chirality and IL properties of the material, modulated by number, position and length of alkyl chain substituents. An overview will be given of the first structures obtained and of their electrochemical properties.

With the contribution of Fondazione Cariplo, grants no. 2011-0417 (inherently chiral electrodes) and no. 2011-1851 (inherently chiral ionic liquids).

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ELE-O26

Studio di celle solari a colorante di tipo catodico con sensibilizzatori squarainici

Danilo Dini[a], *Gaia Naponiello*[a], *Franco Decker*[a], *Davide Saccone*[b], *Claudia Barolo*[b], *Aldo Di Carlo*[c]

a Dip. Chimica, Università di Roma "La Sapienza",p.le Aldo Moro 5, 00185 Roma
b Dip. Chimica Generale ed Organica Applicata, Università di Torino, 10125 Torino
c Dip. Ingegneria Elettronica, Università di Roma "Tor Vergata", 00133 Roma

danilo.dini@uniroma1.it

Celle solari a colorante di tipo catodico (*p*-DSC)[1] sono state costruite con elettrodi fotoattivi di NiO mesoporoso[2] sensibilizzato nel vis-NIR da squaraine[3] a struttura simmetrica ed asimmetrica. I catodi di NiO (spessore < 5 micron) sono stati depositati col metodo dello screen-printing[4] utilizzando sospensioni di nanoparticelle di NiO di diametro 50 nm in matrice di etilcellulosa e terpineolo. Per il processo di sensibilizzazione di NiO colle squaraine sono state adottate condizioni variate nei tempi di colorazione e nel trattamento dell'ossido allo scopo di analizzarne l'effetto sulla prestazione del corrispondente dispositivo *p*-DSC. Il grado di sensibilizzazione di NiO è stato valutato per via spettrofotometrica mentre la determinazione quantitativa del colorante chemisorbito su NiO è stata condotta attraverso il metodo dell'assorbimento/desorbimento.[5] Le celle sono state caratterizzate tramite determinazione delle curve caratteristiche J-V al buio e sotto irraggiamento con sun simulator, e tramite misura degli spettri di efficienza di conversione (IPCE). Particolarmente interessanti sono stati i risultati riguardanti i fotopotenziali di circuito aperto (OCV) che cadono nell'intervallo $0.13 \leq OCV \leq 0.15$ V, cioè tra i più alti riportati in letteratura per le *p*-DSC basate su fotocatodi di NiO quando la coppia redox e' I_3^-/I^-.[6] In particolare, fra le squaraine investigate, quelle con il gruppo ancorante (-COOH) legato al sistema con maggior estensione di coniugazione elettronica generalmente davano origine ai fotopotenziali più elevati.

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ELE-O27

Nanostructures for energy conversion: synergic effects between carbon nanotubes and metal oxides

Giovanni Valenti,[a] *Alessandro Boni,*[a] *Matteo Cargnello,*[b] *Stefania Rapino,*[a] *Paolo Fornasiero,* [b] *Maurizio Prato,*[b] *Massimo Marcaccio,*[a] *and Francesco Paolucci.*[a]

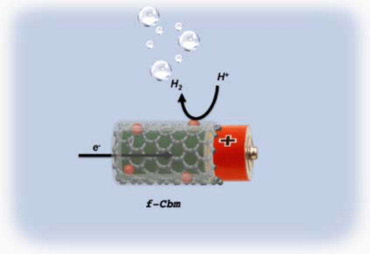
a Department of Chemistry University of Bologna, via Selmi 2, 40126 Bologna, Italy

b Department of Chemical and Pharmaceutical Sciences, University of Trieste, Italy

g.valenti@unibo.it

The growing need for energy on global scale and the realization that the so called oil-based economy cannot sustain our world anymore, prompted researchers to find new ways to "power" the planet.[1] The splitting of water to high energy chemical fuels is one of the most attractive and pursued alternatives; among the major issues there is the need to find catalytic systems that are able to boost the overall reaction efficiently and durably.

In this context our group recently focused the attention on the study of catalytic systems for the oxygen evolution reaction.[2] Our last efforts have been done in the development of new C-based nanocomposites that combine the unique properties of multiwall carbon nanotubes, metal oxides (TiO_2 and CeO_2) and Pd nanoparticles.[3] The nanocomposites have been designed and evaluated as electrocatalyst for the reaction of hydrogen evolution and for the CO_2 reduction. Both systems exhibit very good performances and efficiencies, showing physical and chemical properties that differ to those expected from the simple sum of the individual building blocks.



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ELE-O28

In-operando, time-resolved energy dispersive XANES on IrO_2 as catalyst for water oxidation

Alessandro Minguzzi[a], *Ottavio Lugaresi*[a], *Elisabetta Achilli*[b], *Giovanni Agostini*[c], *Cristina Locatelli*[a], *Alberto Vertova*[a], *Paolo Ghigna*[b], *and Sandra Rondinini*[a]

a Università degli Studi di Milano, Dipartimento di Chimica, Via Golgi 19, 20133, Milano, Italy.
b Università di Pavia, Dipartimento di Chimica, Via Taramelli 16, 27100, Pavia, Italy
c European Synchrotron Radiation Facility, B.P. 220, 38043 Grenoble, France

alessandro.minguzzi@unimi.it

Electrocatalysis, i.e. the study of the electrode material influence on reaction kinetics, is gaining growing attention due to its importance in energy convertion/storage and environmental protection devices.

In the last decade, new synthetic methods for nanostructuring coupled to new characterization techniques allowed a more rapid, efficient and detailed research effort for all the most advanced electrochemistry-based systems. Notwithstanding this, most reaction mechanisms remain not fully understood and the role of the electrocatalyst is often controversial. For example, in photoelectrochemical water splitting, it is not clear whether the catalyst acts as simple surface defects quencher [1] or as reaction catalyst.

The developement of new syncrothron light-based techniques is helping in shining light on these aspects [2] as previously demonstrated by recent *in-operando* electrochemical experiments aimed to introduce the FEXRAV [3] and in turn a better understandings of water oxidation mechanism on IrO_2, one of the most active catalyst for water oxidation. In this work we introduce *in-operando*, time-resolved analysis on IrO_2 electrodes carried out using an innovative set-up based on energy dispersive XANES. With this method we demonstrate the time-lenght of redox transitions of Ir sites involved in water oxidation catalytic cycle.

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Elettrohimica

Poster

ELE-P1

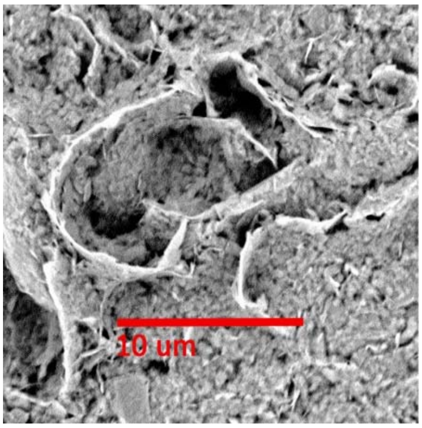
Characteristics of an advanced Graphene / $Pyr_{1,4}$TFSI-LiTFSI / $LiFePO_4$ lithium-ion battery

Marco Agostini [a], *Laura Rizzi* [b], *Bruno Scrosati* [c], *Jusef Hassoun* [a].

a Dipartimento di Chimica, "Sapienza" Università di Roma", Rome, Italy
b Directa Plus, Como, Italy
c Italian Institute of Technology, Genova, Italy

marco.agostini@uniroma1.it

Safety is considered one of the major issues preventing the worldwide diffusion of the high energy lithium ion batteries as storage system for free-emission, electric vehicles. Recently many efforts aimed to reduce the safety hazard considering the replacement of conventional, high flammable and volatile organic electrolyte with thermally stable, non flammable ionic liquid (IL) solutions. Moreover, ILs may be considered valid solution to avoid issues associated with the use of lithium metal anode, such as dendrite growth with cell shorting and possible fire evolution[1]. In this work we focus the attention on the use of a $Py_{1,4}$TFSI-LiTFSI-based electrolyte solution in a novel lithium ion battery employing a Cu-supported graphene anode and a lithium iron phosphate cathode. This cell expected to be characterized by low cost and high performances in terms of stability and safety content. Furthermore, the use of the attractive graphene-based anode in combination with the safe ionic liquid-based electrolyte increases the novelty content of the cell making it of interest for the lithium-ion battery community. The material structure and morphology are characterized by X ray diffraction (XRD) and scanning electronic microscopy (SEM) while the lithium ion cell is studied by galvanostatic cycling (GC).



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ELE-P2

Electrochemistry of Inherently Chiral Thiophene-Based Materials in Achiral and Chiral Ionic Liquids

F. Sannicolò[a], S. Arnaboldi[a], P. R. Mussini[a], S. Rizzo[b], V. Mihali[a], A. Gennaro[c], A. A. Isse[c]

a Dip. di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milano
b CNR ISTM, Via Golgi 19, 20133 Milano
c Dip. di Scienze Chimiche, Univ. degli Studi di Padova, Via Marzolo 1, 35131 Padova

serena.arnaboldi@unimi.it

Recently, ionic liquids have been frequently proposed as convenient substitutes for VOCs-supporting electrolyte systems in a variety of electrochemical processes. In particular, recent studies show that they are very good electrodeposition media for inorganic and organic conducting films, on account of their peculiar features. In this frame, our ongoing studies on redox properties and electrooligomerization of inherently chiral thiophene-based molecular materials [1] provide a particularly significant and attractive test for both achiral and chiral ionic liquids as reaction media.

1) Achiral ionic liquids (AILs) employed as electrodeposition media for the preparation of inherently chiral electrode surfaces of outstanding reproducibility and enantioselectivity.

2) Electrochemical tests in chiral ionic liquids (CILs) by comparing possible reciprocal recognition manifestations between our inherently chiral substrates (monomers and oligomer films) and the chiral working environment.

For this aim we are considering both commercially available CILs and a new series of CILs based on the same innovative inherent chiral approach developed in our laboratories.

With the contribution of Fondazione Cariplo, grant no. 2011-1851.

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ELE-P3

Contributo Ritirato

M. Battaglia[a], *R. Inguanta*[a], *S. Piazza*[a], *C. Sunseri*[a]

a Laboratorio di Chimica Fisica Applicata, Dipartimento di Ingegneria Chimica Gestionale Informatica Meccanica, Università di Palermo, Viale delle Scienze - 90128 Palermo (Italy)

mirko.battaglia@unipa.it

Recently, quaternary compounds, like $CuInGaSe_2$ (CIGS) and Cu_2ZnSnS_4 (CZTS), have been intensively investigated as alternative PV materials due to their very interesting properties. In fact, CIGS and CZTS are semiconductor compounds with a high absorption coefficient values and a direct band-gap that can be tuned at a value of about 1.5 eV by controlling their composition. These properties make CIGS and CZTS thin films excellent PV materials. Theoretical calculations have shown that conversion efficiency as high as 32% is possible for CIGS and CZTS layer of several micrometers.

Electrodeposition is one of the promising technologies for fabrication of low-cost photovoltaic absorber because of the low-cost equipment, scalability to a large scale and good control of composition and morphology. For these reasons, we have examined single step electrodeposition syntheses into polycarbonate membranes in order to obtain nanowires (NWs) of CIGS and CZTS. With this method, all of four components are deposited simultaneously from the working solutions. After extensive investigations we have found the best conditions for the deposition of elements having different standard electrochemical potential in a confined ambient and in the presence of H_2 evolution.

Characterization of the nanowires was performed by SEM, EDS, XRD, and Raman spectroscopy. Their photoelectrochemical behaviour under illumination was also investigated.

This work was partially funded by the European Community through the "Programma Operativo Nazionale Ricerca e Competitività 2007-2013" (PON01_01725 and PON02_00355 Projects).

ELE-P4

Electrodes/Electrolyte interfaces in the presence of a Si-modified photopolymer electrolyte: application in DSSCs

Federico Bella[a,b], *Adriano Sacco*[a], *Stefano De La Pierre*[b], *Micaela Castellino*[a], *Stefano Bianco*[a], *Roberta Bongiovanni*[b]

a Center for Space Human Robotics @Polito, Istituto Italiano di Tecnologia, Corso Trento 21, 10129 Torino, Italia
b Dipartimento di Scienza Applicata e Tecnologia - DISAT, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italia

federico.bella@polito.it

The conversion of solar energy by photovoltaic effect is the most quoted reality in the world of renewable resources. As a feasible option for photovoltaic technology to meet the growing energy demand, dye-sensitized solar cells (DSSCs) have attracted much attention due to their low cost, ease of fabrication and good performance.

We have recently proposed polymer electrolyte membranes as a promising strategy to solve the poor long-term stability of standard liquid-state DSSCs [1-2]. Membranes were prepared by a rapid, energy-saving and environment friendly technique of light-induced polymerization, that can find an appropriate location also in the nascent industrial production plants of third generation photovoltaic cells.

In this work, we propose a combined (photo)electrochemical/XPS investigation of the TiO_2- and Pt-based electrodes interfaces with a polymer electrolyte membrane whose surface composition has been enriched with a Si-based monomer. The improvement of photovoltaic performance and long-term stability will be showed, emphasizing the positive effect of the gradient-tailored composition of the photopolymer electrolyte.

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ELE-P5

Towards flexible DSSCs combining vertically aligned TiO_2 nanotubes array and UV-cured polymer networks

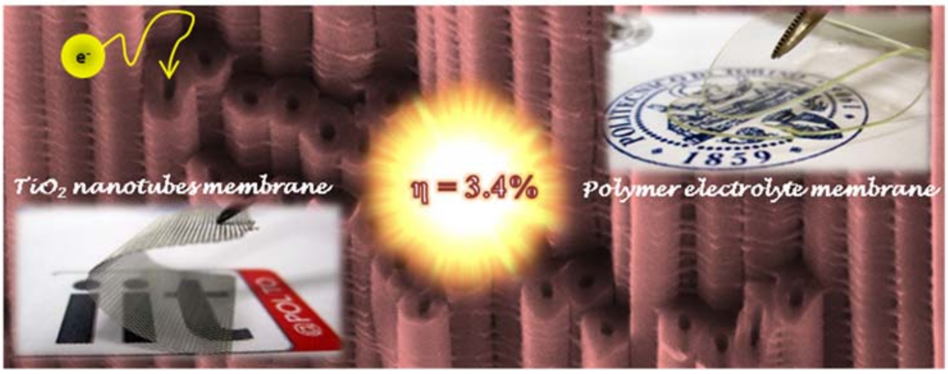
Federico Bella[a,b], *Andrea Lamberti*[b], *Adriano Sacco*[a], *Angelica Chiodoni*[a], *Stefano Bianco*[a], *Roberta Bongiovanni*[b]

a Center for Space Human Robotics @Polito, Istituto Italiano di Tecnologia, Corso Trento 21, 10129 Torino, Italia
b Dipartimento di Scienza Applicata e Tecnologia - DISAT, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italia

federico.bella@polito.it

One of the possible applications of dye-sensitized solar cells (DSSCs) is the biasing of low-power portable devices. In this framework, the cells should be flexible and adaptable to complex shapes. Therefore, it is necessary to prepare suitable electrodic and electrolytic materials.

Here we report for the first time the combination of a methacrylic crosslinked polymer electrolyte membrane (whose polymeric network has been deeply characterized by charge-transfer measurements and dynamo-mechanical analysis) and vertically oriented TiO_2 nanotubes grown by anodic oxidation of flexible Ti mesh in order to fabricate a flexible and transparent DSSC. The photovoltaic behavior was exhaustively investigated by electrical measurements and impedance spectroscopy. To the state-of-the-art, the appropriate selection and optimization of all the materials allowed us to obtain the most efficient quasi-solid flexible DSSC ever produced.



ELE-P6

Physico-chemical characterization of passive films on 316L stainless steel grown in high temperature water

F. Di Franco[a], *M. Santamaria*[a], *F. Di Quarto*[a], *P. Marcus*[b]

a Electrochemical Materials Science Laboratory, Faculty of Engineering, University of Palermo, Viale delle Scienze, 90128 Palermo, Italy

b Laboratoire de Physico-Chimie des Surfaces, CNRS - Chimie ParisTech, Ecole Nationale Supérieure de Chimie de Paris, France.

francesco.difranco@unipa.it

One of the major materials challenge for continued safe, reliable and cost-effective utilization of water-cooled nuclear reactors for electricity production is development of improved understanding of the synergistic fundamental mechanisms responsible for corrosion and stress corrosion cracking degradation of austenitic steels and nickel base alloys [1]. A key factor in determining the corrosion resistance of the materials is played by the properties of the passive films grown on the employed stainless steel during operating conditions. In the last decades, photoelectrochemical techniques have been employed increasingly for investigating thin photo-conducting surface films and corrosion layers on metals and alloys. In this work, we studied the solid state properties of oxide layers grown on 316L stainless steel in high temperature water, exposing the specimens to Pressurized Water Reactor (PWR) primary water at $P = 60$ bar for different immersion times (from 2 min to 100 hours). X-Ray Photoelectron Spectroscopy (XPS) analysis was performed to monitor the change of film composition due the selective dissolution of passive film constituents. A photoelectrochemical investigation was performed in order to estimate the band gap, E_g of the oxide layers as a function of the immersion time. The dependence of E_g on the immersion time has been rationalized considering changes of the passive layer composition.

[1] S.J. Zinkle, G.S. Was, Acta Mater, 61, (2013), 735.

ELE-P7

Effect of the iron doping on the crystal structure and electrochemical performances of $LiCoPO_4$

D. Di Lecce [a], *S. Brutti*[b], *S. Panero* [a]

a Dipartimento di Chimica, "Sapienza" Università di Roma La Sa, Piazzale Aldo Moro 5, 00185, Roma, Italy
b Dipartimento di Scienze, Università della Basilicata, Via Nazario Sauro 85, 85100 Potenza, Italy

daniele.dilecce@uniroma1.it

Current research in lithium-ion battery field focuses on the improvement of energy density and power performances. One way to increase the battery energy is the use of high voltage cathode materials with a large charge capacity and cycling capability. The $LiCoPO_4$ olivine is an interesting candidate as high-voltage cathode for lithium cells due to its high working potential cells (4.8 V vs. Li/Li^+), still within the working limits of the carbonate-based liquid electrolytes, its flat voltage profile and a theoretical capacity of about 167 mAh g^{-1}. However the poor electronic conductivity and the low Li-ion diffusion coefficient limit its practical application [1].
Herein we present our recent results about the study of the synthesis of lithium cobalt phosphate materials and the effect of the iron doping on its structural features and electrochemical properties in lithium cell. In particular X-ray diffraction experiments have been carried out at the MCX beamline in the ELETTRA facility in order to elucidate the role played by iron doping on the lattice structure and local ordering of the cation sublattice. Furthermore a careful analysis of the performances in lithium cells have been carried out by comparing materials prepared in different experimental conditions with and without iron doping, in order to decouple the concurrent effects that drive the ability of this material to reversibly cycle lithium (e.g. particle size, lattice disorder, iron doping).

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ELE-P8

$Py_{14}TFSI$ added PEG500LiTSFI electrolyte for advanced lithium batteries

Giuseppe Antonio Elia[a], *Bruno Scrosati*[b]. *Jusef Hassoun*[a]

a Department of Chemistry, Sapienza University, Piazzale Aldo Moro 5, 00185 Rome
b Italian institute of Technology, Genova, Italy

giuseppeantonio.elia@uniroma1.it

This work reports the behavior of an electrolyte based on poly(ethyleneglycol)500-dimethylether (PEG500) , and a 1-Methyl-4-Butyl-Bis-(trifluoromethanesulfonyl)-Imide ($Py_{14}TFSI$) ionic liquid and lithium-bis-(trifluoromethanesulfonyl)-imide (LiTFSI) for application in safe lithium batteries. The high molecular weight and a high relative viscosity of the electrolyte leaded to a low vapor pressure and an excellent thermal stability [1]. The addition of the $Py_{14}TFSI$ ionic liquid induced a further increase of thermal stability, with higher decomposition temperature, and to a freezing point depression, as resulting by thermal gravimetric analysis and differential scanning calorimetry, respectively. All mixtures show a wide electrochemical window extending up 4.7 V vs. Lithium and, as well, an excellent reversible lithium stripping/deposition behavior. Furthermore, the electrolyte has shown depressed electrochemical aluminum corrosion by LiTFSI, even at the higher temperatures, compared to the common carbonate electrolytes containing LiTFSI salt. See table and figure reporting the electrolytes characteristics

Solvent	$Py_{1,4}TFSI$	Salt (1 mol/kg)	σ [mS/cm] at RT	E_A [eV]	t_{Li+}
PEG500DME	0 %	LiTFSI	0.5 ± 0.1	0.272 ± 0.024	0.47
PEG500DME	10 %	LiTFSI	0.52 ± 0.104	0.286 ± 0.011	0.39
PEG500DME	30 %	LiTFSI	0.757 ± 0.151	0.274 ± 0.024	0.19

Table: prepared electrolytes

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ELE-P9

A new way to deposit Carbon Nanotubes: Application to o-toluidine Determination

Luigi Falciola[a], Valentina Pifferi[a], Andrea Mardegan[b], Ligia Maria Moretto[c]

a Università degli Studi di Milano, Dipartimento di Chimica, via Golgi 19, 20133, Milano (MI)
b Veneto Nanotech, via delle Industrie 5, 30175 Marghera (VE)
c Università Ca' Foscari di Venezia, Dipartimento di Scienze Molecolari e Nanosistemi, Santa Marta 2137, 30123 Venezia (VE)

luigi.falciola@unimi.it

Pyrolized Photoresist Carbon Electrodes (PPCEs) are fabricated by photolithographic micro-fabrication and pyrolysis of an epoxy-based photoresist named SU-8 [1]. After the electrochemical characterization of these electrodes as a function of the pyrolysis time and SU-8 film thickness, the modification of the PPCE with carbon nanotubes (CNT) is proposed in order to enhance the analytical potentialities of PPCE, improving sensitivity and lowering detection limits, as well as permitting the production of disposable and low cost sensors.

Carbon nanotubes are usually dispersed through ultrasonication and diluted in an organic solvent, such as DMF. Cast coating is the most commonly used deposition technique due to its fast and simple procedure, however it lacks in reproducibility and uniformity. A new technique based on two-steps approach has been developed. CNT are first dispersed in a liquid medium and then deposited onto the surface by spray-coating technique.

These devices have been completely characterized and employed for the development of a sensor for the detection of o-toluidine, an organic carcinogenic synthetic pollutant, mainly used as an intermediate in production of azo-dyes. In particular, using the optimized electrode configuration, o-toluidine was detected by Linear Sweep Voltammetry in the range 0.5-5 ppm, obtaining a limit of detection of 89 ppb. The new devices are competitive with respect to other carbon-based electrodes, which present problems of fouling.

[1] S. Ranganathan, R. McCreery, S. M. Majji, M. Madou, J. Electrochem. Soc. 147 (2000) 277.

ELE-P10

Fast and well-controlled atom transfer radical polymerization in water

Marco Fantin, Abdirisak A. Isse, Armando Gennaro

Dipartimento di Scienze Chimiche, Università degli Studi di Padova
Via Marzolo 1, 35131 Padova, Italia

marco.fantin.1@studenti.unipd.it

Aqueous controlled radical polymerization is a powerful technique for the synthesis of well-defined water-soluble polymers, for potential biomedical and pharmaceutical applications.[1] Unfortunately, however, a poor level of control on polymer growth has so far limited the extensive application of atom transfer radical polymerization (ATRP) in water.

The mechanism of ATRP in aprotic solvents involves a well-known equilibrium markedly shifted towards the left (Fig. 1), which allows suppression of radical-radical termination reactions. On the contrary, in aqueous environments, the catalysts are highly active (high k_{act} and $K_{ATRP} \sim 1$) and are involved in a series of competitive reactions that may undermine their efficiency.

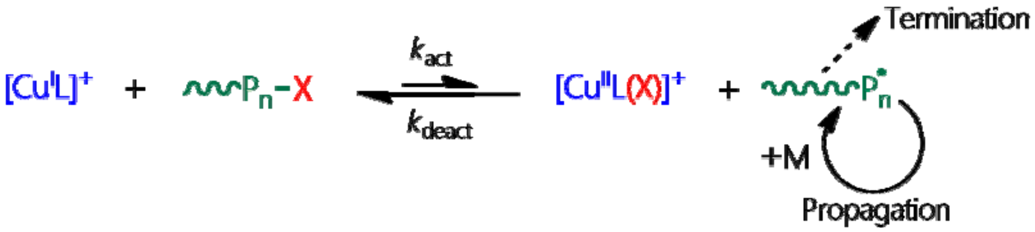

Fig. 1. ATRP mechanism.

To gain control on polymer growth in water, the following aspects must be taken into account: accurate pH control, proper [X$^-$], use of ligands that stabilize Cu^I and suitable polymerization initiators. All these parameters, together with the applied potential in electrochemically mediated ATRP (*e*ATRP)[2], need to be appropriately adjusted for each monomer and catalyst. Overall the results obtained in this study allow defining a set of guidelines that have been used to conduct several fast and efficient aqueous *e*ATRP reactions.

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ELE-P11

Atom transfer radical polymerization in the presence of metallic copper: Is activation due to Cu^0 or Cu^I?

Francesca Lorandi, Marco Fantin, Abdirisak A. Isse, Armando Gennaro

Dipartimento di Scienze Chimiche, Università degli Studi di Padova
Via Marzolo 1, 35131 Padova, Italia

marco.fantin.1@studenti.unipd.it

Atom transfer radical polymerization (ATRP) is a versatile and mild method of synthesis of polymers with good control over the molecular weight and architecture. The process is catalyzed by transition metal complexes and the mechanism is well understood. Recently, use of Cu^0/ligand as catalyst has become very popular, sparking however a vigorous mechanistic debate over the role of Cu^0. Percec et al.[1] propose a mechanism named SET-LRP, based on exclusive activation by Cu^0 and deactivation by Cu^{II}, whereas Matyjaszewski and co-workers[2] propose a reaction mechanism, named SARA ATRP, in which Cu^0 plays the role of a supplemental activator and reducing agent for the conversion of Cu^{II} to Cu^I, which is the principal activator (Fig. 1).

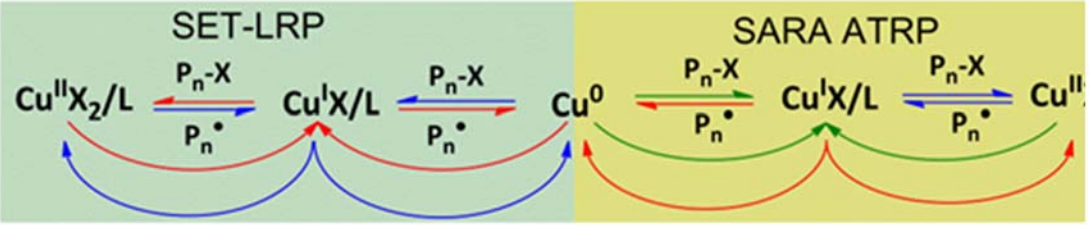

Fig.1. SET-LRP vs. SARA ATRP; arrow colors indicate degree of contribution: main (blue), minor (green), negligible (red).

One of the fundamental differences between the two mechanisms is whether Cu^I principally undergoes disproportionation or reacts with the initiator P_nX. This study was performed to provide a clear answer to this question and it will be shown that under various experimental conditions activation is much faster than disproportionation.

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ELE-P12

A sodium-ion battery based on a P2-$Na_{0.5}Ni_{0.22}Fe_{0.11}Mn_{0.66}O_2$ cathode and a nanostructured Sb-C anode in a ionic liquid based electrolyte

Ivana Hasa[a], *Stefano Passerini*[b], *Bruno Scrosati*[c], *Jusef Hassoun*[a]

a Department of Chemistry, Sapienza University, Piazzale Aldo Moro 5, 00185, Rome, Italy
b Helmholtz-Institut, Karlsruhe Institute of Technology, Albert-Einstein-Allee 11,89081, Ulm, Germany
c Italian Institute of Technology, Via Morego, 30 16163 Genova, Italy

ivana.hasa@uniroma1.it

Na-based storage systems working at room-temperature have recently gained the interest of the research community thanks to the large availability and low cost of sodium.[1,2] The real challenge in the sodium-based battery field is represented by the substitution of the extremely reactive metallic sodium anode that represents a serious issue to face in order to increase the intrinsic safety of the sodium cells. To further improve the safety level of sodium cells, we propose here the substitution of the more common organic-carbonate based electrolytes with an ionic liquid-based electrolyte characterized by higher thermal stability, lower volatility and non flammability.[3] Here we propose the study of a sodium-ion battery based on a P2-type, $Na_{0.5}Ni_{0.22}Fe_{0.11}Mn_{0.66}O_2$ transition metal layered oxide cathode material and a nanostructured Sb-C alloying anode in a 0.2m NaTFSI-Py_{14}TFSI electrolyte. The improved morphology of the electrode materials here investigated ensure an enhanced electrochemical behavior in terms of cycle stability and delivered capacity.

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ELE-P13

Use of Electrochemical Impedance Spectroscopy for membrane and interface characterization

Diego Messana[a,b], *Enrico Drioil*[a,b], *Enrica Fontananova*[a]

[a]*Institute on Membrane Technology of the National Research Council of Italy (ITM-CNR), Via P. Bucci, cubo 17/C, at University of Calabria, 87036 Rende (CS), Italy*
[b]*Department of Environmental Engineering and Land and Chemical Engineering, University of Calabria, 87036 Rende (CS), Italy*

diego.messana.ded@gmail.com

One of the major concerns of membranologists working with electro-membranes processes (e.g. electrodialysis, reverse electrodialysis, fuel cells, capacitive deionization) is the depth knowledge of the membrane electrical properties. It is well known that at the interfaces between a solid ionic conductor and a liquid electrolyte, physical and electrical properties change suddenly because of an heterogeneous charges distribution (polarization), which reduces the overall electrical conductivity of the system .
The Electrochemical Impedance Spectroscopy (EIS) is a powerful technique for measuring the ability to oppose the flow of electric current in the bulk and interfacial regions of solid and liquid electrolyte materials, as a function of the frequency [2]. During an EIS experiment a small sine wave voltage or current excitation is applied to a sample while the amplitude and phase relationship of the corresponding current or voltage signal is monitored, over a frequency range. In this work several IEMs were characterized by EIS with various electrolyte solutions in order to investigate the effect of the electrolyte solution composition and concentration on membrane and interface electrical properties. Moreover, apparent permselectivity was calculated using the static membrane potential measurement.

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ELE-P14

PtY on Mesoporous Carbon as New Catalysts for Oxygen Reduction Reaction

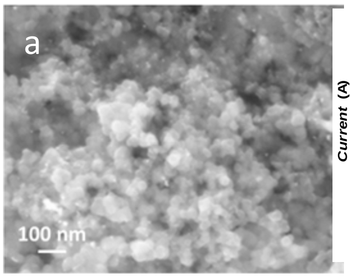
Valentina Perazzolo,[a] *Christian Durante,*[a] *Emilia Grądzka,*[b]
Marco Favaro,[a] *Gaetano Granozzi,*[a] *Armando Gennaro,*[a]

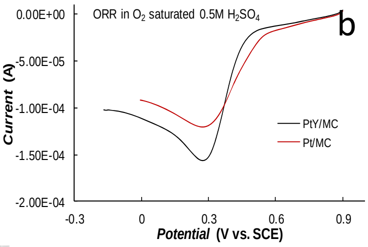
a Dept. of Chemical Sciences, University of Padova, Via Marzolo 1, 35131 Padova Italy
b Institute of Chemistry, University of Bialystok, Hurtowa 1, 15-399 Bialystok, Poland

perazzolo.valentina@gmail.com

Pt-based catalysts are widely used and studied in the oxygen reduction reaction (ORR). Recently, preparation of Pt-based bimetallic systems has attracted considerable attention since the amount of Pt could be reduced while the catalytic activity and stability could be maintained or even enhanced due to the so called "ligand effect" and "geometric effect". According to Nørskov's computational investigations, the alloy Pt_3Y is one of the most promising materials for ORR.[1]

In this paper, we report the synthesis and characterization of nanoparticles (NPs) of PtY alloys supported on mesoporous carbon and nitrogen-doped mesoporous carbon (N-MC). The NPs were prepared from appropriate precursor salts in a tubular furnace under H_2 stream. The synthesis gave small PtY NPs on the surface of MC (Fig. a). The electrochemical properties of PtY/MC and PtY/N-MC thin films were investigated with a special attention to their catalytic properties. The first results in ORR studies showed that PtY/MC exhibits a slightly higher catalytic activity for oxygen reduction as compared to Pt/MC (Fig. b). The influence of the stoichiometry and type of MC on the catalytic properties of PtY alloys were also investigated.





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ELE-P15

PYR_{14}TFSI-LiTFSI as electrolyte for lithium ion batteries

U. Ulissi[1], M. Agostini[1], Y. Aihara[2], B. Scrosati[3], J. Hassoun[1]

[1] "Sapienza Università di Roma", Chemistry Dep., P.le Aldo Moro 5 00185 Rome
[2] Samsung Yokohama Research Institute, Japan
[3] Italian Institute of Technology, Genova, Italy

ulderico.ulissi@uniroma1.it

The safety issue is a matter of great concern, effectively slowing down the wide diffusion of lithium-ion batteries. Unwanted, dangerous side reactions are mainly associated with the liquid organic electrolytes. [1-2] These exothermic side reactions can easily lead to inconvenient events, as the thermal runaway favors fire or, even worse, explosions. Ionic liquids, with a very low flammability and volatility and a high thermal and electrochemical stability [1-2] can be considered as the solvents of choice for next generation, safe, lithium-ion batteries. Here we report a battery using both uncoated $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) and a surface stabilized, Li_2O-ZrO_2 coated $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (Figure 1) cathode material, in a Pyr_{14}TFSI-LiTFSI electrolyte solution. ZrO_2 can effectively stabilize the structure of layered materials [3], while Li_2O is used to facilitate lithium diffusion at the interface [4]. Finally, a novel full cell employing a high capacity tin carbon composite anode [5] , i.e. SnC, and the selected NCA cathode, has been prepared and tested (Figure 2).

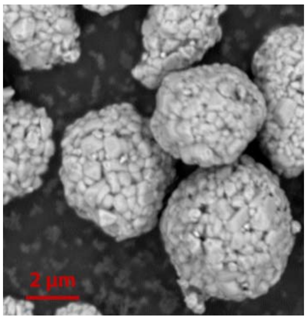

Fig.1 SEM image of coated NCA

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ELE-P16

Electrochemical Investigations of Heteroarylethylene Class

Lucia Viglianti[a], *Alessandro Bolzoni*[a], *Andrea Figini*[a], *Patrizia R. Mussini*[a]
Clara Baldoli[b], *Emanuela Licandro*[a], *Stefano Maiorana*[a]

[a]*Dipartimento di Chimica, Università degli Studi di Milano, via Golgi 19, 20133 Milano, Italy,*
[b]*CNR ISTM, via Golgi 19, 20133 Milano, Italy*

lucia.viglianti@unimi.it

Well-known simple molecules such as diphenylethylene (DPE), dithienylethylene (DTE), and tetraphenylethylene (TPE) show interesting optical properties; for instance, TPE has been extensively studied because of its tunable luminescent properties and some of its derivatives show aggregation-induced emission (AIE). The corresponding thiophene based system: tetra-(2-thienyl)-ethylene (TTE), also giving AIE, has not been as widely studied as TPE, but it and the peculiar electronic properties of the thiophene ring make it much more appealing than TPE for applications in photovoltaics and optoelectronics, both in itself and as building block in wider π-conjugated systems. A few TTE derivatives had been reported in Literature, but no systematic investigation of the structural and electronic features of the thienylethylene class was available. Extension of the study to other heteroaromatic rings, such as the furane based ones, was also overdue. To fill these gaps, we have performed an electrochemical study, supported by spectroscopic experiments, on the aryl- and heteroarylethylene molecules shown in Figure, most of them new, synthesized by us according to an advantageous synthetic pathway. [1]

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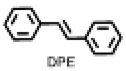
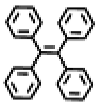
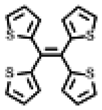
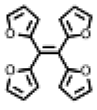

DPE


TPE


DTE


TTE


DFE


TFE

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ELE-P17

Contributo Ritirato

Etica e Chimica

Poster

ETI-P1

Competenza chimica, etica professionale e correttezza di informazione

L. Campanella, V. Balzani, L. Dei, C. Della Volpe, V. Domenici, F. Dondi, C. Franchini, M. Guidotti, F. Trifirò, M. Venturi

Gruppo di Lavoro Etica e Chimica, Società Chimica Italiana

luigi.campanella@uniroma1.it

La sperimentazione animale è ancora riconosciuta come metodica essenziale ai fini della valutazione di tossicità. L´UE ne ha però limitato l´applicazione. Alla chimica sono riconosciute da tutti le potenziali capacità di proporre metodi alternativi. E´ un impegno etico per i chimici impegnarsi in questa direzione. All´interno della SCI sono una decina i gruppi di ricerca che proprio spinti da motivazioni etiche si sono impegnati in questa direzione.

Si calcola che circa il 3% del territorio nazionale debba essere bonificato da residui di precedenti insediamenti industriali. L´etica ambientale ha stimolato la Società Chimica Italiana a proporsi come responsabile scientifico per l´applicazione di metodi innovativi sostenibili sul piano del loro impatto e dei loro costi, rinunciando quindi esplicitamente a qualunque fine speculativo.

Particolare attenzione verrà dedicata all'analisi della esagerata attenzione dei media per tutto ciò che riguarda la salute e il benessere fisico, anche attraverso una corretta alimentazione, rappresenta una delle esigenze più diffuse e di conseguenza un pericolo per spinte commerciali e consumistiche a volte non supportate da sufficienti evidenze scientifiche. E' evidente che in tali argomenti vi sono implicazioni di etica professionale per tutte i professionisti coinvolti, dalla sintesi della nuova molecola da immettere sul mercato al suo controllo chimico analitico, tossicologico e farmacologico. Nel poster verranno valutati e discussi aspetti etico-professionale su farmaci con meccanismo di azione simile, ma caratteristiche chimico-fisiche e farmacocinetiche differenti, o proprietà salutistiche attribuite a prodotti naturali che invece sarebbero da caratterizzare a livello molecolare per definirne proprietà e variazioni metaboliche di ciascun componente.

ETI-P2

Chimica ed Etica nella Formazione

L. Campanella, V. Balzani, L. Dei, C. Della Volpe, V. Domenici, F. Dondi, C. Franchini, M. Guidotti, F. Trifirò, M. Venturi

Gruppo di Lavoro Etica e Chimica, Società Chimica Italiana

luigi.campanella@uniroma1.it

La chimica dovrebbe far parte del bagaglio culturale di ogni cittadino perché costituisce una parte importante della scienza ed è protagonista dello sviluppo tecnologico. È necessario, quindi, gettare ponti fra la chimica e la società e stabilire una relazione positiva fra la chimica e la gente.

Come tutte le scienze, anche la chimica può essere usata male e, in effetti, questo è accaduto e ha causato danni all'uomo e all'ambiente. Oggi un uso incosciente o semplicemente non accurato della chimica, oltre ad essere sanzionato dalle autorità, è moralmente intollerabile. Questo concetto deve farsi strada anzitutto fra i chimici che, oltre a condividerlo, devono osservarlo nella loro attività, dimostrando un senso di rispetto ed una visione di servizio verso il pianeta che ci ospita e le persone che lo abitano. Solo così i chimici potranno illustrare a testa alta i benefici che la chimica ha portato e che ancora porterà per un vero progresso umano.

Nelle università, a tutti i livelli di formazione, l'insegnamento teorico e sperimentale della chimica dovrebbe essere accompagnato da riflessioni e discussioni sugli scopi della ricerca e, in particolare, sulla dualità che caratterizza la Chimica, affrontando alcuni principi generali e imprescindibili: la scienza va usata per la pace e non per la guerra, per diminuire e non per aumentare le già intollerabili disuguaglianze sociali, per colmare e non per accentuare le differenze tecnologiche e culturali fra le varie nazioni, per armonizzare l'uso delle risorse e, in definitiva, per custodire il pianeta Terra che ci è stato dato in prestito dalle prossime generazioni, come recita un antico proverbio africano.

Nelle scuole, ancora una volta a qualsiasi livello di formazione, la chimica deve essere presentata agli insegnanti e agli studenti come la scienza che, se ben usata, può giocare un ruolo fondamentale per garantire la sostenibilità ecologica e sociale contribuendo a risolvere i grandi problemi planetari: cibo, salute, energia e ambiente.

ETI-P3

Dalle armi chimiche alle convenzioni internazionali per il controllo delle sostanze ad elevata tossicità

L. Campanella, V. Balzani, L. Dei, C. Della Volpe, V. Domenici, F. Dondi, C. Franchini, M. Guidotti, F. Trifirò, M. Venturi

Gruppo di Lavoro Etica e Chimica, Società Chimica Italiana

luigi.campanella@uniroma1.it

Così come nel campo della tutela dell'ecosistema si è gradualmente passati da una Chimica noncurante dell'ambiente, ad una Chimica del disinquinamento e, in seguito, ad una Chimica sostenibile, per "prevenire, anziché curare", allo stesso modo, nell'ambito delle sostanze chimiche altamente tossiche, si sta passando da uno studio delle contromisure per minimizzare i danni causati da un uso deliberato di aggressivi chimici bellici, ad una valutazione della cosiddetta *Chimica duale* (*dual Chemistry*), per studiare anticipatamente i potenziali sviluppi positivi e negativi di composti nuovi o poco conosciuti.

Da questo principio è scaturita una serie di protocolli e convenzioni impiegati da organismi sopranazionali, come l'Organizzazione per la Proibizione delle Armi Chimiche, (con sede all'Aia per l'attuazione della Convenzione internazionale sul bando delle armi chimiche, CWC). Si ha così una periodica revisione delle liste di tutte le sostanze chimiche proibite o fortemente regolamentate, a causa del loro potenziale uso come arma chimica, per far sì che gli elenchi siano aperti e aggiornabili, in funzione dei nuovi composti chimici sintetizzati o delle nuove linee-guida dettate dai vari enti di controllo nazionali o dal diritto internazionale. In tal modo, queste convenzioni non invecchiano, ma rimangono al passo con i tempi e possono beneficiare di un continuo benefico apporto della comunità scientifica di tutto il mondo e di una sorta di valutazione del ciclo di vita "etico" di una nuova molecola o di un nuovo prodotto.

La Società Chimica Italiana, grazie alla sua natura multi- e interdisciplinare, è un importante catalizzatore di contatti tra il mondo accademico, l'industria, gli enti di ricerca, le scuole, le istituzioni e gli organismi nazionali e internazionali preposti al controllo, alla regolamentazione e alla sviluppo di nuove linee-guida per un impiego responsabile e sicuro della Chimica.

Spettrometria di Massa

Keynote

MAS-K1

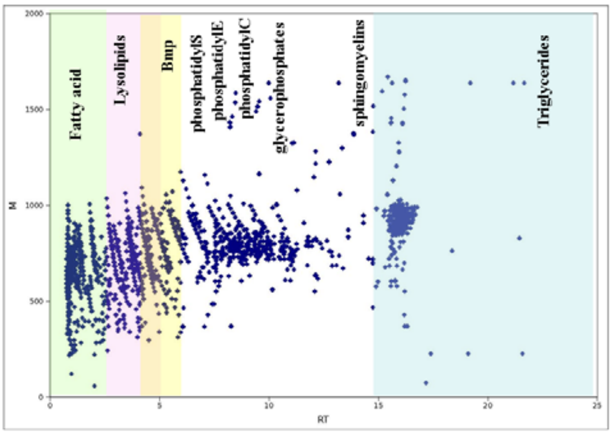
Lipid*omics* or Randomo*mics*?

Gabriele Cruciani[a], *Laura Goracci*[a], *Roberto Pellegrino*[a], *Aurora Valeri*[a]

a Dipartimento di Chimica, Biologia e Biotecnologia, Università di Perugia, Via Elce di Sotto 8 , 06123, Perugia, Italy

gabriele.cruciani@unipg.it

Lipidomics is a branch of metabolomics and is the study of pathways and networks of cellular lipids used to describe the complete lipid profile within a cell. Lipidomic research is mainly aimed to find lipid fingerprinting and lipid biomarkers, and has been applied to study a number on health-related issues like artheriosclerosis, diabetes, obesity, Alzheimer, allergies, rheumatoid arthritis, systemic lupus erythematous, autoimmune/inflammatory diseases and leukodystrophy.



Lipidomics is a ‘difficult’ omics since the analysis of the lipid mixtures is more complex than the analysis of other mixtures. One of the main reasons for this is the structural similarity of the molecular species belonging to same lipid class, which makes their separation very difficult. Another reason is that the abundances of different lipids can vary of several orders of magnitude which pose problems in their detection.

Multivariate Statistical Analysis can help to increase the signal to noise ratio in several aspects of lipidomic analyses, but one should be aware that the results of the statistical models will strongly depend on the experimental procedures, on the biological process (like metabolism), on the experimental design and on the spectral data superposition. When one or more of these aspects are ignored, results may be misleading and useless.

MAS-K2

Comprehensive Metabolomics Investigations by FTICR High Resolution Mass Spectrometry

Giuliana Bianco

Dipartimento di Scienze, Università della Basilicata, Potenza, Italy.

giuliana.bianco@unibas.it

Metabolomics aims at the qualitative and quantitative analysis of wide arrays of metabolites in biological samples. Taken all together, these numerous analytes possess diverse physico-chemical properties (i.e., MW and polarity) and usually occur at very different abundance levels. Consequently, comprehensive metabolomics investigations are really challenging for analytical chemistry, especially when untargeted metabolites are involved. Mass spectrometry (MS) is a dynamically emerging field and numerous MS-based platforms have been currently developed for metabolomic applications. Valuable information can be obtained by Fourier-transform ion cyclotron resonance MS (FTICR-MS) due to its ultra-high resolution (100,000–1,000,000) and high mass accuracy (< 1 ppm), which allows determination of elemental composition. Moreover, when high-resolution MS^n experiments can be performed, detailed molecular structure information are allowed [1]. Liquid chromatography (LC) in conjunction high resolution MS is required in order to overcome the drawbacks of directly injecting complex samples, as reduced ion suppression caused by coeluting compounds. For example, the structure of *N*-acyl homoserine lactones, representing an important class of bacterial metabolites, was identified by LC with electrospray ionization (ESI) and FTICR-MS accurate mass measurements [2]. In this presentation, the tremendous LC-ESI-FTICR-MS performances to investigate the occurrence of metabolites in plant and biological sample, is presented [3].

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MAS-K3

Fingerprints: "the insider mole" amongst offenders

S. Francese

Biomedical research Centre, Sheffield Hallam University, Howard Street, S1 1WW, Sheffield, UK

s.francese@shu.ac.uk

Fingerprints still remain one of the most powerful means of biometric identification. However, ridge pattern physical information may occasionally be insufficient to match a suspect with a record in the National database; such instances are partial, distorted or smudged marks, fingertips' extensive scarring/abrasion or record absence of the suspect prints.

In all of these situations it is very desirable to have a technology able to provide additional intelligence from a fingermark exploiting its endogenous and exogenous chemistry. In recent years Matrix Assisted Laser Desorption Ionisation Mass Spectrometry Imaging (MALDI MSI) has proven its ability to provide multiple images of the same fingermark simultaneous with additional intelligence[1]. The opportunity to detect chemical information (aminoacids, fatty acids, peptides, proteins, drugs, toiletry products, condom lubricants as a few examples) could provide investigative leads on the suspect's lifestyle and activity prior to leaving the mark. In a recent publication, for example, we demonstrate that it is possible to determine the sex of the donor through detection of peptides from their fingermark with high level of accuracy[5].

Here, the pioneering use and rapid developments of MALDI MS and MSI for the analysis of latent marks is presented along insights into the research carried out at crime scenes in collaboration with the West Yorkshire Police.

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Spettrometria di Massa

Oral

MAS-O1

A rapid centrifugal elution procedure for reliable MALDI-TOF profiling of gingival crevicular fluid

Rosa Terracciano, Mariaimmacolata Preianò, Daniela Falcone, Giuseppina Maggisano, Sergio Paduano, Rocco Savino

Dipartimento di Scienze della Salute, Università di Catanzaro, Via , 88100, Catanzaro, Italia

terracciano@unicz.it

Gingival crevicular fluid (GCF) has captured an increasing interest for its potential diagnostic and prognostic value in periodontal diseases [1]. Comparative MALDI-TOF MS analysis of GCF between healthy and periodontal diseases subjects may help in monitoring changes of expression patterns of disease specific peptides and proteins. However, the sub-microliter volumes of GCF obtained by healthy subjects limit significantly proteomic analysis. In this study, we describe a rapid and standardized procedure aimed at obtaining reproducible MALDI-TOF MS peptidome profiles from the limited volume of GCF obtained from clinically healthy gingival tissue. We carefully evaluated analytical variables during sample collection and sample processing which could significantly influence the quality and the reproducibility of MALDI-TOF profiles. GCF was collected from the four maxillary incisors in 4 healthy subjects according to two common sampling techniques based on the use of paper strips and paper points in a sampling time of 30 seconds. Peptides and proteins were extracted by centrifugal elution in different acidic solutions with and without protease inhibitor cocktail. MALDI-TOF MS analysis was performed varying matrix composition. We found that MALDI-TOF fingerprints of GCF were most largely influenced by extracting solution and matrix composition. In conclusion, we proposed a rapid and an optimized procedure enabling the generation of qualitative and reproducible MALDI-TOF fingerprints from limited volume of GCF, which could be useful for high-throughput screening for the identification of peptide-biomarkers of gingival inflammation.

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MAS-O2

The Triple TOF: the Right Mass Spectrometer for the Next Generation Proteomics

Dr. Nicolas Fraysse

Business development specialist academia -omics
AB SCIEX
Parc Technopolis, bâtiment Sigma
3 avenue du Canada
F - 91940 Les Ulis
nicolas.fraysse@absciex.com

AB SCIEX, introduced at ASMS conference in June 2014 the new high-resolution mass spectrometer TripleTOF 6600 with SWATH Acquisition 2.0. This is the company's revolutionary solution for quantitative proteomics.

As the emphasis in proteomics research shifts from cataloguing to comprehensive quantitation, the AB SCIEX solution is uniquely positioned, enabling the quantification of thousands of proteins across large sample sets with a level of data completeness and quantitative accuracy and precision that have only been achievable by "gold-standard," targeted MRM in the past.

AB SCIEX SWATH Acquisition incorporates a *data-independent* acquisition strategy and has re-invigorated the proteomics community's interest in comprehensive data by fragmenting every detectable peptide in the sample in order to acquire quantitative MS/MS data. This approach has been shown to increase the capacity of targeted proteomics experiments by over 30-fold and reduce study time by as much as 90 percent. Now, with the increased dynamic range of the TripleTOF 6600 System, researchers can more deeply interrogate complex samples. Combined with innovative variable window acquisition and the SWATH 2.0 processing software, a significant improvement in quantitative results has been realized.

Early experiments comparing TripleTOF 6600 System with SWATH 2.0 to other systems have demonstrated the quantification of up to 90 percent more peptides with CVs of less than 20 percent (a threshold often used to determine good limits of quantitation in LC/MS data).

MAS-O3

Analisi di sialoproteine sieriche di interesse diagnostico mediante spettrometria di massa ad alta risoluzione

Marco Gaspari, Annalisa Nicastri, Shibu Krishnan, Caterina Gabriele, Giovanni Cuda

Proteomics@UMG, Dipartimento di Medicina Sperimentale e Clinica, Università "Magna Græcia" di Catanzaro, Viale Europa, 88100, Catanzaro, Italia

gaspari@unicz.it

La glicosilazione è una modifica post-traduzionale delle proteine di fondamentale importanza nello studio della trasformazione e progressione neoplastica. Il dosaggio di glicoproteine in fluidi biologici, quindi, potrebbe rappresentare una fonte di nuovi marcatori diagnostici di patologie tumorali. Questo lavoro presenta l'analisi di glicoproteine sieriche sialilate ottenuta mediante: (i) digestione triptica della miscela proteica, (ii) arricchimento con biglie al biossido di titanio, (iii) analisi mediante nanocromatografia liquida interfacciata con spettrometria di massa ad alta risoluzione (Q-Exactive).

Un primo esperimento di analisi qualitativa, condotto su sieri provenienti da pazienti affetti da carcinoma del colon o carcinoma della prostata, è stato effettuato utilizzando cromatografia bidimensionale e analisi spettrometrica in *data-dependent mode*. Tale analisi ha permesso di identificare oltre 700 glicopeptidi totali, molti dei quali appartenenti a proteine presenti a bassa concentrazione nel siero (ng/mL) e mai rivelate come glicoforme in fluidi biologici (EGFR, MMP8, MMP9, TGFBI, VGFR3). Questo ricco data set ha permesso di costruire successivamente dei metodi più rapidi, basati su cromatografia a nanoflussi e spettrometria di massa in tandem (*targeted-*MS^2), per il dosaggio *high-throughput* di decine di sialopeptidi di interesse.

In conclusione, l'arricchimento di digeriti triptici provenienti da fluidi biologici mediante biglie al titanio e la successiva analisi mediante *targeted-*MS^2 su uno spettrometro di massa ad alta risoluzione ha consentito il dosaggio rapido di glicoproteine aventi potenziale interesse in diagnostica oncologica.

MAS-O4

Contributo Ritirato

MAS-O5

Determinazione degli elementi in tracce nel cibo per celiaci tramite ICP-MS

Santino Orecchio[a], *Diana Amorello*[a], *Maria Raso*[b] , *Salvatore Barreca*[a], *Claudia Lino, Francesca Di Gaudio*[b]

a Dipartimento di Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche (STEBICEF), Università di Palermo, Viale delle scienze , 90128, Palermo, Italia
b Dipartimento di Biopatologia e Biotecnologie Mediche e Forensi (DiBiMeF) Sez. Chimica e Biochimica Medica Azienda Ospedaliera Universitaria Paolo Giaccone, Università di Palermo, Via del Vespro ,90128,Palermo, Italia

santino.orecchio@unipa.it

Il presente studio descrive un approccio analitico, mediante ICP-MS, per la quantificazione di venti metalli in prodotti senza glutine.
Le più alte concentrazioni di arsenico e molibdeno sono state riscontrate in campioni di spaghetti di riso provenienti dalla Cina (rispettivamente 0.088 e 0.47 mg Kg^{-1}) mentre alte concentrazioni di alcuni metalli (Cu, Ba, Cd, Pb, Hg, Sr e V) sono state rivelate in campioni di pane e grissini prodotti in diversi panifici di Palermo.
Inoltre, al fine di valutare globalmente le concentrazioni di tutti gli analiti nei campioni analizzati, è stato calcolato il Metal Pollution Index che, per alcuni campioni, ha mostrato un possibile rischio chimico per la salute a causa delle conentrazioni di cadmio, piombo e nichel.
Dall’analisi dei dati raccolti è possibile affermare che la concentrazione degli oligo elementi determinati nei campioni sono sotto i limiti tollerabili dalla legge e che il loro apporto all’organismo umano risulta, in alcuni casi, insufficiente se paragonati all’assunzione giornaliera raccomandata dagli organismi internazionali. In dettaglio, i campioni presi in considerazione nel presente studio forniscono dall’1,1 al 53 % della dose giornaliera raccomandata per i metalli essenziali.

MAS-O6

MALDI-IMS in Papillary Thyroid Carcinoma

Gabriele De Sio MS [a], V. Mainini PhD [a], F.o Pagni MD [b], M. Garancini MD [c], V. Giardini MD [c] C. Cusi MS [b], C. Arosi [d], G. Roversi MD[e], C. Chinello PhD [a], P. Caria PhD [f], R. Vanni PhD [f], F. Magni PhD [a]

[a]Department of Health Sciences, Univ. Milano-Bicocca, Monza, Italy
[b]Department of Surgery and Interdisciplinary Medicine, Univ. Milano-Bicocca, Monza, Italy
[c]Department of Surgery, San Gerardo Hospital, Monza, Italy
[d]Consortium of Human Molecular Genetics, Univ. Milano-Bicocca, Monza, Italy
[e]Department of Surgery and Interdisciplinary Medicine, Univ. Milano-Bicocca, Monza, Italy
[f]Department of Biomedical Sciences, Univ. of Cagliari, Cagliari, Italy

g.desio@campus.unimib.it

None of the numerous molecular techniques have been able to resolve the diagnostic problem associated with indeterminate thyroid lesions (THY3). Therefore, we investigated the potential role of MALDI-IMS in detecting new diagnostic targets in papillary thyroid carcinoma (PTC), integrating the genomic profile of the main genes of interest with the proteomic profile generated by MALDI-IMS analysis [2]. Hierarchical cluster analysis (HCA) confirmed that MALDI-IMS can potentially discriminate between benign and malignant thyroid lesions. Moreover, the homologies between follicular variant (fv) of PTC and a nodule histologically classified as uncertain malignant potential (UMP) tumour, highlights that MALDI-IMS is able to identify a PTC even when the classic diagnostic morphological aspects are still unclear and ambiguous as well as distinguish between different architectural patterns associated with distinct histotypes. Additionally, HCA allowed us to group the specimens in base of the BRAF mutation (BRAFV600E vs BRAFwt). Finally, the Principal Component Analysis (PCA) plot also showed that the proteomic profile of hyperplasic nodules was significantly different when compared to both malignant lesions and those with ambiguous morphology, with the latter cases further divided in to BRAFV600E and wtBRAF. The identification of potential targets of interest would provide the possibility to translate the proteomic information into cost-effective tools, such as immunohistochemistry, thus providing the pathologist with a reliable supporting tool in the FNA diagnostic process and improving the preoperative diagnosis of indeterminate thyroid nodules.

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MAS-O7

Multiplexed Molecular Imaging Mass Spectrometry: Analysis of Different Molecular types on a Single Tissue Section

Domenico Taverna[a], *Erin H Seeley*[b], *Jeremy L Norris*[b], *Sindona G*[a], *Caprioli RM*[b]

a Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Via P.Bucci, cubo 12/C ,87036, Arcavacata di Rende, Italy
b Mass Spectrometry Research Center, Vanderbilt University School of Medicine, 465 21st Ave. So., MRB III, 9160 , 37232, Nashville - TN, USA

domenico.taverna@unical.it

Imaging MS (IMS) is a consolidated tool for the analysis of biological and clinical tissue samples allowing intact tissue sections to be directly analyzed.[1] Most on-tissue sample preparation protocols are developed towards a single MS analysis, i.e. focusing only on proteins or phospholipids.[2] We have developed a sample preparation method for multiple IMS analysis with different target classes from a single tissue section. The method was optimized using a single tissue section at 8 µm thickness from a fresh frozen rat kidney. First, lipids IMS sequences are consecutively acquired into the 600-2000 Da mass range and respectively 55 and 68 peaks (S/N > 3) were recorded for positive and negative mode analyses. Many ions were localized within the kidney cortex (e.g.: m/z 703, pos; m/z 668, neg) while others, are instead restricted to the medulla. The third step focuses on proteins within 3-25 kDa mass range. Most of the highly relative intense signals were recorded into the 3-5 kDa range and ion density maps display the distribution of m/z 8713 and 6156 both into the cortex while m/z 7757 is restricted to the medulla. In the fourth step proteins are digested and peptides-focused IMS is carried out within the mass range 500-3000 Da. The localization of most of the peptide signals within the kidney regions closely matches the localization of both proteins and lipids.

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Spettrometria di Massa

Poster

MAS-P1

Comparative survey on nine Pistachio Cultivars grown in Sicily regarding their volatile fraction and fatty acids content.

M.Arnone [a], *R. Damiano*[a], *G. Avellone* [a], *V. Di Stefano*[a], *P. Agozzino*[a]

[a] *Department of Biological Chemical and Pharmaceutical Sciences and Technologies (STEBICEF) Università di Palermo, Via Archirafi 32 90123, Palermo, Italy*

mariafrancesca.arnone@unipa.it

The pistachio (*Pistacia vera L.*) is a nut having peculiar organoleptic characteristics. Iran, the USA, Turkey, Syria, Italy and Greece are the main producers of pistachio nut, and the global production increases steadily.

A tendency for increasing nut consumption is attributed to their nutritional components.

In this study was analyzed the volatile composition and fatty acids contents of nine pistachio cultivars namely *Aegina, Bianca, Bronte, Cerasuola, Iran, Kerman, Larnaka, Rhastig, Sfax* grown in the geographical area of Agrigento in the same soil and climatic conditions.

The volatile components from fresh sample were identified and quantified with HeadSpace Solid-Phase Microextraction (HS-SPME) and gaschromatography coupled with mass spectrometry (GC/MS) using *n-hexanol-*d_{13} as internal standard [1]

The fatty acid composition was determinate as a mixture of Fatty Acid Methyl Esters (FAMEs) after extraction of the oil of pistachio nut using *Welmann* method [2] followed by transesterification with a methanolic solution of potassium hydroxide [3]. The analysis was performed by GC-MS techique.

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MAS-P2

Comparative study on volatile compounds and FAMEs profile from Sicilian monovarietal virgin olive oils.

R. Damiano[a], *M. Arnone* [a], *G. Avellone* [a], *V. Di Stefano*[a], *P. Agozzino*[a], *Rosa Pitonzo*[b]

[a] *Department of Biological Chemical and Pharmaceutical Sciences and Technologies*
Università degli Studi di Palermo, Via Archirafi 32 90123, Palermo, Italy
[b]*Centro Grandi Apparecchiature (CGA)*
Università degli Studi di Palermo, Via F. Marini 14, 90128, Palermo, Italy

roberta.damiano@unipa.it

Monovarietal virgin olive oils (VOO) were collected at two different ripening degree (unripe and ripe). Four Sicilian cultivars were investigated (*Nocellara del Belice*, *Biancolilla*, *Cerasuola* and *Arbequina)* to evaluate the effects of ripeness stages on volatile profile and fatty acid composition. The VOO were obtained by the same extraction method.

The volatile compounds of the monovarietal VOO were identified and quantitatively analyzed by HeadSpace Solid-Phase Micro-Extraction (HS-SPME) technique coupled to GC-MS [1].

The fatty acid composition was determinate after cold transesterification with a methanolic solution of potassium hydroxide by GC-MS analysis as a mixture of Fatty Acid Methyl Esters (FAMEs) [2,3].

In monovarietal olive oils analyzed, the results show that the volatile profile could be considered a parameter for the characterization of an olive oil fingerprint, in according to the varieties and ripeness degree; while no significant differences were found in FAMEs composition.

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ELENCO PARTECIPANTI SCI 2014

Cognome:	Nome:	Ente:	E-Mail:
ABBA'	FABIO	VINAVIL S.P.A.	f.abba@vinavil.it
ABBOTTO	ALESSANDRO	UNIVERSITA' MILANO-BICOCCA	alessandro.abbotto@unimib.it
ACOCELLA	MARIA ROSARIA	UNIVERSITA' DI SALERNO	rosyaco@hotmail.it
ADAMI	GIANPIERO	UNIVERSITA' DI TRIESTE	gadami@units.it
ADORNETTO	GIANLUCA	UNIVERSITA' DI ROMA TOR VERGATA	gianluca.adornetto@uniroma2.it
AGOSTIANO	ANGELA	UNIVERSITA' DI BARI	angela.agostiano@uniba.it
AGOSTINI	MARCO	UNIVERSITA' ROMA LA SAPIENZA	marco.agostini@uniroma1.it
AIELLO	FRANCESCA	UNIVERSITA' DI RENDE	francesca.aiello@unical.it
AIME	SILVIO	UNIVERSITA' DI TORINO	silvio.aime@unito.it
AIROLDI	CRISTINA	UNIVERSITA' DI MILANO-BICOCCA	cristina.airoldi@unimib.it
ALAM	MD MAHBUBUL	UNIVERSITA CA' FOSCARI VENEZIA	mahbubul.alam@unive.it
ALBANESE	ELISA	UNIVERSITA' DI TORINO	elisa.albanese@unito.it
ALBERTO	MARTA ERMINIA	UNIVERSITA' DELLA CALABRIA	marta.alberto@unical.it
ALBINATI	ALBERTO	UNIVERSITA' DI MILANO	alberto.albinati@unimi.it
ALCARO	STEFANO	UNIVERSITA' MAGNA GRAECIA DI CATANZARO	alcaro@unicz.it
ALFEI	SILVANA	UNIVERSITA' DI GENOVA	alfei@difar.unige.it
ALGIERI	CATIA	ITM CNR RENDE	c.algieri@itm.cnr.it
ALHAIQUE	FRANCO	SAPIENZA UNIVERSITA' DI ROMA	franco.alhaique@uniroma1.it
ALIBONI	ANDREA	ENEA-UTRINN-BIO	andrea.aliboni@enea.it
ALLEGRINI	PIETRO	DIPHARMA FRANCIS SRL	pietro.allegrini@dipharma.it
ALMERICO	ANNAMARIA	UNIVERSITA' DI PALERMO	annamaria.almerico@unipa.it
ALTOMARE	COSIMO DAMIANO	UNIVERSITA' DI BARI	cosimodamiano.altomare@uniba.it
ALTOMARE	MARCO	UNIVERSITA' ERLANGEN-NORIMBERGA	
AMADIO	EMANUELE	ITM-CNR PADOVA	emanuele.amadio@unipd.it
AMATO	JUSSARA	UNIVERSITA' DI NAPOLI FEDERICO II	jussara.amato@unina.it
AMBROSIO	LUIGI		
AMINE	AZIZ	UNIVERSITÉ HASSAN II MOHAMMEDIA	azizamine@yahoo.fr
AMODIO	ALESSIA	UNIVERSITA' ROMA TOR VERGATA	alessia.amodio0@gmail.com
ANGIONI	SIMONE		
ANNESE	COSIMO	UNIVERSITA' DI BARI	annese@ba.iccom.cnr.it
ANTONELLI	MARTA LETIZIA	UNIVERSITA' ROMA LA SAPIENZA	marta.antonelli@uniroma1.it
ANTONUCCI	DANIELA	UNIVERSITA' DEL SALENTO	antonucci.daniela@gmail.com
APRILE	SILVIO	UNIVERSITA' PIEMONTE ORIENTALE	silvio.aprile@pharm.unipmn.it
AQUILINI	ELEONORA	LICEO ARTISTICO PISA	ele.aquilini@tin.it
ARDUINI	FABIANA	UNIVERSITA' DI ROMA "TOR V	fabiana.arduini@uniroma2.it
ARGURIO	PIETRO	UNIVERSITA' DELLA CALABRIA	pietro.argurio@unical.it
ARMAROLI	NICOLA	CNR ISOF BOLOGNA	nicola.armaroli@isof.cnr.it
ARMELAO	LIDIA	CNR IENI, PADOVA	lidia.armelao@unipd.it
ARMENTANO	ANTONIO	IZS DELLA PUGLIA E DELLA BASILICATA	a_arm@hotmail.it
ARMENTANO	DONATELLA	UNIVERSITA' DELLA CALABRI	donatella.armentano@unical.it

ARNABOLDI	SERENA	UNIVERSITA' DI MILANO	serena.arnaboldi@unimi.it
ARNESANO	FABIO	UNIVERSITA' DI BARI	fabio.arnesano@uniba.it
ARNOLDI	ANNA	UNIVERSITA' DI MILANO	anna.arnoldi@unimi.it
ARNONE	MARIAFRANCESCA	UNIVERSITA' DI PALERMO	mariafra25@libero.it
ASCENZI	PAOLO		
ASCHI	MASSIMILIANO	UNIVERSITA' L'AQUILA	massimiliano.aschi@univaq.it
ASSFALG	MICHAEL	UNIVERSITA' DI VERONA	michael.assfalg@univr.it
ATZEI	DAVIDE	UNIVERSITA' DI CAGLIARI	datzei@unica.it
AURA	ANGELA MARGHERITA	UNIVERSITA' DI CATANIA	amaura@unict.it
AZZENA	UGO	UNIVERSITA' DI SASSARI	ugo@uniss.it
BADETTI	ELENA	UNIVERSITA' DI PADOVA	elena.badetti@unipd.it
BADOLATO	MARIATERESA	UNIVERSITA' DELLA CALABRIA	mary.badolato@libero.it
BAGLIO	VINCENZO	CNR	vincenzo.baglio@itae.cnr.it
BALANTSEVA	ELENA	UNIVERSITA' DI TORINO	elena.balantseva@unito.it
BALDUCCHI	ROBERTO		
BALLINI	ROBERTO	UNIVERSITA' DI CAMERINO	roberto.ballini@unicam.it
BANDIERA	TIZIANO	ISTITUTO ITALIANO DI TECNOLOGIA (GE)	d3segreteria@iit.it
BARATTUCCI	ANNA	UNIVERSITA' DI MESSINA	abarattucci@unime.it
BARBANTE	CARLO	UNIVERSITA' CA' FOSCARI DI VENEZIA	
BARBIERI	GIUSEPPE	CNR-ITM, RENDE	g.barbieri@itm.cnr.it
BARBIERI	PIERLUIGI	UNIVERSITA' DI TRIESTE	barbierp@units.it
BARRAJA	PAOLA	UNIVERSITA' DI PALERMO	paola.barraja@unipa.it
BARRECA	SALVATORE	UNIVERSITA' DI PALERMO	salvatore.barreca@unipa.it
BARTOCCI	SILVIA	UNIVERSITA' DI PADOVA	silvia.bartocci@unipd.it
BARTOLI	FRANCESCO	UNIVERSITA' DI FIRENZE	francesco.bartoli@unifi.it
BARTOLI	MATTIA	UNIVERSITA' DI FIRENZE	mattia.bartoli@unifi.it
BASATO	MARINO	UNIVERSITA' DI PADOVA	marino.basato@unipd.it
BASILE	FRANCESCO	UNIVERSITA' DI BOLOGNA	f.basile@unibo.it
BASOSI	RICCARDO	UNIVERSITA' DI SIENA	riccardo.basosi@unisi.it
BASTIANONI	SIMONE	UNIVERSITA' DI SIENA	bastianoni@unisi.it
BATTISTEL	DARIO	UNIVERSITA' CA' FOSCARI VENEZIA	dario.battistel@gmail.com
BECAGLI	SILVIA	UNIVERSITA' DI FIRENZE	silvia.becagli@unifi.it
BELLA	FEDERICO	POLITECNICO DI TORINO	federico.bella@polito.it
BELLIA	FRANCESCO	CNR-IBB CATANIA	francesco.bellia@cnr.it
BELLINA	FABIO	UNIVERSITA' DI PISA	fabio.bellina@unipi.it
BELLUCCI	LUCA	CNR MODENA	luca.bellucci_s3@unimore.it
BELVISO	BENNY DANILO	CNR-IC BARI	danilo.belviso@ic.cnr.it
BENEDETTI	FABIO	UNIVERSITA' DI TRIESTE	benedett@units.it
BENEDETTI	MICHELE	UNIVERSITA' DEL SALENTO	michele.benedetti@unisalento.it
BENEDUCI	AMERIGO	UNIVERSITA' DELLA CALABRIA	amerigo.beneduci@unical.it
BENINCORI	TIZIANA	UNIVERSITA' DELL'INSUBRIA	tiziana.benincori@uninsubria.it
BERISIO	RITA	CNR-IBB, NAPOLI	
BERNARDI	ANNA	UNIVERSITA' DI MILANO	anna.bernardi@unimi.it
BERNI	ALEX	UNIVERSITA' DI MODENA E REGGIO EMILIA	alex.berni@unimore.it
BERNINI	ROBERTA	UNIVERSITA' DELLA TUSCIA	berninir@unitus.it
BETTINI	SIMONA	UNIVERSITA' DEL SALENTO	simona.bettini@unisalento.it
BIANCO	GIULIANA	UNIVERSITA' DELLA BASILICATA	giuliana.bianco@unibas.it

BIANCO	ARMANDODORIANO	UNIVERSITA' ROMA LA SAPIENZA	armandodoriano.bianco@uniroma1.it
BIASIOLO	LUCA	UNIVERSITA' DI UDINE	luca.biasiolo@aol.com
BIAVA	MARIANGELA	SAPIENZA UNIVERSITA' DI ROMA	mariangela.biava@uniroma1.it
BINETTI	SIMONA OLGA	UNIVERSITA' MILANO BICOCCA	simona.binetti@unimib.it
BIONDI	STEFANO	ALLECRA THERAPEUTICS SAS	sdb@allecra.com
BISI	ALESSANDRA	UNIVERSITA' DI BOLOGNA	alessandra.bisi@unibo.it
BISIO	CHIARA	UNIVERSITA' DEL PIEMONTE ORIENTALE	chiara.bisio@mfn.unipmn.it
BLOINO	JULIEN	CNR-ICCOM-PISA	julien.bloino@pi.iccom.cnr.it
BOCCALON	MARIANGELA	UNIVERSITA' DI TRIESTE	mboccalon@units.it
BOCHICCHIO	ANTONELLA	UNIVERSITA' DELLA BASILICATA	antella.bochicchio@gmail.com
BOLLELLA	PAOLO	UNIVERSITA' ROMA LA SAPIENZA	bollella1989@hotmail.it
BOLZACCHINI	EZIO	UNIVERSITA' DI MILANO BICO	ezio.bolzacchini@unimib.it
BONACCI	SONIA	UNIVERSITA' MAGNA GRAECIA DI CATANZARO	s.bonacci@unicz.it
BONACCORSI	PAOLA	UNIVERSITA' DI MESSINA	pbonaccorsi@unime.it
BONACCORSO	CARMELA	UNIVERSITA' DI CATANIA	bonaccorsoc@gmail.com
BONCHIO	MARCELLA	UNIVERSITA' DI PADOVA	marcella.bonchio@unipd.it
BONIFAZI	DAVIDE	UNIVERSITA' DI TRIESTE	dbonifazi@units.it
BONURA	GIUSEPPE	ITAE-CNR MESSINA	giuseppe.bonura@itae.cnr.it
BORBONE	FABIO	UNIVERSITA' DI NAPOLI FEDERICO II	fabio.borbone@unina.it
BORDIGA	SILVIA	UNIVERSITA' DI TORINO	silvia.bordiga@unito.it
BORTOLINI	OLGA	UNIVERSITA' DI FERRARA	olga.bortolini@unife.it
BOSI	VALENTINA	UNIVERSITA' DI FERRARA	bsovnt@unife.it
BOSSOLA	FILIPPO	UNIVERSITA' DELL'INSUBRIA	filippo.bossola@gmail.com
BOTTA	MAURIZIO		
BRANDI	ALBERTO	UNIVERSITA' DI FIRENZE	alberto.brandi@unifi.it
BRETTI	CLEMENTE	UNIVERSITA' DI MESSINA	cbretti@unime.it
BRIZZI	ANTONELLA	UNIVERSITA' DI SIENA	antonella.brizzi@unisi.it
BRUNETTI	ADELE	ITM-CNR, RENDE	a.brunetti@itm.cnr.it
BRUNI	PANTALEONE		
BRUNO	MAURIZIO	UNIVERSITA' DI PALERMO	maurizio.bruno@unipa.it
BRUNO	INES	UNIVERSITA' DI SALERNO	brunoin@unisa.it
BRUTTI	SERGIO	UNIVERSITA' DELLA BASILICATA	sergio.brutti@unibas.it
BRUZZONITI	M. CONCETTA	UNIVERSITA' DI TORINO	mariaconcetta.bruzzoniti@unito.it
BUCCI	ALBERTO	UNIVERSITA' DI PERUGIA	albechm@gmail.com
BUEMI	CARMELA		
BUFO	SABINO AURELIO	UNIVERSITÀ DELLA BASILICATA	sabino.bufo@unibas.it
BUTERA	VALERIA	UNIVERSITA' MILANO BICOCCA	valeria.butera@libero.it
CALABRESE	VALENTINA	UNIVERSITA' DI MILANO BICOCCA	valentina.calabrese@unimib.it
CALANDRUCCIO	CARLA	UNIVERSITA' MAGNA GRECIA DI CATANZARO	calandrucciocarla@gmail.com
CALIANDRO	ROCCO		
CALOGERO	GIUSEPPE	CNR-IST. PROCESSI CHIMICO-FISICI,MESSINA	calogero@me.cnr.it
CALUGI	CHIARA	UNIVERSITA' DI FIRENZE	chiara.calugi@unifi.it
CALVANESE	LUISA	UNIVERSITA' DI NAPOLI FEDERICO II	luisa.calvanese@unina.it

CALVILLO	LAURA	UNIVERSITA' DI PADOVA	laura.calvillolamana@unipd.it
CAMAIONI	EMIDIO	UNIVERSITA' DI PERUGIA	emidio.camaioni@unipg.it
CAMILLE SIMON	OUMAROU	UNIVERSITY OF CAMERINO	camillesimon.oumarou@unicam.it
CAMPANELLA	LUIGI	IMT SRL - ROMA	imtsrl@imtsrl.it
CAMPIGLIA	PIETRO	UNIVERSITA' DI SALERNO	pcampigl@unisa.it
CAMPISCIANO	VINCENZO	UNIVERSITA' DI PALERMO	vincenzo.campisciano@unipa.it
CANESCHI	ANDREA	UNIVERSITA' DI FIRENZE	andrea.caneschi@unifi.it
CANNILLA	CATIA	CNR	cannilla@itae.cnr.it
CANOLA	SOFIA	UNIVERSITA' DI BOLOGNA	sofia.canola2@unibo.it
CANTI	LORENZO	UNIVERSITA' DEL PIEMONTE ORIENTALE	lorenzo.canti@mfn.unipmn.it
CANTONE	VINCENZA	UNIVERSITA' DI SALERNO	vcantone@unisa.it
CAPASSO	SANTE	SECONDA UNIVERSITA' DI NAPOLI	sante.capasso@unina2.it
CAPODILUPO	AGOSTINA		
CAPONETTI	EUGENIO		
CAPOLUPO	ANGELA	UNIVERSITA' DI SALERNO	ancapolupo@unisa.it
CAPORALE	ANGELAMARIA	UNIVERSITA' DI SALERNO	acaporale@unisa.it
CAPPIELLO	ACHILLE	UNIVERSITA' DI URBINO	achille.cappiello@uniurb.it
CAPRIATI	VITO	UNIVERSITA' DI BARI	vito.capriati@uniba.it
CAPRIOTTI	ANNA LAURA	UNIVERSITA' ROMA LA SAPIENZA	annalaura.capriotti@uniroma1.it
CARASTRO	ISABELLA	UNIVERSITA' DELLA TUSCIA	i.carastro@unitus.it
CARATTO	VALENTINA	UNIVERSITA' DI GENOVA	caratto@chimica.unige.it
CARBONE	MARIA ELVIRA EGIDIA	UNIVERSITA' DELLA BASILICATA	maria.carbone@unibas.it
CARBONI	MARCO	UNIVERSITA' ROMA LA SAPIENZA	m.carboni@uniroma1.it
CARDELLICCHIO	NICOLA	CNR-IAMC TARANTO	n.cardellicchio@iamc.cnr.it
CARDULLO	NUNZIO	UNIVERSITA' DI CATANIA	nunzio.cardullo@hotmail.it
CARELLA	ANTONIO	UNIVERSITA' DI NAPOLI FEDERICO II	antonio.carella@unina.it
CARLUCCI	GIUSEPPE	UNIVERSITA' DI CHIETI	g.carlucci@unich.it
CARNIATO	FABIO	UNIVERSITA' DEL PIEMONTE ORIENTALE	fabio.carniato@mfn.unipmn.it
CAROLI	ANTONIO	UNIVERSITA' DEL SALENTO	antonio.caroli@hotmail.com
CARONIA	ANNA	MIUR - ISTRUZIONE	anna.caronia@tin.it
CAROTENUTO	ALFONSO	UNIVERSITA' DI NAPOLI "FEDERICO II"	alfonso.carotenuto@unina.it
CARRADORI	SIMONE	SAPIENZA UNIVERSITA' DI ROMA	simone.carradori@uniroma1.it
CARRARO	MAURO	UNIVERSITA' DI PADOVA	mauro.carraro@unipd.it
CARRERA	ANDREA	POLITECNICO DI MILANO	andrea.carrera@polimi.it
CARUSO	ANNA	UNICAL	
CARRIERI	ANTONIO		
CARNASCIALI	MARIA MADDALENA	DIP CHIMICA E CHIMICA INDUSTRIALE GENOVA	marilena@chimica.unige.it
CARUSO	FRANCESCO	ETH ZüRICH	fcaruso@ethz.ch
CARUSO	TONINO		
CASAPULLO	AGOSTINO	UNIVERSITA' DI SALERNO	casapullo@unisa.it
CASELLA	INNOCENZO GIUSEPPE	UNIVERSITA' DELLA BASILICATA	innocenzo.casella@unibas.it
CASNATI	ALESSANDRO	UNIVERSITA' DI PARMA	casnati@unipr.it
CASO	JOLANDA VALENTINA	SECONDA UNIVERSITA' DI NAPOLI	valentina.caso@unina2.it
CASOLI	ANTONELLA	UNIVERSITA' DI PARMA	
CASSANI	STEFANO	UNIVERSITA' DELL'INSUBRIA	stefano.cassanitaz@gmail.com

CASTOLDI	LIDIA	POLITECNICO DI MILANO	lidia.castoldi@polimi.it
CATALANO	FEDERICO	UNIVERSITA' DI TORINO	federico.catalano@unito.it
CATALDI	TOMMASO	UNIVERSITA' DI BARI	tommaso.cataldi@uniba.it
CATALDO	SALVATORE	UNIVERSITA' DI PALERMO	salvatore.cataldo@unipa.it
CATARZI	DANIELA	UNIVERSITA' DI FIRENZE	daniela.catarzi@unifi.it
CAUTERUCCIO	SILVIA	UNIVERSITA' DI MILANO	silvia.cauteruccio@unimi.it
CAVALIERE	CHIARA	SAPIENZA UNIVERSITA' DI ROMA	chiara.cavaliere@uniroma1.it
CAVALLI	MICHAELA	MILANO	
CAVANI	FABRIZIO	UNIVERSITA' DI BOLOGNA	fabrizio.cavani@unibo.it
CELENTANO	VERONICA	CNR NAPOLI	veronicacelentano@yahoo.it
CELESTINO	TERESA	UNIVERSITA' DI CAMERINO	teresa.celestino@unicam.it
CEOTTO	MICHELE	UNIVERSITA' DI MILANO	michele.ceotto@unimi.it
CEREZO BASTIDA	JAVIER	ICCOM-CNR UOS DI PISA	j.cerezo@pi.iccom.cnr.it
CERRA	MARCO	VINAVIL SPA	m.cerra@vinavil.it
CERSOSIMO	MAURIZIO	ITM-CNR, RENDE	m.cersosimo@itm.cnr.it
CESAROTTI	EDOARDO	UNIVERSITA' DI MILANO	edoardo.cesarotti@unimi.it
CEVASCO	GIORGIO	UNIVERSITA' DI GENOVA	giorgio.cevasco@unige.it
CHIAPPE	CINZIA	UNIVERSITA' DI PISA	cinziac@farm.unipi.it
CHIARELLO	GIANLUCA		
CHIDICHIMO	GIUSEPPE	UNIVERSITA' DELLA CALABRIA	chidichi@unical.it
CHIMINAZZO	ANDREA	UNIVERSITA' CA' FOSCARI DI VENEZIA	andrea.chiminazzo@unive.it
CHINI	MARIA GIOVANNA	UNIVERSITA' DI SALERNO	mchini@unisa.it
CHIOZZA	FABIO	VINAVIL SPA	f.chiozza@vinavil.it
CIABATTI	IACOPO	UNIVERSITA' DI BOLOGNA	iacopo.ciabatti2@unibo.it
CICERI	SAMUELE	UNIVERSITA' DI MILANO	samuele.ciceri@guest.unimi.it
CIGALA	ROSALIA MARIA	UNIVERSITA' DI MESSINA	rmcigala@unime.it
CILURZO	FRANCESCO	UNIVERSITA' DI MILANO	francesco.cilurzo@unimi.it
CIMINO	RITA		
CINCINELLI	ALESSANDRA	UNIVERSITA' DI FIRENZE	
CIOFFI	NICOLA	UNIVERSITA' DI BARI	nicola.cioffi@uniba.it
CIRRINCIONE	GIROLAMO	UNIVERSITA' DI PALERMO	girolamo.cirrincione@unipa.it
CITRO	ILARIA	CNR-IPCF MESSINA	citro@ipcf.cnr.it
CITTI	CINZIA	UNIVERSITA' DEL SALENTO	cinzia.citti@unisalento.it
CIVALLERI	BARTOLOMEO	UNIVERSITA' DI TORINO	bartolomeo.civalleri@unito.it
CLEMENTI	CATIA	UNIVERSITA' DI PERUGIA	catia.clementi@unipg.it
COCCHI	MARINA	UNIVERSITA' DI MODENA E REGGIO EMILIA	marina.cocchi@unimore.it
COCCO	FEDERICA	UNIVERSITA' DI CAGLIARI	fcocco@unica.it
COLLINA	AMILCARE	MAPEI S.P.A.	a.collina@mapei.it
COLOMBO	GIORGIO	CNR-ICMR MILANO	g.colombo@icrm.cnr.it
COLOTTA	VITTORIA	UNIVERSITA' DI FIRENZE	vittoria.colotta@unifi.it
COLUCCIA	ANTONIO	SAPIENZA UNIVERSITA' DI ROMA	antonio.coluccia@uniroma1.it
COLUCCIA	SALVATORE	UNIVERSITA' DI TORINO	
COMISSO	NICOLA	CNR-IENI-PADOVA	nicola.comisso@ieni.cnr.it
COMPAGNONE	DARIO	UNIVERSITA' DI TERAMO	dcompagnone@unite.it
COMPAGNONI	MATTEO	UNIVERSITA' DI MILANO	matteo.compagnoni1@studenti.unimi.it
COMPARELLI	ROBERTO	CNR-IPCF	r.comparelli@ba.ipcf.cnr.it
CONCILIO	GERARDO	UNIVERSITA' DI SALERNO	gconcilio@unisa.it
CONCILIO	SIMONA	UNIVERSITA' DI SALERNO	sconcilio@unisa.it
CONTE	VALERIA	UNIVERSITA' ROMA TOR VERGATA	valeria.conte@uniroma2.it
CONTI	LUCA	UNIVERSITA' DI FIRENZE	luca.conti@unifi.it

CONTURSI	MICHELA		
CORELLI	FEDERICO	UNIVERSITA' DI SIENA	federico.corelli@unisi.it
CORNO	MARTA	UNIVERSITA' DI TORINO	marta.corno@unito.it
CORRADINI	DANILO	CNR	danilo.corradini@cnr.it
CORRADINI	ROBERTO	UNIVERSITA' DI PARMA	roberto.corradini@unipr.it
CORTESE	REMEDIOS	UNIVERSITÀ DI PALERMO	remedios.cortese@unipa.it
COSENTINO	KATIA	MAX PLANCK INSTITUTE FOR INTELLIGENT SYSTEMS	cosentino@is.mpg.de
COSENTINO	UGO	UNIVERSITA' MILANO-BICOCCA	ugo.cosentino@unimib.it
COSPITO	SANTE	UNIVERSITA' DELLA CALABRIA	sante.cospito@unical.it
COSTENARO	DANIELE	UNIVERSITA' DEL PIEMONTE ORIENTALE "A. AVOGADRO"	daniele.costenaro@unipmn.it
COSTI	ROBERTA	UNIVERSITA' ROMA LA SAPIENZA	roberta.costi@uniroma1.it
CREA	FRANCESCO	UNIVERSITA' DI MESSINA	fcrea@unime.it
CRISCUOLO	VALERIA	UNIVERSITA' DI NAPOLI FEDERICO II	valeria.criscuolo@hotmail.it
CRISTIANO	MARIA CHIARA	UNIVERSITA' MAGNA GRAECIA DI CATANZARO	mchiara.cristiano@unicz.it
CRITTO	ANDREA	UNIVERSITA' CA' FOSCARI VENEZIA	critto@unive.it
CRUCIANELLI	MARCELLO	UNIVERSITA' DELL'AQUILA	marcello.crucianelli@univaq.it
CRUCIANI	GABRIELE	UNIVERSITA' DI PERUGIA	gabriele.cruciani@unipg.it
CUCCINIELLO	RAFFAELE	UNIVERSITA' DI SALERNO	rcucciniello@unisa.it
CUNSOLO	ALESSANDRA	UNIVERSITA' DI CATANIA	acunsolo@unict.it
CUPELLINI	LORENZO	UNIVERSITA' DI PISA	lorenzo.cupellini@for.unipi.it
CURULLI	ANTONELLA	CNR ISMN ROMA	antonella.curulli@cnr.it
DA ROS	TATIANA	UNIVERSITà DEGLI STUDI DI TRIESTE	daros@units.it
DA SETTIMO	FEDERICO	UNIVERSITA' DI PISA	federico.dasettimo@farm.unipi.it
D'ABROSCA	GIANLUCA	SECONDA UNIVERSITA' DI NAPOLI	gianluca.dabrosca@unina2.it
DAGLIA	MARIA	UNIVERSITA' DI PAVIA	maria.daglia@unipv.it
DAIDONE	GIUSEPPE	UNIVERSITA' DI PALERMO	giuseppe.daidone@unipa.it
DAL BEN	DIEGO	UNIVERSITA' DI CAMERINO	diego.dalben@unicam.it
DALLA CORT	ANTONELLA	UNIVERSITA' ROMA LA SAPIENZA	antonella.dallacort@uniroma1.it
DALLA VALLE	CHIARA	UNIVERSITA' DI PADOVA	chia.dllavalle.1@studenti.unipd.it
DALL'ANTONIA	PATRIZIA	IST. TECN. INDUSTRIALE TRIESTE	patriziadallantonia@libero.it
DALLE CARBONARE	NICOLA	CNR- ISOF-UNIVERSITA' DI FERRARA	dllncl@unife.it
DAMIANO	ROBERTA	UNIVERSITA' DI PALERMO	roberta.damiano@unipa.it
D'ANDREA	LUCA DOMENICO	CNR, NAPOLI	ldandrea@unina.it
DANIELE	SALVATORE	UNIVERSITA' CA' FOSCARI VENEZIA	sig@unive.it
DANIELE	PIER GIUSEPPE	UNIVERSITA' DI TORINO	piergiuseppe.daniele@unito.it
D'AURIA	VALERIA	UNIVERSITA' DI NAPOLI FEDERICO II	madauria@unina.it
D'AURIA	GABRIELLA	UNIVERSITA' DI NAPOLI "FEDERICO II"	gabriella.dauria@unina.it
DE ANGELIS	FILIPPO	CNR-ISTM PERUGIA	filippo.d.angelis@gmail.com
DE ANGELIS	FRANCESCO	UNIVERSITA' DELL'AQUILA	francesco.deangelis@univaq.it
DE BARTOLO	LOREDANA	CNR ITM RENDE	l.debartolo@itm.cnr.it
DE BONIS	ANGELA	UNIVERSITA' DELLA BASILICATA	angela.debonis@unibas.it
DE CARLO	ROSA MARIA	UNIVERSITA' DI TORINO	rosa.decarlo@unito.it

DE CASTRO	FEDERICA	UNIVERSITA' DEL SALENTO	decastrofederica87@gmail.com
DE GENNARO	GIANLUIGI	UNIVERSITA' DI BARI	gianluigi.degennaro@uniba.it
DE LAURENTIIS	ELISA	UNIVERSITA' DI TORINO	elisa.delaurentiis@unito.it
DE LEO	VINCENZO		
DE LORENZI	ERSILIA	UNIVERSITA' DI PAVIA	ersidelo@unipv.it
DE LUCA	LAURA		
DE LUCA	MICHELE	UNIVERSITA' DELLA CALABRIA	michele.deluca@unical.it
DE MUNNO	GIOVANNI	UNIVERSITA' DELLA CALABRIA	demunno@unical.it
DE NEGRI	SERENA	UNIVERSITA' DI GENOVA	serena.denegri@unige.it
DE NISI	ASSUNTA	UNIVERSITA' DI SALERNO	assunta.denisi@gmail.com
DE ROSA	LUCIA	CNR - NAPOLI	lucia.derosa@unina.it
DE SIO	GABRIELE	UNIVERSITA' DI MILANO-BICOCCA	g.desio@campus.unimib.it
DE STEFANO	CONCETTA	UNIVERSITA' DI MESSINA	cdestefano@unime.it
DE STEFANO	ALESSIA	UNIVERSITA' DI ROMA "TOR VERGATA"	alessia.de.stefano@uniroma2.it
DE TOMMASO	GAETANO	UNIVERSITA' DI NAPOLI FEDERICO II	gaetano.detommaso@unina.it
DE VIVO	MARCO	ITALIAN INSTITUTE OF TECHNOLOGY, GENOVA	
DE ZOTTI	MARTA	UNIVERSITA' DI PADOVA	marta.dezotti@unipd.it
DECKER	FRANCO		
DEGANO	ILARIA	UNIVERSITA' DI PISA	ilaria.degano@unipi.it
DEHNEN	STEFANIE	UNIVERSITY OF MARBURG	dehnen@chemie.uni-marburg.de
DEI	LUIGI	UNIVERSITA' DI FIRENZE	luigi.dei@unifi.it
DEL GAUDIO	PASQUALE	UNIVERSITA' DI SALERNO	pdelgaudio@unisa.it
DEL GIACCO	TIZIANA	UNIVERSITA' DI PERUGIA	tiziana.delgiacco@unipg.it
DEL PIVO	CAMILLA	ISTEC-CNR FAENZA	camilla.delpivo@istec.cnr.it
DELLA CA	NICOLA	UNIVERSITA' DI PARMA	nicola.dellaca@unipr.it
DELLA PELLE	FLAVIO	UNIVERSITA' DI TERAMO	flaviod.p.86@hotmail.it
DELLA SALA	FABIO		
DELL'ERBA	FRANCO	TARANTO	
DEODATO	DAVIDE		
D'ERRICO	STEFANO	UNIVERSITA' DI NAPOLI 'FEDERICO II'	stefano.derrico@unina.it
D'ERRICO	GERARDINO	UNIVERSITA' DI NAPOLI	gerardino.derrico@unina.it
DI DONNA	LEONARDO	UNIVERSITA' DELLA CALABRIA	l.didonna@unical.it
DI FRANCESCO	FABIO	UNIVERSITA' DI PISA	fdifra@dcci.unipi.it
DI FRANCO	FRANCESCO	UNIVERSITA' DI PALERMO	francesco.difranco@unipa.it
DI GREGORIO	ENZA	UNIVERSITA' DI TORINO	enza.digregorio@unito.it
DI IORIO	NICOLA	UNIVERSITA' DI BOLOGNA	nicola.diiorio2@unibo.it
DI LECCE	DANIELE		
DI LORENZO	ROSALIA	UNIVERSITA' DI PADOVA	rosalia.dilorenzo@studenti.unipd.it
DI MICCO	SIMONE	UNIVERSITA' DI SALERNO	sdimicco@unisa.it
DI PIETRO	PATRIZIA	UNIVERSITA' DI CATANIA	pdipietro@unict.it
DI PIETRO	MARIA ENRICA	UNIVERSITA' DELLA CALABRIA	mariaenrica.dipietro@unical.it
DI PROFIO	GIANLUCA	ITM CNR RENDE	g.diprofio@itm.cnr.it
DI SANTO	EMANUELA	UNIVERSITA' DELLA CALABRIA	emanuela.disanto@unical.it
DI SANZO	GIUSEPPE	ENEA	giuseppe.disanzo@enea.it
DI SERIO	MARTINO	UNIVERSITA' DI NAPOLI	diserio@unina.it
DI STASI	ROSSELLA	CNR - NAPOLI	rossella.distasi@cnr.it
DI VITA	GLORIA	UNIVERSITA' DI PALERMO	gloria.divita@unipa.it
DIANA	PATRIZIA	UNIVERSITA' DI PALERMO	patrizia.diana@unipa.it

DIETZ	LUCA	POLITECNICO DI MILANO	luca.dietz.89@gmail.com
DINI	DANILO	UNIVERSITA' DI ROMA SAPIENZA	danilo.dini@uniroma1.it
D'ISCHIA	MARCO	UNIVERSITA' DI NAPOLI FEDERICO II	dischia@unina.it
DOBERDO'	ITALO		
DOMENICI	VALENTINA	UNIVERSITA' DI PISA	valentina.domenici@unipi.it
DONATO	LAURA	ITM CNR RENDE	l.donato@itm.cnr.it
DONAZZI	ALESSANDRO	POLITECNICO DI MILANO	alessandro.donazzi@polimi.it
DONDI	DANIELE	UNIVERSITA' DI PAVIA	dondi@unipv.it
DOSSI	CARLO	UNIVERSITA' DELL' INSUBRIA	carlo.dossi@uninsubria.it
DOVA	DAVIDE	UNIVERSITA' DI MILANO	davide.dova@unimi.it
D'URSO	ALESSANDRO	UNIVERSITA' DI CATANIA	adurso@unict.it
ELISEI	FAUSTO	UNIVERSITA' DI PERUGIA	fausto.elisei@unipg.it
EVIDENTE	ANTONIO	UNIVERSITA' DI NAPOLI FEDERICO II	antonio.evidente@unina.it
EVIDENTE	MARCO	UNIVERSITA' DI NAPOLI FEDERICO II	marco.evidente@unina.it
FAHAMI	AMIR REZA	POLITECNICO DI MILANO	amirreza.fahami@polimi.it
FALBO	FRANCESCO	ITM-CNR, RENDE	f.falbo@itm.cnr.it
FALCIGNO	LUCIA	UNIVERSITA' DI NAPOLI	falcigno@unina.it
FALCIOLA	LUIGI	UNIVERSITA' DI MILANO	luigi.falciola@unimi.it
FAMENGO	ALESSIA	CNR PADOVA	a.famengo@ieni.cnr.it
FANIZZI	FRANCESCO PAOLO	UNIVERSITA' DEL SALENTO	fp.fanizzi@unisalento.it
FANTAUZZI	MARZIA	UNIVERSITA DI CAGLIARI	fantauzzi@unica.it
FANTIN	MARCO	UNIVERSITA' DI PADOVA	marco.fantin.1@studenti.unipd.it
FARINA	VITTORIO	JANSSEN	vfarina@its.jnj.com
FARINA	ROBERTA	UNIVERSITA' DI BARI	roberta-farina@libero.it
FARINOLA	GIANLUCA MARIA	UNIVERSITA' DI BARI	gianlucamaria.farinola@uniba.it
FARROTTI	ANDREA	UNIVERSITA' DI ROMA TOR VERGATA	andrea.farrotti@uniroma2.it
FATTORUSSO	ROBERTO	SECONDA UNIVERSITA' DI NAPOLI	roberto.fattorusso@unina2.it
FAVERO	GABRIELE	UNIVERSITA' ROMA LA SAPIENZA	gabriele.favero@uniroma1.it
FAZZINI	SILVIA	UNIVERSITA' DI BOLOGNA	silvia.fazzini2@unibo.it
FEDELI	STEFANO	UNIVERSITA' DI FIRENZE	stefano.fedeli@unifi.it
FEDERICO	STEPHANIE	UNIVERSITA' DI TRIESTE	sfederico@units.it
FILICE	MONICA	Unical	
FELLUGA	FULVIA	UNIVERSITA' DI TRIESTE	ffelluga@units.it
FERMO	PAOLA	UNIVERSITA' DI MILANO	paola.fermo@unimi.it
FERRANTE	FRANCESCO	UNIVERSITA' DI PALERMO	francesco.ferrante@unipa.it
FERRERO	LUCA	UNIVERSITA' DI MILANO-BICOCCA	luca.ferrero@unimib.it
FERRETTI	FRANCESCO	UNIVERSITA' DI MILANO	francesco.ferretti@unimi.it
FERRO	STEFANIA	UNIVERSITA' DI MESSINA	sferro@unime.it
FESTA	CARMEN	UNIVERSITA' DI NAPOLI FEDERICO II	carmen.festa@unina.it
FINAMORE	CLAUDIA	UNIVERSITA' DI NAPOLI FEDERICO II	claudiafinamore@gmail.com
FINI	PAOLA		
FIORICA	CALOGERO		
FLORIANO	MICHELE ANTONIO	UNIVERSITA' DI PALERMO	michele.floriano@unipa.it
FONTANA	GIANFRANCO	UNIVERSITA' DI PALERMO	gianfranco.fontana@unipa.it
FONTANANOVA	ENRICA	ITM-CNR RENDE	e.fontananova@itm.cnr.it
FORMAGGIO	FERNANDO	UNIVERSITA' DI PADOVA	fernando.formaggio@unipd.it
FORTINO	MARIAGRAZIA	UNIVERSITA' DELLA CALABRIA	mariagrazia.fortino@gmail.com

FORZATTI	PIO	POLITECNICO DI MILANO	pio.forzatti@polimi.it
FOSSATI	GIANLUCA	ITALFARMACO	g.fossati@italfarmaco.com
FOTI	CLAUDIA	UNIVERSITA' DI MESSINA	cfoti@unime.it
FOTI	SALVATORE	UNIVERSITA' DI CATANIA	sfoti@unict.it
FRANCESCONI	OSCAR	UNIVERSITA' DI FIRENZE	oscar.francesconi@unifi.it
FRANCESE	SIMONA	SHEFFIELD HALLAM UNIVERSITY	s.francese@shu.ac.uk
FRANCHINI	CARLO	UNIVERSITA' DI BARI	carlo.franchini@uniba.it
FRANCO	FEDERICO	UNIVERSITA' DI TORINO	federico.franco@unito.it
FRATALOCCHI	LAURA	POLITECNICO DI MILANO	laura.fratalocchi@polimi.it
FREZZATO	DIEGO	UNIVERSITA' DI PADOVA	diego.frezzato@unipd.it
FRONZONI	GIOVANNA	UNIVERSITA' DI TRIESTE	fronzoni@units.it
FRUSTERI	FRANCESCO	ISTITUTO CNR-ITAE	francesco.frusteri@itae.cnr.it
FUNICELLO	MARIA	UNIVERSITA' DELLA BASILICATA	maria.funicello@unibas.it
FURIA	EMILIA	UNIVERSITA' DELLA CALABRIA	e.furia@unical.it
FURLANETTO	SANDRA	UNIVERSITA' DI FIRENZE	sandra.furlanetto@unifi.it
FUSCO	CATERINA	CNR-ICCOM	fusco@ba.iccom.cnr.it
FUSCO	ROBERTO		roberto.fusco1@eni.com
FUSE'	MARCO	UNIVERSITA' DI MILANO	marco.fuse@unimi.it
FUSINI	GRAZIANO	UNIVERSITA' DI PISA	graziano.fusini@for.unipi.it
GAGGIOLI	CARLO ALBERTO	UNIVERSITA' DI PERUGIA	
GALASSI	ROSSANA		
GALIANO	FRANCESCO	ITM-CNR-RENDE	galiano.francesco@hotmail.it
GALLIANI	ANGELA	UNIVERSITA' DI BARI	angelagalliani@libero.it
GALLO	EMMA	UNIVERSITA' DI MILANO	emma.gallo@unimi.it
GALLONI	PIERLUCA	UNIVERSITA' DI ROMA TOR VERGATA	galloni@scienze.uniroma2.it
GAMBUZZI	ELISA	UNIVERSITA' DI MODENA E REGGIO EMILIA	elisa.gambuzzi@hotmail.com
GARDOSSI	LUCIA	UNIVERSITA' DI TRIESTE	gardossi@units.it
GAROFALO	ANTONIO	UNIVERSITA' DELLA CALABRIA	antonio.garofalo@unical.it
GASPARI	MARCO		
GEDA	GIUSEPPE	ORDINE CHIMICI PIEMONTE E VDA	segreteria@chimicipiemonte.it
GELAIN	ARIANNA	UNIVERSITA' DI MILANO	arianna.gelain@unimi.it
GENGA	ALESSANDRA		
GENTILE	LUIGI	UNIVERSITA' DELLA CALABRIA	luigi.gentile@unical.it
GENTILI	ALESSANDRA	UNIVERSITA' ROMA LA SAPIENZA	alessandra.gentili@uniroma1.it
GENTILUOMO	SERENA	UNIVERSITA' DI MESSINA	sgentiluomo@unime.it
GERACE	ENRICO	CENTRO REGIONALE ANTIDOPING	enrico.gerace@antidoping.piemonte.it
GERARDI	CHIARA		chiaragerardi89@gmail.com
GHIBAUDI	ELENA	UNIVERSITA' DI TORINO	elena.ghibaudi@unito.it
GHILARDI	TIZIANA	UNIVERSITA' DI PISA	tiz.ghilardi@gmail.com
GHIMENTI	SILVIA	UNIVERSITA' DI PISA	silvia.ghimenti@ifc.cnr.it
GIACALONE	VALENTINA	UNIVERSITA' DI PALERMO	valentina.giacalone03@unipa.it
GIAMPA'	FELICIA		felicia.giampa@istruzione.it
GIANCANE	GABRIELE		gabriele.giancane@unisalento.it
GIANNETTO	ANTONINO	UNIVERSITA' DEL SALENTO	giannettoa@unime.it
GIANNICCHI	ILARIA	SAPIENZA UNIVERSITA' DI ROMA	ilaria.giannicchi@uniroma1.it
GINEPRO	MARCO	UNIVERSITA' DI TORINO	marco.ginepro@unito.it
GIOFRE'	SALVATORE VINCENZO	UNIVERSITA' DI MESSINA	sgiofre@unime.it

GIORGI	SIMONE	UNIVERSITA' DI CAMERINO	sim.giorgi@gmail.com
GIORGI	GIANLUCA	UNIVERSITA' DI SIENA	gianluca.giorgi@unisi.it
GIORNO	LIDIETTA	CNR-ITM RENDE	l.giorno@itm.cnr.it
GIUFFRE'	OTTAVIA	UNIVERSITA' DI MESSINA	ogiuffre@unime.it
GOBBI	SILVIA	UNIVERSITA' DI BOLOGNA	silvia.gobbi@unibo.it
GOBETTO	ROBERTO	UNIVERSITA' DI TORINO	roberto.gobetto@unito.it
GOLEMME	GIOVANNI	UNIVERSITA' DELLA CALABRIA	ggolemme@unical.it
GOMEZ MONTERREY	I.M.		
GORACCI	LAURA	UNIVERSITA' DI PERUGIA	laura.goracci@unipg.it
GORI	SILVIO EUGENIO	MILANO	
GOSETTI	FABIO	UNIVERSITA' DEL PIEMONTE ORIENTALE	fabio.gosetti@unipmn.it
GRAMATICA	PAOLA	UNIVERSITA' INSUBRIA	paola.gramatica@uninsubria.it
GRANAFEI	SARA	UNIVERSITA' DI BARI	sara.granafei@uniba.it
GRANDE	FEDORA	UNIVERSITA' DELLA CALABRIA	fedora.grande@unical.it
GRANOZZI	GAETANO		
GRASSO	GIUSEPPE	UNIVERSITA' DI CATANIA	grassog@unict.it
GRAZIADIO	ALESSANDRA	UNIVERSITA' DI BOLOGNA	alessandra.graziadi3@unibo.it
GRECO	CLAUDIO	UNIVERSITA' DI MILANO BICOCCA	claudio.greco@unimib.it
GROPPI	GIANPIERO	POLITECNICO DI MILANO	gianpiero.groppi@polimi.it
GROPPO	ELENA	UNIVERSITA' DI TORINO	elena.groppo@unito.it
GROSSO	VALENTINA	ITM-CNR RENDE	v.grosso@itm.cnr.it
GRUTTADAURIA	MICHELANGELO	UNIVERSITA' DI PALERMO	michelangelo.gruttadauria@unipa.it
GUERRA	GAETANO		
GUIDOTTI	MATTEO	CNR-ISTM MILANO	m.guidotti@istm.cnr.it
GUISO	MARCELLA	UNIVERSITA' ROMA LA SAPIENZA	marcella.guiso@uniroma1.it
HASA	IVANA	UNIVERSITA' ROMA LA SAPIENZA	ivana.hasa@uniroma1.it
IACOVINO	ROSA	UNIVERSITA' DI NAPOLI FEDERICO II	rosa.iacovino@unina2.it
IELPO	PIERINA	CNR-IRSA	piera.ielpo@ba.irsa.cnr.it
IENCO	ANDREA	CNR ICCOM FIRENZE	andrea.ienco@iccom.cnr.it
ILLUMINATI	SILVIA	UNIVERSITA' POLITECNICA DELLE MARCHE	s.illuminati@univpm.it
IMPERIO	ELEONORA	UNIVERSITA' DEL SALENTO	eleonora.imperio@unisalento.it
IMPROTA	ROBERTO		
INGROSSO	CHIARA	CNR	c.ingrosso@ba.ipcf.cnr.it
INTAGLIATA	SEBASTIANO	UNIVERSITA' DI CATANIA	s.intagliata@hotmail.it
IONESCU	ANDREEA	UNIVERSITA' DELLA CALABRIA	andreea.ionescu@unical.it
IOVINO	PASQUALE	SECONDA UNIVERSITA' DI NAPOLI	pasquale.iovino@unina2.it
IRRERA	SIMONA	SAPIENZA UNIVERSITA' DI ROMA	simona.irrera@uniroma1.it
ISERNIA	CARLA	SECONDA UNIVERSITA' DI NAPOLI	carla.isernia@unina2.it
ISSE	ABDIRISAK AHMED	UNIVERSITA' DI PADOVA	abdirisak.ahmedisse@unipd.it
JUMDE	RAVINDRA	ISTM-CNR MILANO	jumde.ravindra@istm.cnr.it
JURINOVICH	SANDRO	UNIVERSITA' DI PISA	sandro.jurinovich@for.unipi.it
KHAN	MD BADIUZZAMAN	UNIVERSITA' CA' FOSCARI VENEZIA	md.khan@unive.it
KOHNKE	FRANZ		
LA MENDOLA	DIEGO	UNIVERSITA' DI PISA	lamendola@farm.unipi.it

LA REGINA	GIUSEPPE	SAPIENZA UNIVERSITA' DI ROMA	giuseppe.laregina@uniroma1.it
LA ROSA	MARCELLO	UNIVERSITA' DI BOLOGNA	marcello.larosa3@unibo.it
LA SORELLA	GIORGIO	UNIVERSITA' CA' FOSCARI VENEZIA	giosister@yahoo.it
LABELLA	CRISTIANA	UNIVERSITA' DELLA BASILICATA	cristiana.labella@unibas.it
LACHOWICZ	JOANNA IZABELA	UNIVERSITA' DI CAGLIARI	lachowicz@unica.it
LAGANA'	ALDO	UNIVERSITA' ROMA LA SAPIENZA	aldo.lagana@uniroma1.it
LAMBERTUCCI	CATIA	UNIVERSITA' DI CAMERINO	catia.lambertucci@unicam.it
LAMMI	CARMEN	UNIVERSITA' DI MILANO	
LANDO	GABRIELE	UNIVERSITA' DI MESSINA	glando@unime.it
LANGE	HEIKO	UNIVERSITA' DI ROMA 'TOR VERGATA'	heiko.lange@uniroma2.it
LANTERI	SILVIA	UNIVERSITA' DI GENOVA	silvia@difar.unige.it
LASSO	JOSE'	UNIVERSITA' DI MILANO	
LAURIA	ANTONINO	UNIVERSITA' DI PALERMO	antonino.lauria@unipa.it
LENCI	ELENA	UNIVERSITA' DI FIRENZE	elena.lenci@unifi.it
LEONE	VINCENZO	SECONDA UNIVERSITA' DI NAPOLI	enzoleone83@alice.it
LEOPOLDO	MARCELLO	UNIVERSITA' DI BARI	marcello.leopoldo@uniba.it
LEPRI	SUSAN	UNIVERSITA' DI PERUGIA	susanlepri@gmail.com
LESCI	ISIDORO GIORGIO	UNIVERSITA' DI BOLOGNA	isidorogiorgio.lesci@unibo.it
LI VIGNI	MARIO	UNIVERSITA' DI MODENA E REGGIO EMILIA	mario.livigni@unimore.it
LIBANI	GIULIA	UNIVERSITA' POLITECNICA DELLE MARCHE	g.libani@univpm.it
LICANDRO	EMANUELA	UNIVERSITA' DI MILANO	emanuela.licandro@unimi.it
LICINI	GIULIA	UNIVERSITA' DI PADOVA	giulia.licini@unipd.it
LIETTI	LUCA		
LIGUORI	PAOLA FRANCESCA	UNIVERSITA' DELLA CALABRIA	paolafrancesca.liguori@unical.it
LILL	ROLAND	PHILIPPS-UNIVERSITÄT MERBURG	lill@staff.uni-marburg.de
LIMONGELLI	VITTORIO		vittoriolimongelli@gmail.com
LOMBARDI	LIVIA	SAPIENZA UNIVERSITA' DI ROMA	livia.lombardi@uniroma1.it
LOMBARDO	MARCO	UNIVERSITA' DI BOLOGNA	marco.lombardo@unibo.it
LOMONACO	TOMMASO	UNIVERSITA' DI PISA	tommaso.lomonaco@ifc.cnr.it
LONA	LUIGIA		
LONGO	SIMONA	UNIVERSITA' DI SALERNO	simmylongo@hotmail.it
LOSITO	ILARIO	UNIVERSITA' DI BARI	ilario.losito@uniba.it
LUCCHESINI	FRANCESCO	UNIVERSITA' DI GENOVA	lucchesini@difar.unige.it
LUCCHINI	MATTIA ALBERTO	UNIVERSITA' DI GENOVA	mattia.lucchini@unige.it
LUCHINAT	CLAUDIO	UNIVERSITA' DI FIRENZE	
LUCONI	LAPO	ICOMC-CNR FIRENZE	lapo.luconi@iccom.cnr.it
LUSVARDI	GIGLIOLA	UNIVERSITA' DI MODENA E REGGIO EMILIA	gigliola.lusvardi@unimore.it
MACCARI	GIORGIO	UNIVERSITA' DI SIENA	giorgio.maccari@gmail.com
MACCHIONI	ALCEO	UNIVERSITA' DI PERUGIA	alceo.macchioni@unipg.it
MAFESSANTI	RODOLFO	UNIVERSITA' DI BOLOGNA	
MAGGINI	MICHELE	UNIVERSITA' DI PADOVA	michele.maggini@unipd.it
MAGGISANO	GIUSEPPINA		
MAGI	EMANUELE	UNIVERSITA' DI GENOVA	emanuele.magi@unige.it
MAGISTRIS	ALDO	UNIVERSITA' DI PAVIA	aldo.magistris@unipv.it
MAGLIONE	CIRA	UNIVERSITA' DI NAPOLI FEDERICO II	
MAGLIULO	MARIA	UNIVERSITA' DI BARI	maria.magliulo@uniba.it

MAGNANO	GIULIA	UNIVERSITA' DI MILANO	giulia.magnano@unimi.it
MAGNI	MIRKO	UNIVERSITA' DI MILANO	mirko.magni@unimi.it
MAGRINI	LAURA	UNIVERSITA' DI URBINO	laura.magrini@uniurb.it
MAI	ANTONELLO	UNIVERSITA' ROMA LA SAPIENZA	antonello.mai@uniroma1.it
MAIONE	VINCENZO	SECONDA UNIVERSITA' DI NAPOLI	vincenzo.maione@unina2.it
MAIORANA	STEFANO	UNIVERSITA' DI MILANO	stefano.maiorana@unimi.it
MAJIDI SALEHI	SHABNAM	UNIVERSITA' DELLA CALABRIA	s.majidi@itm.cnr.it
MALAJ	NAIM	UNIVERSITA' DI MILANO BICOCCA	naim.malaj@unimib.it
MALANDRINO	MERY	UNIVERSITA' DI TORINO	mery.malandrino@unito.it
MALAVOLTI	MARINO	UNIVERSITA' DI FIRENZE	marino.malavolti@unifi.it
MALGIERI	GAETANO	SECONDA UNIVERSITA' DI NAPOLI	gaetano.malgieri@unina2.it
MALITESTA	COSIMINO	UNIVERSITA' DEL SALENTO	cosimino.malitesta@unisalento.it
MALTESE	VITO	UNIVERSITA' DELLA CALABRIA	metalsoviet@tiscali.it
MAMONE CAPRIA	ORNELLA		
MANCIN	FABRIZIO	UNIVERSITA' DI PADOVA	fabrizio.mancin@unipd.it
MANCUSO	RAFFAELLA	UNIVERSITA' DELLA CALABRIA	raffaella.mancuso@unical.it
MANDIC'	EMANUELA	SAPIENZA UNIVERSITA' DI ROMA	emanuela.mandic@gmail.com
MANFREDI	CARLA	UNIVERSITA' FEDERICO II DI NAPOLI	carla.manfredi@unina.it
MANFREDI	NORBERTO	UNIVERSITA' DI MILANO BICOCCA	norberto.manfredi@unimib.it
MANGOLINI	FILIPPO	UNIVERSITY OF PENNSYLVANIA	
MANIACI	ROBERTA	UNIVERSITA' DI PALERMO	roberta.maniaci@unipa.it
MANNINA	LUISA	UNIVERSITA' DI ROMA "LA SAPIENZA"	luisa.mannina@uniroma1.it
MANSUETI	ENRICO		ENRICO.MAN@LIBERO.IT
MARCANTONI	ENRICO	UNIVERSITA' DI CAMERINO	enrico.marcantoni@unicam.it
MARCHETTI	FABIO	UNIVERSITA' DI PISA	fabmar@dcci.unipi.it
MARCHETTI	FABIO	POLITECNICO DI MILANO	fabio.marchitti@polimi.it
MARCHETTINI	NADIA	UNIVERSITA' DI SIENA	nadia.marchettini@unisi.it
MARCHINI	MARIANNA	UNIVERSITA' DI BOLOGNA	marianna.marchini2@unibo.it
MARCHIONNA	MARIO	SAIPEM	mario.marchionna@saipem.com
MARCHIONNI	VALENTINA	PAUL SCHERRER INSTITUTE (CH)	valentina.marchionni@psi.ch
MARCI'	GIUSEPPE	UNIVERSITA' DI PALERMO	giuseppe.marci@unipa.it
MARCOALDI	CATERINA	ENEA - ROMA	kate-12@hotmail.it
MARCOMINI	ANTONIO	UNIVERSITY CA' FOSCARI VENICE	marcom@unive.it
MARCONI	ROBERTO PAOLO	UNIVERSITA' DI PAVIA	robymarcoz@hotmail.it
MARIANETTI	GIULIA	SCUOLA NORMALE SUPERIORE DI PISA	giulia.marianetti@sns.it
MARIANI	MATTEO	UNIVERSITA' DI MILANO	matteo.mariani@unimi.it
MARIANI	STEFANO	UNIVERSITÀ DI FIRENZE	s.mariani@unifi.it
MARINI	FEDERICO	UNIVERSITA' DI ROMA "LA SAPIENZA"	federico.marini@uniroma1.it
MARINO	TIZIANA	UNIVERSITA' DELLA CALABRIA	tmarino@unical.it
MARINO	TIZIANA	ITM-CNR, RENDE	tiziana.marino@yahoo.it
MARRANI	ANDREA GIACOMO	UNIVERSITA' DI ROMA "LA SAPIENZA"	andrea.marrani@uniroma1.it
MARTELLINI	TANIA	UNIVERSITA' DI FIRENZE	tania.martellini@unifi.it

MARTRA	GIANMARIO	UNIVERSITA' DI TORINO	gianmario.martra@unito.it
MASSA	ANTONIO	UNIVERSITA' DI SALERNO	amassa@unisa.it
MASSANISSO	PAOLO		
MASSARENTI	CHIARA	UNIVERSITA' DI FERRARA	msschr@unife.it
MASTROPASQUA TALAMO	MAURIZIO	UNIVERSITA' DI BARI	maurizio.mastropasquatalamo@uniba.it
MASTROPIETRO	TERESA FINA	UNIVERSITA' DELLA CALABRIA	teresafina.mastropietro@gmail.com
MASULLO	DARIO	UNIVERSITA' DI NAPOLI FEDERICO II	dario.masullo@unina.it
MATERAZZI	STEFANO	UNIVERSITA' DI ROMA "LA SAPIENZA"	stefano.materazzi@uniroma1.it
MAURIELLO	FRANCESCO		francesco.mauriello@unirc.it
MAZZEI	ROSALINDA	ITM-CNR RENDE	r.mazzei@itm.cnr.it
MAZZEI	PATRIZIA	SCUOLA SECONDARIA DI II GRADO	patrizia.mazzei@istruzione.it
MAZZEO	ROCCO		
MAZZEO	PIETRO	ROMA	pietromazzeo35@gmail.com
MAZZONE	GLORIA	UNIVERSITA' DELLA CALABRIA	gloria.mazzone@unical.it
MAZZOTTI	FABIO	UNIVERSITA' DELLA CALABRIA	fmazzotti@unical.it
MEDURI	ANGELO	UNIVERSITA' DI SALERNO	ameduri@unisa.it
MEILLE	STEFANO VALDO	POLITECNICO MILANO	valdo.meille@polimi.it
MELLONI	MATTIA	UNIVERSITA' DI BOLOGNA	mattia.melloni2@unibo.it
MENABUE	LEDI	UNIVERSITA' DI MODENA E REGGIO EMILIA	ledi.menabue@unimore.it
MENEGAZZO	FEDERICA	UNIVERSITA' CA FOSCARI VENEZIA	fmenegaz@unive.it
MENINNO	SARA	UNIVERSITA' DI SALERNO	smeninno@unisa.it
MENNUCCI	BENEDETTA	UNIVERSITA' DI PISA	benedetta.mennucci@unipi.it
MENZIANI	MARIA CRISTINA	UNIVERSITA' DI MODENA E REGGIO EMILIA	menziani@unimore.it
MERCOLINI	LAURA	UNIVERSITA' DI BOLOGNA	laura.mercolini@unibo.it
MERCURIO	MARIA EMILIA	SECONDA UNIVERSITA' DI NAPOLI	mariaemilia.mercurio@unina2.it
MESSANA	DIEGO	ITM-CNR RENDE	diego.messana.ded@gmail.com
METRANGOLO	PIERANGELO	POLITECNICO DI MILANO	pierangelo.metrangolo@polimi.it
MICHELI	LAURA	UNIVERSITA' DI ROMA TOR VERGATA	laura.micheli@uniroma2.it
MICHELINI	ELISA	UNIVERSITA' DI BOLOGNA	elisa.michelini8@unibo.it
MIELE	CARMELA		
MIGLIORI	MASSIMO	UNIVERSITA' DELLA CALABRIA	
MILARDI	DANILO	UNIVERSITA' DI CATANIA	danilo.milardi@unict.it
MILEA	DEMETRIO	UNIVERSITA' DI MESSINA	dmilea@unime.it
MILIOTO	STEFANIA	UNIVERSITA' DI PALERMO	milioto@unipa.it
MILITANO	FRANCESCA	ITM-CNR RENDE	f.militano@itm.cnr.it
MILLI	LORENZO	UNIVERSITA' DI BOLOGNA	lorenzo.milli2@unibo.it
MINARINI	ANNA	UNIVERSITA' DI BOLOGNA	anna.minarini@unibo.it
MINELLA	MARCO	UNIVERSITA' DI TORINO	marco.minella@unito.it
MINERO	CLAUDIO	UNIVERSITA' DI TORINO	claudio.minero@unito.it
MINGHETTI	PAOLA	UNIVERSITA' DI MILANO	paola.minghetti@unimi.it
MINGUZZI	ALESSANDRO	UNIVERSITA' DI MILANO	alessandro.minguzzi@unimi.it
MINUNNI	MARIA	UNIVERSITA' DI FIRENZE	maria.minunni@unifi.it
MINUTI	LUCIO	UNIVERSITA' DI PERUGIA	lucio.minuti@unipg.it
MIRASOLI	MARA	UNIVERSITA' DI BOLOGNA	mara.mirasoli@unibo.it
MODICA	MARIA NUNZIATA	UNIVERSITA' DI CATANIA	mmodica@unict.it
MOLINARI	RAFFAELE	UNIVERSITA' DELLA CALABRIA	r.molinari@unical.it

MOLINARI	CHIARA	UNIVERSITA' DI BOLOGNA	ciara.molinari10@unibo.it
MONACO	SIMONE	UNIVERSITA' DI BOLOGNA	simone.monaco2@unibo.it
MONACO	GUGLIELMO	UNIVERSITA' DI SALERNO	gmonaco@unisa.it
MONARI	MAGDA	UNIVERSITA' DI BOLOGNA	magda.monari@unibo.it
MONTALBANO	ALESSANDRA	UNIVERSITA' DI PALERMO	alessandra.montalbano@unipa.it
MONTANARI	SERENA	UNIVERSITA' DI BOLOGNA	serena.montanari5@unibo.it
MONTESARCHIO	DANIELA	UNIVERSITA' "FEDERICO II" DI NAPOLI	daniela.montesarchio@unina.it
MONTI	MARIA CHIARA	UNIVERSITA' DI SALERNO	mcmonti@unisa.it
MONTINI	TIZIANO	UNIVERSITA' DI TRIESTE	tmontini@units.it
MOR	MARCO	UNIVERSITA' DI PARMA	marco.mor@unipr.it
MORACA	FEDERICA	UNIVERSITA' DI CATANZARO	
MORELLI	SABRINA	ITM-CNR, RENDE	s.morelli@itm.cnr.it
MORETTI	ELISA	UNIVERSITA' CA' FOSCARI VENEZIA	elisa.moretti@unive.it
MORO	GIORGIO	UNIVERSITA' DI MILANO-BICOCCA	giorgio.moro@unimib.it
MORSELLI	LUCIANO	UNIVERSITA' DI BOLOGNA	luciano.morselli@unibo.it
MOSCONE	DANILA	UNIVERSITA' TOR VERGATA	moscone@uniroma2.it
MUñOZ GARCIA	ANA BELEN	UNIVERSITA' DI NAPOLI FEDERICO II	anabelen.munozgarcia@unina.it
MURATORE	NICOLA	UNIVERSITA' DI PALERMO	nicola.muratore@unipa.it
MURGIA	IRENE	UNIVERSITA' DI SASSARI	irenemurgia@gmail.com
MUSCO	GIOVANNA	UNIVERSITA' VITA-SALUTE S. RAFFAELE	
MUSIANI	MARCO	CNR-IENI PADOVA	m.musiani@ieni.cnr.it
MUSTARELLI	PIERCARLO	UNIVERSITA' DI PAVIA	piercarlo.mustarelli@unipv.it
MUSUMARRA	GIUSEPPE	UNIVERSITA' DI CATANIA	gmusumarra@unict.it
MUSUMECI	DOMENICA	UNIVERSITA' DI NAPOLI FEDERICO II	domymusu@alice.it
NAPOLI	ANNA	UNIVERSITA' DELLA CALABRIA	amc.napoli@unical.it
NARDI	MONICA	UNIVERSITA' DELLA CALABRIA	monica.nardi@unical.it
NATALINI	BENEDETTO	UNIVERSITA' DI PERUGIA	benedetto.natalini@unipg.it
NEGRI	FABRIZIA	UNIVERSITA' DI BOLOGNA	fabrizia.negri@unibo.it
NENCINI	LUCA	UNIVERSITA' DI TORINO	luca.nencini@unito.it
NERI	ESMERALDA	UNIVERSITA' DI BOLOGNA	esmeralda.neri@unibo.it
NERI	GIULIA	UNIVERSITA' DI MESSINA	nerig@unime.it
NERVI	CARLO	UNIVERSITA' DI TORINO	carlo.nervi@unito.it
NEVE	FRANCESCO	UNIVERSITA' DELLA CALABRIA	f.neve@unical.it
NICOTERA	ISABELLA	UNIVERSITA' DELLA CALABRIA	isabella.nicotera@unical.it
NICOTRA	FRANCESCO	UNIVERSITA' DI MILANO-BICOCCA	francesco.nicotra@unimib.it
NITTI	ANDREA	UNIVERSITA' DI PAVIA	andrea.nitti01@universitadipavia.it
NOBILI	LARA	UNIVERSITA' DI BOLOGNA	laranobili@yahoo.it
NOSCHESE	ANNARITA	UNIVERSITA' DI SALERNO	annaritanoschese@gmail.com
OLIVA	ROSANGELA	UNIVERSITA' DI FIRENZE	rosangela.oliva@unifi.it
OLIVERI	PAOLO	UNIVERSITA' DI GENOVA	oliveri@dictfa.unige.it
OLIVERIO	MANUELA	UNIVERSITA' MAGNA GRECIA DI CATANZARO	m.oliverio@unicz.it
OLIVO	GIORGIO	UNIVERSITA' "LA SAPIENZA" DI ROMA	giorgio.olivo@uniroma1.it
OLIVO	ALBERTO	UNIVERSITA' CA' FOSCARI VENEZIA	albertoolivo@hotmail.it
ONGARO	MICHAEL	UNIVERSITA' CA'FOSCARI DI VENEZIA	michael.ongaro@unive.it

ORTICA	FAUSTO	UNIVERSITA' DI PERUGIA	fausto.ortica@unipg.it
OTTANA'	ROSARIA	UNIVERSITA' DI MESSINA	rottana@unime.it
PACCHIONI	GIANFRANCO	UNIVERSITA' MILANO BICOCCA	gianfranco.pacchioni@unimib.it
PAGANINI	MARIA CRISTINA	UNIVERSITA' DI TORINO	mariacristina.paganini@unito.it
PAGANO	BRUNO	UNIVERSITA' DI NAPOLI FEDERICO II	bruno.pagano@unina.it
PALATINO	VITO	WATERS SPA	vito_palatino@waters.com
PALAZZI	SERGIO	ISIS DI SETIFICIO COMO	sergio@kemia.it
PALCHETTI	ILARIA	UNIVERSITA' DI FIRENZE	ilaria.palchetti@unifi.it
PALLESCHI	GIUSEPPE	UNIVERSITA' DI ROMA TOR VERGATA	palleschi@uniroma2.it
PALMIERI	MADDALENA	SECONDA UNIVERSITA' DI NAPOLI	maddalena.palmieri@unina2.it
PALMIERI	ALESSANDRO	UNIVERSITA' DI CAMERINO	alessandro.palmieri@unicam.it
PALMISANO	FRANCESCO	UNIVERSITA' DI BARI	francesco.palmisano@uniba.it
PALMISANO	LEONARDO	UNIVERSITA' DI PALERMO	leonardo.palmisano@unipa.it
PALUMBO	FABIO SALVATORE	UNIVERSITA' DI PALERMO	fabiosalvatore.palumbo@unipa.it
PALUMBO	CHIARA	ISTM-CNR MILANO	c.palumbo@istm.cnr.it
PANNUZZO	MARTINA	UNIVERSITA' DI CATANIA	martina.pannuzzo@gmail.com
PANZELLA	LUCIA	UNIVERSITA' DI NAPOLI "FEDERICO II"	panzella@unina.it
PAOLINO	MARCO	UNIVERSITA' DI SIENA	paomar@oneonline.it
PAPA	ELETTRA	ISTEC-CNR - FAENZA	elettra.papa@istec.cnr.it
PAPALIA	TERESA	UNIVERSITA' DI MESSINA	tpapalia@unime.it
PAPPALARDO	VALERIA	ISTM-CNR MILANO	valeria.pappalardo@istm.cnr.it
PAPPALARDO	MATTEO	UNIVERSITA' DI CATANIA	mpappala@unict.it
PARISI	MELCHIORRE	UNIVERSITA' DI MESSINA	mparisi@unime.it
PARRI	ERICA	UNIVERSITA' DI PISA	erica.parri86@gmail.com
PARRINO	FRANCESCO	UNIVERSITA' DI PALERMO	francesco.parrino@unipa.it
PASQUINI	BENEDETTA	UNIVERSITA' DI FIRENZE	benedetta.pasquini@unifi.it
PASSARINI	FABRIZIO	UNIVERSITA' DI BOLOGNA	fabrizio.passarini@unibo.it
PATERNO'	ALESSIO	UNIVERSITA' DI CATANIA	paternoalessio@unict.it
PAVARELLI	GIULIA	UNIVERSITA' DI BOLOGNA	
PAVONE	MICHELE	UNIVERSITA DI NAPOLI FEDERICO II	michele.pavone@unina.it
PECORARO	CLAUDIO MARIA	UNIVERSITA' DI PALERMO	claudiompecoraro@gmail.com
PEDONE	ALFONSO	UNIVERSITA' DI MODENA E REGGIO EMILIA	alfonso.pedone@unimore.it
PELLACANI	LUCIO	UNIVERSITA' DI ROMA LA SAPIENZA	lucio.pellacani@uniroma1.it
PERATHONER	SIGLINDA	UNIVERSITA' DI MESSINA	perathon@unime.it
PERAZZOLO	VALENTINA	UNIVERSITA' DI PADOVA	valentina.perazzolo@studenti.unipd.it
PEREZ	VIRGINIA	UNIVERSITA' ROMA LA SAPIENZA	virginia.perez@uniroma1.it
PERI	FRANCESCO	UNIVERSITA' MILANO BICOCCA	francesco.peri@unimib.it
PERNA	FILIPPO MARIA	UNIVERSITA' DI BARI	filippo.perna@uniba.it
PERRI	ENZO		enzo.perri@entecra.it
PERRONE	MARIA GRAZIA	UNIVERSITA' DI MILANO BICOCCA	grazia.perrone@unimib.it
PERRONE	SERENA	UNIVERSITA' DEL SALENTO	serena.perrone@unisalento.it
PERUZZINI	MAURIZIO	ICCOM CNR FIRENZE	maurizio.peruzzini@iccom.cnr.it
PESAVENTO	MARIA		
PETROPOULOS	KONSTANTINOS	UNIVERSITA' DI ROMA TOR VERGATA	konstantinos.petropoulos@uniroma2.it
PETTIGNANO	ALBERTO	UNIVERSITA' DI PALERMO	alberto.pettignano@unipa.it

PETTINARI	CLAUDIO	UNIVERSITA' DI CAMERINO	claudio.pettinari@unicam.it
PETTINARI	RICCARDO	UNIVERSITA' DI CAMERINO	riccardo.pettinari@unicam.it
PIAZZALUNGA	ANDREA	UNIVERSITA' MILANO BICOCCA	andrea.piazzalunga@unimib.it
PIAZZESE	DANIELA	UNIVERSITA' DI PALERMO	daniela.piazzese@unipa.it
PIAZZETTA	PAOLO	UNIVERSITA' DELLA CALABRIA	paolo.piazzetta@unical.it
PICCI	NEVIO	UNIVERSITA' DELLA CALABRIA	nevio.picci@unical.it
PICCIALLI	GENNARO	UNIVERSITA' DI NAPOLI FEDERICO II	picciall@unina.it
PICCOLO	ORESTE	STUDIO CONSULENZA SCIENTIFICA	contact@scsop.it
PIERINI	MARCO	UNIVERSITA' ROMA LA SAPIENZA	marco.pierini@uniroma1.it
PIETROPAOLO	ADRIANA	UNIVERSITA' DI CATANZARO	apietropaolo@unicz.it
PIFFERI	VALENTINA	UNIVERSITA' DI MILANO	
PIGNATARO	LUCA LUIGI	UNIVERSITA' DI MILANO	luca.pignataro@unimi.it
PIGNATARO	FRANCESCO	MAPEI S.P.A.	f.pignataro@vinavil.it
PINI	MARTINA	UNIVERSITA' DI MODENA E REGGIO EMILIA	martina.pini@unimore.it
PINZAUTI	SERGIO	UNIVERSITA' DI FIRENZE	pinz@unifi.it
PIOTTO PIOTTO	STEFANO	UNIVERSITA' DI SALERNO	piotto@unisa.it
PIPERNO	ANNA	UNIVERSITA' DI MESSINA	apiperno@unime.it
PIRILLO	JENNY	UNIVERSITA' DELLA CALABRIA	jenni386@libero.it
PIRRONE	NICOLA		
PISANI	LEONARDO		
PITEA	DEMETRIO	UNIVERSITA' MILANO BICOCCA	demetrio.pitea@unimib.it
PLASTINA	PIERLUIGI	UNIVERSITA' DELLA CALABRIA	pierluigi.plastina@unical.it
POCCI	MARCO	UNIVERSITA' DI GENOVA	pocci@difar.unige.it
POCE	GIOVANNA	SAPIENZA UNIVERSITA' DI ROMA	giovanna.poce@uniroma1.it
POGNI	REBECCA	UNIVERSITA' DI SIENA	rebecca.pogni@unisi.it
POMELLI	CHRISTIAN SILVIO	UNIVERSITA' DI PISA	pomelli@farm.unipi.it
PORCHETTA	ALESSANDRO	UNIVERSITA' DI ROMA TOR VERGATA	alessandro.porchetta@uniroma2.it
PORTALONE	GUSTAVO	"SAPIENZA" UNIVERSITA' DI ROMA	gustavo.portalone@uniroma1.it
POZZI	CECILIA	UNIVERSITA' DI SIENA	pozzi4@unisi.it
PRATI	SILVIA	UNIBO	s.prati@unibo.it
PREDIERI	GIOVANNI	UNIVERSITA' DI PARMA	predieri@unipr.it
PREZIOSO	GINA	IIS "E.SICILIANO" BISIGNANO	gina.prezioso@alice.it
PROFETA	ROBERTO	APTUIT	roberto.profeta@aptuit.com
PROTTI	MICHELE	UNIVERSITA' DI BOLOGNA	michele.protti2@unibo.it
PSARO	RINALDO	CNR-ISTM MILANO	r.psaro@istm.cnr.it
PUCCI	PIETRO	UNIVERSITA' DI NAPOLI FEDERICO II	pucci@unina.it
PULEO	FABRIZIO	ISMN-CNR PALERMO	fabrizio.puleo@mail.pa.ismn.cnr.it
PUNZI	ANGELA	UNIVERSITA' DI BARI	angela.punzi@uniba.it
PURRELLO	ROBERTO	UNIVERSITA' DI CATANIA	rpurrello@unict.it
PYNALYSA	COSMA	UNIVERSITA' DI BARI	pinalysa.cosma@uniba.it
QUAGLIOTTO	PIERLUIGI	UNVIERSITA' DI TORINO	pierluigi.quagliotto@unito.it
RAFFO	SIMONA	UNIVERSITA' DI BOLOGNA	simona.raffo2@unibo.it
RAGAINI	FABIO	UNIVERSITA' DI MILANO	fabio.ragaini@unimi.it

RAGGI	MARIA AUGUSTA	UNIVERSITA' DI BOLOGNA	mariaaugusta.raggi@unibo.it
RAGNO	GAETANO	UNIVERSITA' DELLA CALABRIA	ragno@unical.it
RANALLO	SIMONA	UNIVERSITA' DI ROMA TOR VERGATA	simona.ranallo@uniroma2.it
RANDAZZO	ANTONIO	UNIVERSITA' DI NAPOLI	antranda@unina.it
RANDAZZO	ROSALBA	UNIVERSITA' DI CATANIA	rrandazzo@unict.it
RANIERI	SILVIA	UNIVERSITA' DI BOLOGNA	silvia.ranieri2@unibo.it
RAPINI	RICCARDO	UNIVERSITA' DI FIRENZE	riccardo.rapini@unifi.it
RASTRELLI	FEDERICO	UNIVERSITA' DI PADOVA	federico.rastrelli@unipd.it
RAUT	DNYANESHWAR	UNIVERSITA' DELLA CALABRIA	dsraut47@gmail.com
RE	NAZZARENO	UNIVERSITA' DI CHIETI	nre@unich.it
REBOLLO SAN MIGUEL	ELENA PAZ	CNR-IENI PADOVA	elena.rebollo@ieni.cnr.it
REBUGHINI	STEFANO	POLITECNICO DI MILANO	
RECANATINI	MAURIZIO	UNIVERSITA' DI BOLOGNA	maurizio.recanatini@unibo.it
REGINI	GIORGIA	UNIVERSITA' DI TRIESTE	giorgia.regini@studenti.units.it
REGIS	ALBERTO	DD-SCI	reg.al@alice.it
RELLA	SIMONA	UNIVERSITA' DEL SALENTO	simona.rella@unisalento.it
RICCARDI	CLAUDIA	UNIVERSITA' DI NAPOLI FEDERICO II	riccardiclaudia90@gmail.com
RICCI	FRANCESCO		
RICCI	ANTONIO	FRESENIUS KABI ANTI-INFECTIVES	antonio.ricci@fresenius-kabi.com
RICCI	GIULIA	UNIVERSITA' CA'FOSCARI - VENEZIA	giulia.ricci@stud.unive.it
RICCIARDI	LOREDANA	UNIVERSITA' DELLA CALABRIA	loredana.ricciardi@unical.it
RICCIO	RAFFAELE	UNIVERSITA' DI SALERNO	presidente@soc.chim.it
RIGHINI	ROBERTO		
RISOLUTI	ROBERTA	UNIVERSITA' ROMA LA SAPIENZA	roberta.risoluti@uniroma1.it
RITACCO	IDA	UNIVERSITA' DELLA CALABRIA	ida.ritacco@unical.it
RIVA	RENATA	UNIVERSITA' DI GENOVA	riva@chimica.unige.it
RIVALTA	IVAN	CNRS-LYON	ivan.rivalta@ens-lyon.fr
RIVOIRA	LUCA	UNIVERSITA' DI TORINO	luca.rivoira@unito.it
RIZZATO	SILVIA	UNIVERSITA' DI MILANO	silvia.rizzato@unimi.it
RIZZI	VITO	UNIVERSITA' DI BARI	vito.rizzi@uniba.it
RIZZI	GIAN ANDREA	UNIVERSITA' DI PADOVA	gianandrea.rizzi@unipd.it
RIZZO	SIMONA		
ROCCHIGIANI	LUCA	UNIVERSITA' DI PERUGIA	luca.rocchigiani@progetti.unipg.it
RODRIGUEZ	VICTORIA		
ROMANAZZO	DANIELA	UNIVERSITA' TOR VERGATA ROMA	daniela.romanazzo@uniroma2.it
ROMANELLI	ALESSANDRA	UNIVERSITA' DI NAPOLI "FEDERICO II"	alessandra.romanelli@unina.it
ROMBOLA'	ALESSANDRO GIROLAMO	UNIVERSITA' DI BOLOGNA	alessandro.rombola@unibo.it
ROMEO	ROBERTO		
ROMEO	GIOVANNI	UNIVERSITA' DI MESSINA	gromeo@unime.it
ROMIO	EMANUELA	UNIVERSITA' DELLA CALABRIA	romio.emanuela@yahoo.it
ROSATI	ORNELIO	UNIVERSITA' DI PERUGIA	ornelio.rosati@unipg.it
ROSATO	ANTONIO	UNIVERSITA' DI FIRENZE	rosato@cerm.unifi.it
ROSESTOLATO	DAVIDE	UNIVERSITA' DI FERRARA	rssdvd@unife.it
ROSINI	MICHELA	UNIVERSITA' DI BOLOGNA	michela.rosini@unibo.it
ROSSETTI	ILENIA	UNIVERSITA' DI MILANO	ilenia.rossetti@unimi.it

ROSSI	FEDERICO	UNIVERSITA' DI SALERNO	frossi@unisa.it
ROSSI	BIANCA	POLITCNICO DI MILANO	bianca.rossi@polimi.it
ROSSI	ANTONELLA	UNIVERSITA' DI CAGLIARI	rossi@unica.it
ROVIELLO	ANTONIO	UNIVERSITA' NAPOLI FEDERICO II	antonio.roviello@unina.it
RUSSO	VINCENZO	UNIVERSITA' DI NAPOLI "FEDERICO II"	v.russo@unina.it
RUSSO	FLORIANA	SECONDA UNIVERSITA' DI NAPOLI	floriana.russo@unina2.it
RUSSO	VINCENZO	MAPEI SPA	s_laboratorio@mapei.it
RUSSO	NINO	UNIVERSITA' DELLA CALABRIA	nrusso@unical.it
RUSSO	BEATRICE	UNIVERSITA' DELLA CALABRIA	beatrice.russo@unical.it
RUSSOMANNO	ANNA	CNR NAPOLI	anna.russomanno@gmail.com
SABBATINI	LUIGIA	UNIVERSITA' DI BARI ALDO MORO	luigia.sabbatini@uniba.it
SABUZI	FEDERICA	UNIVERSITA' ROMA TOR VERGATA	federica.sabuzi@uniroma2.it
SAIANO	FILIPPO	UNIVERSITA' DI PALERMO	filippo.saiano@unipa.it
SAIELLI	GIACOMO	CNR ITM PADOVA	giacomo.saielli@unipd.it
SAIELLO	SILVANA	UNIVERSITA' DI NAPOLI	silvana.saiello@unina.it
SAKHNO	YURIY	UNIVERSITA' DI TORINO	sakhnoyura@alice.it
SALADINO	MARIA LUISA	UNIVERSITA' DI PALERMO	marialuisa.saladino@unipa.it
SALASSA	GIOVANNI	UNIVERSITA' DI PADOVA	giovanni.salassa@gmail.com
SALVADORI	SEVERO	UNIVERSITA' DI FERRARA	severo.salvadori@unife.it
SALVAGGIO	MARIA GRAZIA	UNIVERSITA' DI MESSINA	mgsalvaggio@unime.it
SALVESTRINI	STEFANO	SECONDA UNIVERSITA' DI NAPOLI	stefano.salvestrini@unina2.it
SALVI	ANNA MARIA	UNIVERSITA' DELLA BASILICATA	anna.salvi@unibas.it
SALVINI	ANTONELLA	UNIVERSITA' DI FIRENZE	antonella.salvini@unifi.it
SAMMARTANO	SILVIO	UNIVERSITA' DI MESSINA	ssammartano@unime.it
SANGION	ALESSANDRO	UNIVERSITA' DELL' INSUBRIA	a.sangion@hotmail.it
SANGUINETI	ELISA	UNIVERSITA' DI GENOVA	elisa.sanguineti@unige.it
SANNICOLO'	FRANCESCO	UNIVERSITA' DI MILANO	francesco.sannicolo@unimi.it
SANTORO	ANNA MARIA		
SANZ MENDIGUCHÍA	BÁRBARA	UNIVERSITA' DELLA CALABRIA	barbara.sanz@unical.it
SARACINO	MICHELA	CNR ISOF, BOLOGNA	michela.saracino@isof.cnr.it
SARACINO	MARIA ADDOLORATA	UNIVERSITA' DI BOLOGNA	maria.saracino5@unibo.it
SARDELLA	ROCCALDO	UNIVERSITA' DI PERUGIA	roccaldo.sardella@unipg.it
SARTI	ELENA	UNIVERSITA' DI FERRARA	srtlne@unife.it
SASSONE	FRANCESCA	UNIVERSITA' DI BARI	sassonefrancesca@gmail.com
SAVIANO	MICHELE	CNR BARI	msaviano@unina.it
SCAFATO	PATRIZIA	UNIVERSITA' DELLA BASILICATA	patrizia.scafato@unibas.it
SCARPONI	GIUSEPPE	UNIVERSITA' POLITECNICA DELLE MARCHE	g.scarponi@univpm.it
SCARSO	ALESSANDRO	UNIVERSITA' CA' FOSCARI DI VENEZIA	alesca@unive.it
SCHIMMENTI	ROBERTO	UNIVERSITA' DI PALERMO	robertoschimmenti89@gmail.com
SCIUTTO	GIORGIA	UNIVERSITA' DI BOLOGNA	giorgia.sciutto2@unibo.it
SCRIMIN	PAOLO	UNIVERSITA' DI PADOVA	paolo.scrimin@unipd.it
SEEBER	RENATO	UNIVERSITA' DI MODENA E REGGIO EMILIA	renato.seeber@unimore.it
SELLARO	MIRIAM	ITM-CNR, RENDE	m.sellaro@itm.cnr.it
SELLERI	TOMMASO	POLITECNICO DI MILANO	
SELLI	ELENA	UNIVERSITA' DI MILANO	elena.selli@unimi.it

SEMENZIN	ELENA	UNIVERSITA' CA' FOSCARI DI VENEZIA	semenzin@unive.it
SEMERANO	PAOLA	UNIVERSITA' DI BARI	paola.semeraro@uniba.it
SENOCRATE	ALESSANDRO	UNIVERSITA' DI PAVIA	haloxp@gmail.com
SEPE	VALENTINA	UNIVERSITA' DI NAPOLI "FEDERICO II"	valentina.sepe@unina.it
SERAFINI	ILARIA	UNIVERSITA' ROMA LA SAPIENZA	ilaria.serafini@uniroma1.it
SEVERI	MIRKO		
SGANAPPA	AURORA	POLITECNICO DI MILANO	aurora.sganappa@polimi.it
SIANI	GABRIELLA	UNIVERSITA' CHIETI-PESCARA	siani@unich.it
SICILIA	EMILIA	UNIVERSITA' DELLA CALABRIA	siciliae@unical.it
SILVESTRI	ROMANO	SAPIENZA UNIVERSITA' DI ROMA	romano.silvestri@uniroma1.it
SINGH	MANDEEP		
SINICROPI	ADALGISA	UNIVERSITA' DI SIENA	adalgisa.sinicropi@unisi.it
SOLDATI	ROBERTO	UNIVERSITA' DI BOLOGNA	roberto.soldati3@unibo.it
SONEGO	SANDRA	MIUR	
SPADA	LORENZO	UNIVERSITA' DI BOLOGNA	lorenzo.spada5@unibo.it
SPATAFORA	CARMELA	UNIVERSITA' DI CATANIA	cspatafo@unict.it
SPELTINI	ANDREA	UNIVERSITA' DI PAVIA	andrea.speltini@unipv.it
SPOTO	GIUSEPPE	UNIVERSITA' DI CATANIA	spotog@unict.it
STABILE	GAETANO	UNIVERSITA' DELLA CALABRIA	gaetanostabile75@libero.it
STAMA	MADIA LETIZIA	UNIVERSITÀ DI BARI	madiastama@alice.it
STENER	MAURO	UNIVERSITA' DI TRIESTE	stener@units.it
STORARO	LORETTA	UNIVERSITA' DI VENEZIA	storaro@helios.unive.it
STROCCHIA	MARIA	UNIVERSITA' DI SALERNO	mstrocchia@unisa.it
STRUKUL	GIORGIO	UNIVERSITA' CA' FOSCARI VENEZIA	strukul@unive.it
STUCCHI	MATTIA	UNIVERSITA' DI MILANO	
SUFFRITTI	GIUSEPPE BALDOVINO	UNIVERSITA' DI SASSARI	pino@uniss.it
SUGINOME	MICHINORI	KYOTO UNIVERSITY	suginome@sbchem.kyoto-u.ac.jp
SUPERCHI	STEFANO	UNIVERSITA' DELLA BASILICATA	stefano.superchi@unibas.it
TAFUR MARINOS	JANETH ALICIA	UNIVERSITA' DI TORINO	janethalicia.tafurmarinos@unito.it
TAGARELLI	ANTONIO	UNIVERSITA' DELLA CALABRIA	a.tagarelli@unical.it
TALARICO	CARMINE	UNIVERSITA' MAGNA GRAECIA DI CATANZARO	carmine.talaricox@gmail.com
TALARICO	DARIA	UNIVERSITA' DI ROMA TOR VERGATA	daria.talarico@uniroma2.it
TANGORRA	ROCCO ROBERTO	UNIVERSITA' DI BARI	r.tangorra@ba.ipcf.cnr.it
TASSINARI	FRANCESCO		francesco.tassinari@gmail.com
TAVERNA	DOMENICO	UNIVERSITA' DELLA CALABRIA	
TEGHIL	ROBERTO	UNIVERSITA' DELLA BASILICATA	roberto.teghil@unibas.it
TEMPERINI	ANDREA	UNIVERSITA' DI PERUGIA	andrea.temperini@unipg.it
TERENZI	ALESSIO	UNIVERSITA' DI PALERMO	alessio.terenzi@unipa.it
TERRACCIANO	STEFANIA	UNIVERSITA' DI SALERNO	sterracciano@unisa.it
TERZI	FABIO	UNIVERSITA' DI MODENA E REGGIO EMILIA	fabio.terzi@unimore.it
TESTONI	ANTONIO	IIS "COPERNICO CARPEGGIANI"	ajteston@tin.it
TING	TERESA	DIP. CHIMICA	teresa.ting@unical.it
TESTA	MARIA LUISA	CNR-ISMN PALERMO	marialuisa.testa@cnr.it
TOCCI	ELENA	CNR-ITM RENDE	e.tocci@itm.cnr.it

TODESCHINI	ROBERTO	UNIVERSITA' DI MILANO BICOCCA	roberto.todeschini@unimib.it
TOMASINI	CLAUDIA	UNIVERSITA' DI BOLOGNA	claudia.tomasini@unibo.it
TOMMASONE	STEFANO	UNIVERSITA' DI SALERNO	stommasone@unisa.it
TONIOLO	ROSANNA	UNIVERSITA' DI UDINE	rosanna.toniolo@uniud.it
TORRIELLI	GIULIA	UNIVERSITA' DI GENOVA	giulia.torrielli@libero.it
TOSCANO	MARIROSA	UNIVERSITA' DELLA CALABRIA	m.toscano@unical.it
TRAVERSI	RITA	UNIVERSITA' DI FIRENZE	rita.traversi@unifi.it
TREVISAN	VALENTINA	UNIVERSITA' CA' FOSCARI VENEZIA	valentina.trevisan@unive.it
TRIFIRO'	FERRUCCIO	UNIVERSITA' DI BOLOGNA	ferruccio.trifiro@unibo.it
TRIGGIANI	LEONARDO	UNIVERSITA' DI BARI	leonardo.triggiani@uniba.it
TROISI	LUIGINO	UNIVERSITA' DEL SALENTO	luigino.troisi@unisalento.it
TROMBINI	CLAUDIO	UNIVERSITA' DI BOLOGNA	claudio.trombini@unibo.it
TUMMINO	MARIA LAURA	UNIVERSITA' DI TORINO	marialaura.tummino@unito.it
TUNDO	PIETRO		
TURANO	MARIA	MIUR	maria.turano@fastwebnet.it
TURCO	ANTONIO	UNIVERSITA' DEL SALENTO	antonio.turco@unisalento.it
TURCO	ROSA	UNIVERSITA' DI NAPOLI FEDERICO II	rosa.turco@unina.it
UDISTI	ROBERTO	UNIVERSITA' DI FIRENZE	udisti@unifi.it
UGLIENGO	PIERO	UNIVERSITA' DI TORINO	piero.ugliengo@unito.it
ULISSI	ULDERICO	UNIVERSITA' SAPIENZA - ROMA	ulderico.ulissi@uniroma1.it
URSINO	CLAUDIA	ITM-CNR - RENDE	claudiaursino@gmail.com
VALENTI	CRISTINA	I.N.B.B. ROMA	cristy.valenti@gmail.com
VALENTI	GIOVANNI	UNIVERSITA' DI BOLOGNA	g.valenti@unibo.it
VALENTINI	FEDERICA	UNIVERSITA' ROMA TOR VERGATA	federica.valentini@uniroma2.it
VALLI	LUDOVICO	UNIVERSITA' DEL SALENTO	ludovico.valli@unisalento.it
VANGONE	PAOLO	UNIVERSITA' DELLA CALABRIA	paolovangone@gmail.com
VANORE	PAOLA	SECONDA UNIVERSITA' DI NAPOLI	paolavanore@alice.it
VARDE'	MASSIMILIANO	CNR-ITA RENDE	varde@iia.cnr.it
VASSURA	IVANO	UNIVERSITA' DI BOLOGNA	ivano.vassura@unibo.it
VAZQUEZ GOMEZ	LOURDES	IENI-CNR PADOVA	l.vazquez@ieni.cnr.it
VELTRI	LUCIA	UNIVERSITA' DELLA CALABRIA	lucia.veltri@unical.it
VENANZI	MARIANO	UNIVERSITA' DI ROMA 'TOR VERGATA'	venanzi@uniroma2.it
VENDITTI	ALESSANDRO	UNIVERSITA' ROMA LA SAPIENZA	alessandro.venditti@uniroma1.it
VENDITTI	IOLE	UNIVERSITA' DI ROMA SAPIENZA	iole.venditti@uniroma1.it
VERRELLI	ROBERTA	UNIVERSITA' SAPIENZA - ROMA	roberta.verrelli@uniroma1.it
VILLANI	GIOVANNI	ICCOM (UOS PISA)	villani@pi.iccom.cnr.it
VILLANI	VINCENZO	UNIVERSITA' DELLA BASILICATA	vincenzo.villani@unibas.it
VINCENTI	MARCO	UNIVERSITA' DI TORINO	marco.vincenti@unito.it
VIONE	DAVIDE	UNIVERSITA' DI TORINO	davide.vione@unito.it
VITIELLO	ROSA	UNIVERSITA' DI NAPOLI FEDERICO II	rosa.vitiello@unina.it
VITILLO	JENNY G.	UNIVERSITA' DELL' INSUBRIA	jenny.vitillo@uninsubria.it
VIZZA	FRANCESCO	CNR	francesco.vizza@iccom.cnr.it
VOCCIA	DIEGO	UNIVERSITA' DI FIRENZE	diego.voccia@unifi.it

VOLPE	GIULIA	UNIVERSITA' DI ROMA TOR VERGATA	giulia.volpe@uniroma2.it
VURCHIO	CAROLINA	UNIVERSITA' DI FIRENZE	carolina.vurchio@unifi.it
ZAMPELLA	ANGELA	UNIVERSITA' DI NAPOLI FEDERICO II	azampell@unina.it
ZANETTA	TITO	VINAVIL SPA	t.zanetta@vinavil.it
ZANOTTI	VALERIO	UNIVERSITA' DI BOLOGNA	valerio.zanotti@unibo.it
ZAPPALA'	MARIA	UNIVERSITA' DI MESSINA	mzappala@unime.it
ZERBETTO	MIRCO	UNIVERSITA' DI PADOVA	mirco.zerbetto@unipd.it
ZERBETTO	FRANCESCO	UNIVERSITA' DI BOLOGNA	francesco.zerbetto@unibo.it
ZICCARELLI	IDA	UNIVERSITA' DELLA CALABRIA	idaziccarelli@gmail.com
ZIOSI	PAOLO	UNIVERSITA' DI BOLOGNA	
ZITO	PASQUALE FRANCESCO	UNIVERSITA' DELLA CALABRIA	pasqualezito@hotmail.it
ZONTA	CRISTIANO	UNIVERSITA' DI PADOVA	cristiano.zonta@unipd.it