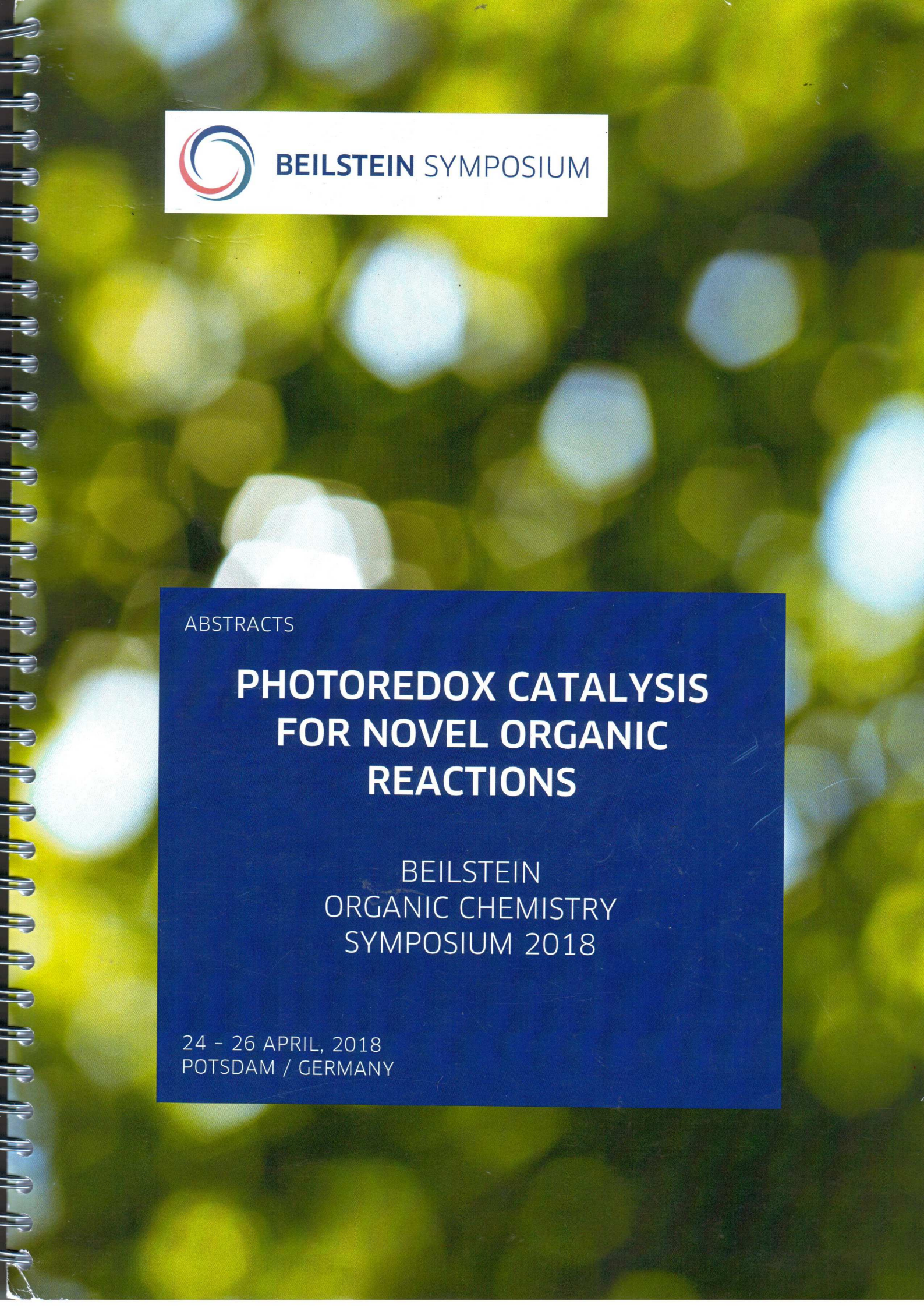
BEILSTEIN SYMPOSIUM
ABSTRACTS
PHOTOREDOX CATALYSIS FOR NOVEL ORGANIC REACTIONS
BEILSTEIN ORGANIC CHEMISTRY SYMPOSIUM 2018
24 - 26 APRIL, 2018
POTSDAM / GERMANY

Poster

No. 18

Carbon nitride-hydrogen peroxide adduct for selective photo-oxidation

Igor Krivtsov[a], M. Ilkaeva[b], E.I. García-López[c], G. Marcì[c], L. Palmisano[c], E. Díaz[a] and S. Ordóñez[a]

[a]Department of Chemical and Environmental Engineering, University of Oviedo, Spain

[b]Department of Organic and Inorganic Chemistry, University of Oviedo, Spain

[c]Dipartimento di Energia, Ingegneria dell'informazione e modelli Matematici, University of Palermo, Italy

Polymeric carbon nitride (PCN) is a semiconductor photocatalyst possessing some exceptional electronic and surface properties. PCN can be activated by UV and visible-light due Its relatively narrow band-gap of 2.7 eV, which makes it a promising material for the solar irradiation harvesting. Moreover, the inability of PCN to produce •OH radicals by the direct water oxidation owing to the low VB potential and its readiness to reduce O_2 to $\bullet O_2^-$ are the prerequisites of the efficient catalyst for partial photo-oxidation of certain organic compounds to high added value chemicals. Nonetheless, achieving high selectivity of organic molecules conversion in aqueous medium is hampered by the presence of partially polymerised and non-polymerised carbon nitride species. The PCN-H_2O_2 adduct synthesised by the reaction of aqueous H_2O_2 with thermally etched PCN favours improved selectivity of the UV- and sunlight-assisted oxidation of benzylic C–H bond, aromatic alcohols to the corresponding aldehydes and a biomass platform molecule 5-hydroxymethyl furfural (HMF) to 2,5-furandicarboxaldehyde (FDC).1,2 Hydrogen peroxide in PCN-H_2O_2 adduct attaches to the carbon nitride surface species by forming strong hydrogen bonds with NH_2 and heptazine nitrogen atoms. The obtained adduct is found to be stable in water, organic solvents under heating or light-irradiation, or if thermally treated in air up to 200 °C. Its high selectivity in partial photo-oxidation reactions is explained by the steric hindrance created by the bonded H_2O_2, which does not permit the interaction of substrate molecules with the non-polymerised carbon nitride species, where supposedly unselective hydroxyl radicals are produced as a consequence of H_2O reaction with NH_2-containing sites.

1. M. Ilkaeva, I. Krivtsov, E. Bartashevich, S.A. Khainakov, J.R. García, E. Díaz, S. Ordóñez, Green Chem., 2017, 19, 4299.
2. M. Ilkaeva, I. Krivtsov, E.I. García-López, G. Marcì, O. Khainakova, J.R. García, L. Palmisano, E. Díaz, S. Ordóñez, J. Catal., 2018, Accepted.