ARTICLE

Solvatochromic behaviour of new donor-acceptor oligothiophenes

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Oligothiophene derivatives play a central role in the formulation of materials used in devices in the field of organic electronics. In this work we report the results of the study of UV-Vis absorption and fluorescence spectra, in several solvents, of a series of oligothiophenes recently synthesized in our laboratory. The studied oligothiophenes present different structures due to several factors: the Donor-Acceptor (D-A) or Acceptor-Donor-Acceptor (A-D-A) architecture; the number of thiophene rings in the backbone (ranging from three to eight); the number and position of solubilizing octyl chains in the backbone, and the type of acceptor moieties (from Knoevenagel condensation either with ethyl cyanoacetate or 3-ethylrhodanine). Since solvents with different polarities were adopted, we provide a detailed analysis on the observed positive and negative solvatochromism effects depending on the symmetry of the oligomers, the lengths of the backbones and the kind of acceptors adopted. Moreover, an electrochemical synthesis of a new donor-acceptor oligothiophene (which can be assumed as a model compound) by anodic dimerization is reported, along with the voltammetric analysis of the obtained product.

Introduction

Organic semiconductors represent the key element on which the concept of Organic Electronics is based.[1,2]
Among them, the most important role is certainly that played by thiophene derivatives, both in polymeric and oligomeric form.[3]
A large number of these compounds can be found, for example, in organic light-emitting diodes,[4-7] organic thin film transistors,[8,9] organic solar cells,[10–15] organic photodetectors.[16]
Thiophene-based materials have excellent charge transport properties, however, oligothiophenes, compared to the more commonly used polythiophenes, have undeniable advantages due to the possibility of being synthesized with exactly defined structures, with greater purity and cost-effectiveness. We have synthesized oligothiophenes with different number of monomer units based on donor-acceptor (D-A) and acceptor-donor-acceptor (A-D-A) architectures, using different donor cores and acceptor end groups. The syntheses were carried out not only by classical organic chemistry but also by means of anodic dimerizations; in this way it has been shown that, in addition to providing important information such as HOMO and LUMO energy levels, electrochemistry is also useful for shortening and simplifying otherwise long synthetic processes.

To have insights into some physico-chemical properties of our oligothiophenes, especially regarding their use in optoelectronic devices, solvatochromic studies can be carried out.
In general, solvatochromism regards the effect of the probe surrounding (solvent) on its spectroscopic properties.[19]
In particular, during energy absorption, the electrons pass from the ground state to the excited state, and, after possible non radiative energy dissipation, they return to the ground state with energy emission. The solvent (probe surrounding) can influence differentially both ground and excited states, leading to a bathochromic or a hypsochromic shift with respect to a reference solvent. The structure of our oligothiophenes (donor, acceptor, π-bridge) allows for both dipole and dispersion interactions, possibly leading to interactions of different extent between solvent and ground state molecule and excited state one varying the nature and thus the physico-chemical properties of the solvent.
As the absorption and emission wavelengths of compounds used in optoelectronics (both pure and in solution) are highly important, a solvatochromic study prior to their use in real devices is of crucial importance.

Experimental

Materials and methods

Compounds **T2T**, **BT2T**, **T1N**, **T2N**, **BT1N**, **BT1C**, **BT2N**, **BT2C**, **BT4N**, **BT6N**, **D8N** were synthesized and characterized as recently reported.[17,18] Thin layer chromatography was carried out using Alugram SIL G/UV254 plates and visualized under UV

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Electronic Supplementary Information (ESI) available: absorption UV-Vis spectra; emission spectra; plots λ_{abs} vs $E_T(30)$; plots λ_{em} vs $E_T(30)$; Lippert-Mataga equation plots. See DOI: 10.1039/x0xx00000x

light (at 254 and/or 365 nm). Flash chromatography was carried out using Silica Gel 60 (0.04-0.063 mm). ^{1}H and ^{13}C-NMR spectra were acquired on a Bruker AVANCE-400 spectrometer at 9.4 T, in $CDCl_3$ at 27 °C. The residual signals for the NMR solvent ($CDCl_3$) are 77.16 ppm (^{13}C) and 7.27 ppm (^{1}H); the following abbreviations have been used for NMR assignment: s for singlet, d for doublet, t for triplet, q for quartet, quint for quintet and m for multiplet.

Voltammetric measurements were performed using an Amel System 5000 electrochemical workstation. Measurements were carried out under a nitrogen atmosphere in a conventional three electrode cell with a 492/GC/3 Amel microelectrode as the working electrode, a Pt wire as the counter electrode and a modified saturated calomel electrode as reference electrode (mSCE: SCE with organic solvent junction; the standard redox potential of the ferrocenium/ferrocene system is $E°(Fc^{+}/Fc)$ = +0.52 V *vs* SCE). All experiments were carried out at 25 °C, in anhydrous dichloromethane (DCM) with 0.1 M tetrabutylammonium tetrafluoroborate (Bu_4NBF_4), the concentration of the substrate was 1×10^{-2} M.

Chemical and electrochemical syntheses

Anodic Dimerization of ethyl 2-cyano-3-(3,3''-dioctyl-[2,2':5',2''-terthiophene]-5-yl)acrylate (T1N)

The electrolysis was carried out under nitrogen atmosphere at room temperature at constant potential of +1.4 V (*vs* mSCE), using an Amel Model 552 potentiostat equipped with an Amel Model 731 integrator. Pt spirals (apparent area 0.8 cm^2) were used as both cathode and anode. Catholyte (5 mL CH_2Cl_2-Bu_4NBF_4 0.1 M) and anolyte (5 mL CH_2Cl_2-Bu_4NBF_4 0.1 M, containing 0.28 mmol of **T1N**) were separated through a G-3 glass septum filled up with a layer of gel (*i.e.*, methyl cellulose 0.5% vol dissolved in DMF-Et_4NBF_4 1.0 M). The electrolysis was stopped after 75 C (2.7 F). Usual workup and flash column chromatography (eluent: petroleum ether/CH_2Cl_2 50/50, R_F=0.7 in CH_2Cl_2) gave Diethyl 3,3'-(3,3'',3'''',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2'''':5'''',2''''':5''''-sexithiophene]-5,5'''''-diyl)bis(2-cyanoacrylate) **D6N** as a dark violet solid with yellow metallic reflections in 62% yield. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.90 (12H, m); 1.31 (40H, m); 1.41 (6H, t, *J* = 7.2 Hz); 1.72 (8H, quint, *J* = 7.6 Hz); 2.80 (4H, t, *J* = 7.6 Hz); 2.86 (4H, t, *J* = 7.6 Hz); 4.38 (4H, q, *J* = 7.2 Hz); 7.06 (2H, s); 7.15 (2H, d, *J* = 4.0 Hz); 7.32 (2H, d, *J* = 4.0 Hz); 7.62 (2H, s); 8.23 (2H, s). ^{13}C NMR ($CDCl_3$) δ (ppm): 14.12, 14.25, 22.68, 29.27, 29.29, 29.39, 29.41, 29.47, 29.54, 29.61, 29.67, 30.24, 30.45, 31.86, 31.90, 62.43, 97.71, 116.07, 120.47, 126.18, 126.94, 128.28, 129.13, 132.96, 134.15, 135.36, 138.52, 140.55, 140.80, 141.30, 141.69, 145.98, 163.07.

Synthesis of 3,3'''',3''''',4'-tetraoctyl-[2,2':5',2'':5'',2''':5''',2'''':5'''',2''''':5'''''-sexithiophene]-5,5'''''-dicarbaldehyde (BT4F) and 3,4'-dioctyl-[2,2':5',2'':5'',2'''-quaterthiophene]-5-carbaldehyde (BTTF).

$Pd(PPh_3)_4$ (2 mol % respect to 5'-bromo-3,4'-dioctyl-[2,2'-bithiophene]-5-carbaldehyde) was added to a solution of 5'-bromo-3,4'-dioctyl-[2,2'-bithiophene]-5-carbaldehyde (0.248 g, 0.5 mmol) and 5,5'-bis(tributylstannyl)-2,2'-bithiophene (0.223 g, 0.30 mmol) in 15 mL of dry toluene under N_2, and the mixture was heated to gentle reflux for 24 h. After pouring the mixture into 20 mL of water, the organic phase was extracted with dichloromethane (DCM). The extract was successively washed with water, dried over Na_2SO_4 and evaporated in vacuo. The crude product was then purified with column chromatography (SiO_2; hexane) to give 3,3'''',3''''',4'-tetraoctyl-[2,2':5',2'':5'',2''':5''',2'''':5'''',2''''':5'''''-sexithiophene]-5,5'''''-dicarbaldehyde (**BT4F**) as a dark red oil (0.090 g, 36.0 % yield) and 0.097 g of 3,4'-dioctyl-[2,2':5',2'':5'',2'''-quaterthiophene]-5-carbaldehyde (**BTTF**) (55.5% yield).

3,3'''',3''''',4'-tetraoctyl-[2,2':5',2'':5'',2''':5''',2'''':5'''',2''''':5'''''-sexithiophene]-5,5'''''-dicarbaldehyde (BT4F): ^{1}H NMR ($CDCl_3$) δ (ppm): 0.88 (6H, m), 0.92 (6H, m), 1.29 (40H, m), 1.65 (4H, m), 2.81 (4H, m), 7.12 (6H, m), 7.58 (2H, s), 9.80 (2H, s). ^{13}C NMR ($CDCl_3$) δ (ppm): 13.69, 14.20, 17.58, 17.63, 20.88, 22.77, 23.93, 26.93, 27.94, 29.36, 29.50, 29.58, 29.80, 30.34, 30.54, 31.98, 124.25, 126.96, 130.50, 132.67, 132.91, 134.60, 137.25, 139.19, 140.16, 140.49, 140.53, 141.18, 182.59.

3,4'-dioctyl-[2,2':5',2'':5'',2'''-quaterthiophene]-5-carbaldehyde (BTTF): ^{1}H NMR ($CDCl_3$) δ (ppm): 0.90 (6H, m), 1.30 (24 H, m), 2.80 (4H, m), 7.05 (3H, m), 7.12 (1H, s), 7.22 (2H, m), 7.56 (1H, s), 9.81 (1H, s). ^{13}C NMR ($CDCl_3$) δ (ppm): 14.14, 22.70, 29.29, 29.36, 29.43, 29.51, 29.54, 30.25, 30.47, 31.90, 123.82, 124.01, 124.70, 126.76, 127.90, 130.34, 132.67, 134.08, 136.86, 137.75, 139.03, 140.03, 140.24, 141.06, 182.37.

Synthesis of ethyl 2-cyano-3-(3,4'-dioctyl-[2,2':5',2'':5'',2'''-quaterthiophene]-5-yl)acrylate (BTTN)

To a solution of 0.097 g (0.17 mmol) 3,4'-dioctyl-[2,2':5',2'':5'',2'''-quaterthiophene]-5-carbaldehyde (**BTTF**) in 20 mL of dry dichloromethane (DCM) were added 0.3 mL of triethylamine. Then 0.177 mL (1.7 mmol, d = 1.063 g mL^{-1}, 10 equiv) of ethyl cyanoacetate were added. The resulting solution was stirred overnight under nitrogen, at room temperature. The reaction mixture was then extracted with dichloromethane (DCM) (2x10 mL), washed with water, then brine and dried over Na_2SO_4. After removal of solvent, the mixture was purified by chromatography on silica gel using ethyl acetate/hexane (1:9) to afford the title compound as a black solid (0.098 g, 88.0 % yield). ^{1}H NMR ($CDCl_3$) δ (ppm): 0.86 (6H, m), 1.33 (27H, m), 2.80 (4H, m), 4.35 (2H, m), 7.16 (6H, m), 7.90 (1H, s), 8.16 (1H, s). ^{13}C NMR ($CDCl_3$) δ (ppm): 14.1, 22.7, 29.4, 30.0, 30.4, 30.5, 31.9, 62.4, 97.4, 116.0, 123.8, 124.0, 124.7, 126.7, 127.9, 130.7, 132.3, 132.6, 133.2, 134.0, 136.8, 137.8, 140.3, 141.0, 141.8, 145.9, 162.9

UV-Vis absorption spectra

Samples for UV and fluorescence measurements were prepared from stock solutions (1×10^{-3} M) in dichloromethane. The proper volumes of the stock solution were transferred into a vial, then the solvent was evaporated, and the residue dissolved in 2 mL of the suitable solvent. All solutions were equilibrated at 25 °C before each measurement.

UV-Vis investigations were carried out on a Beckman DU 800 spectrophotometer equipped with a Peltier temperature controller. In general, UV-Vis spectra were recorded at 25 °C using a quartz cuvette with a light path of 0.2 cm, at a concentration of 1×10^{-5} M.

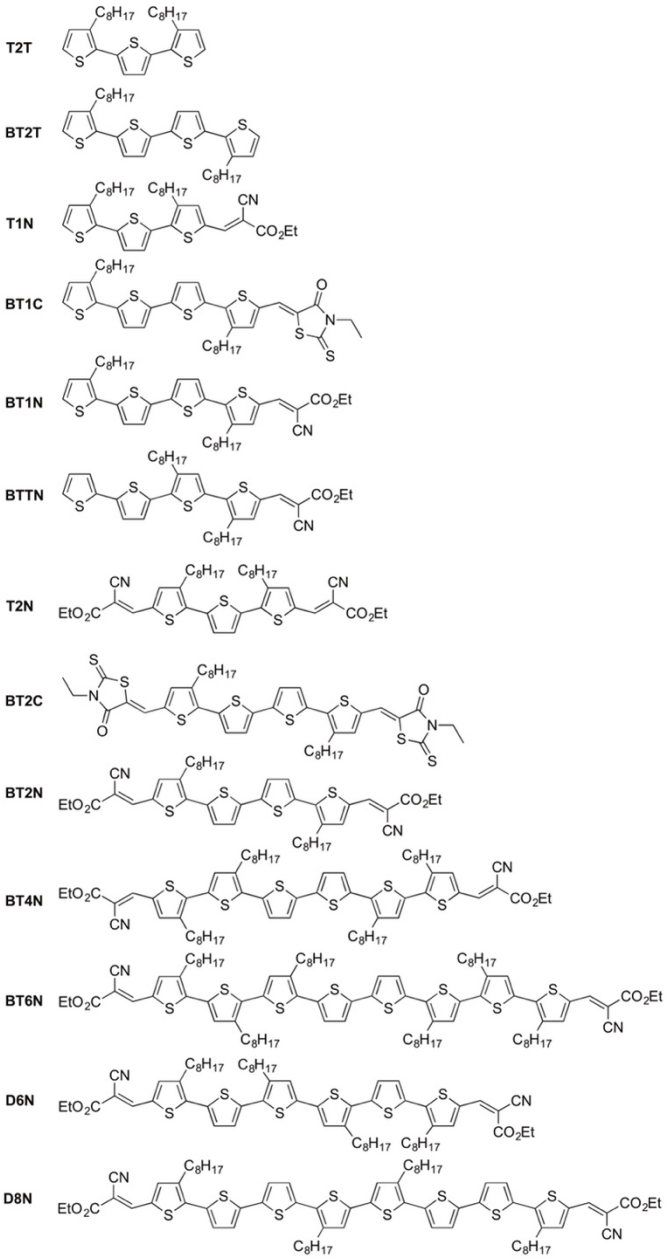
Fluorescence spectra

Fluorescence measurements were performed at 25 °C on a spectrofluorophotometer (Jasco FP-777W) equipped with a system for temperature control. Emission spectra were recorded at 25 °C, at a concentration of 1×10^{-5} M, using a quartz cuvette with a light path of 0.2 cm in excitation and of 1 cm in emission. The excitation wavelength was chosen on the basis of the λ_{max} of the relevant absorption spectra. The spectral width was set at 1.5 nm in excitation and 3 nm in emission mode, respectively.

Results and discussion

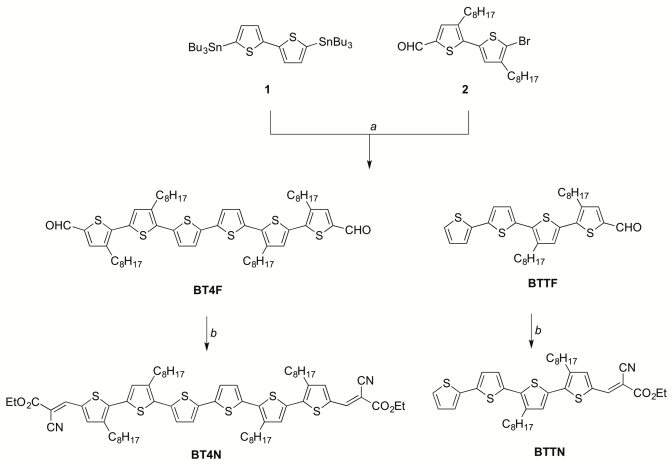
Electrochemical behaviour

In Figure 1 the structures of all oligothiophenes studied in this work are reported.



Among them the compound **BTTN** was obtained as a by-product during the synthesis of **BT4N** reported in our previous work.[17]

Figure 1. Structures of studied oligothiophenes.



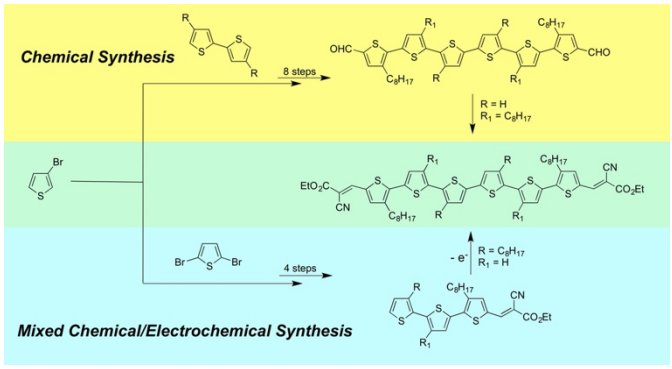
Scheme 1. Synthesis of **BT4N** and **BTTN**. Reaction conditions: (a) $Pd(PPh_3)_4$, toluene; (b) triethylamine, ethyl cyanoacetate, DCM.

The compound **BTTF** is the monosubstituted product of the Stille reaction between compounds **1** and **2**, carried out in presence of tetrakis(triphenylphosphine)-palladium (0) [$Pd(PPh_3)_4$] as catalyst and dry toluene as solvent. **BTTF** was obtained with 55% yield.

The Knoevenagel condensation between **BTTF** and ethyl cyanoacetate gave the final product **BTTN**, as a black powder, with 88% yield.

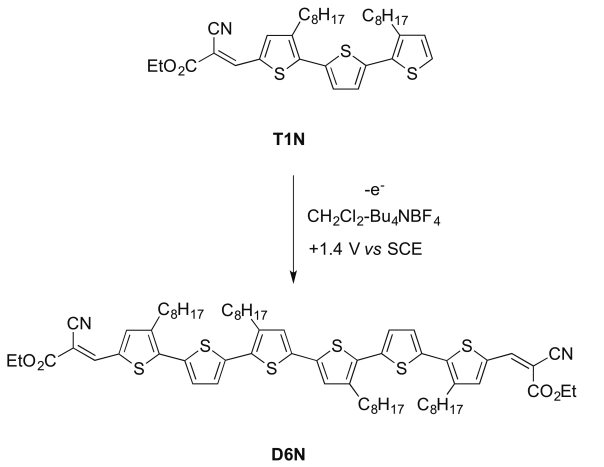
The chemical synthesis of long-chain oligothiophenes, such as **BT4N** and **BT6N** involves many reaction steps, resulting in low overall reaction yields. In addition, toxic organometallic compounds based on nickel and tin are used for some necessary reaction steps, as observed in Scheme 1.

Electrochemistry can be a valid alternative to the classical chemical synthesis to obtain longer oligothiophenes (A-D-A) starting from smaller ones (D-A), decreasing the number of reaction steps and simplifying the synthetic procedure (Scheme 2).



Scheme 2. Comparison of chemical and mixed chemical/electrochemical synthesis of long-chain oligothiophenes.

In our previous work[18] the anodic dimerization of **BT1N** was carried out, obtaining the dimer **D8N** with a good yield. Although we had no information about the application of this electrochemical dimerization to different substrates, this same procedure was successfully applied to **T1N**, precursor of **D6N** (Scheme 3).



Scheme 3. Anodic dimerization of **T1N**.

The electrolysis was performed in a divided glass cell on a solution of CH_2Cl_2-Bu_4NBF_4 0.1 M containing **T1N**, at 25 °C, under nitrogen atmosphere using Pt electrodes. Potentiostatic conditions were chosen to carry out the experiment, by setting the value of +1.4 V (*vs* mSCE). The electrolysis was stopped after the consumption of 2.7 F and the usual workup gave **D6N** in 62% yield. The excellent result obtained was not entirely predictable and it confirmed the possibility of applying the electro synthetic methodology even starting from smaller (three thiophene units) D-A oligothiophenes than **BT1N** (four thiophene units)**.**

The obtained **D6N** can be considered a structural analogous of **BT4N**, as well as **D8N** is for **BT6N**. In fact, they have the same number of thiophene units but different positions of alkyl chains.

By means of cyclic voltammetry, the electrochemical behaviour of **D6N** has been studied (Figure 2) and then compared with that of **BT4N**.

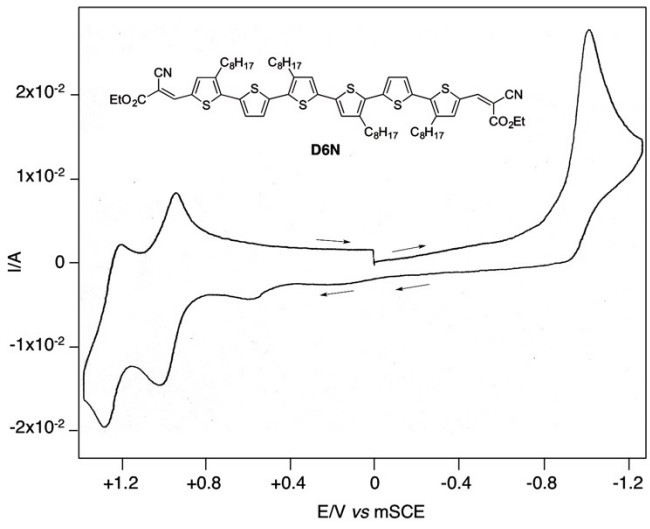


Figure 2. Cyclic voltammogram of **D6N** 1×10^{-2} M in CH_2Cl_2-Bu_4NBF_4 0.1 M. Working electrode: GC. Reference electrode: mSCE. v=0.1 Vs^{-1}, T=25 °C. Potential scan: 0.0 to -1.3 to +1.4 to 0.0 V.

The first oxidation peak of **D6N** is reversible and it has a potential value of +1.00 V *vs* mSCE, higher than the **BT4N** data

(+0.94 V). On the other hand, the cathodic peak of **D6N** (-1.01 V) and **BT4N** (-1.04 V) are similar. The different position of the alkyl chains on the thiophene backbone has therefore influenced the oxidation process, leaving almost unchanged the reduction one, as expected considering the donor effect of the octyl groups.

Cyclic voltammetry is useful also to obtain the energy levels of target compounds and then the electrochemical band gaps. As seen in a previous work,[18] **D8N** showed a lower bandgap than **BT6N**. The same comparison can be carried out with the six-units oligothiophenes: **D6N** and **BT4N**. Again, a lower band gap is observed for the electrodimerized oligothiophene **D6N** ($E_{g(\mathbf{BT4N})}$ = 1.78 eV *vs* $E_{g(\mathbf{D6N})}$ = 1.72 eV).

Solvatochromic investigation

As soon as all the studied compounds are dissolved in dichloromethane (DCM), they reveal their different response to the nature of the solvent, as accounted for by different colours exhibited by the solutions obtained (Figure 3a). Furthermore, when irradiated at 368 nm, they also gave emission of different colours (Figure 3b).

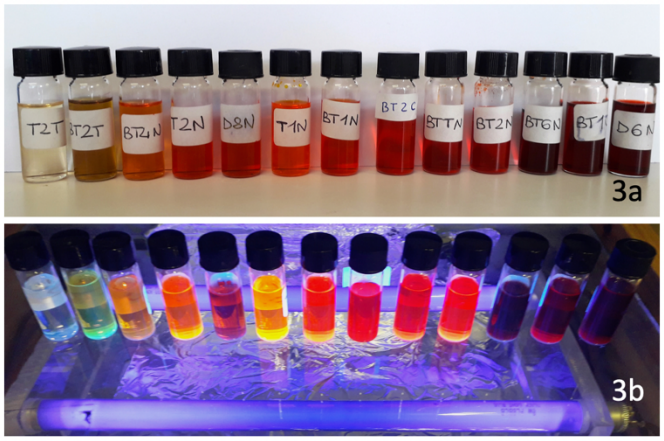


Figure 3. Colour shades of: a) DCM solutions of oligothiophenes; b) irradiated at 368 nm.

To have more insights about the effect of the solvent nature on the photophysical properties of oligothiophenes, UV-Vis and emission spectra were recorded in different solvents. In particular, aprotic solvents having different polarity, like cyclohexane (Cy), chloroform ($CHCl_3$), toluene (Tol), dichloromethane (DCM), acetonitrile (ACN) and ethyl acetate (AcOEt) were used, and the data are presented in Table 1.

Table 1. Absorption data of compounds in all studied solvents. C=1×10^{-5} M. λ_{max} absorption (nm). [a]Low solubility.

	DCM	$CHCl_3$	ACN	AcOEt	Cy	Tol
T2T	338	338	337	335	332	338
BT2T	382	383	375	375	369	376
T1N	448	452	437	437	432	446
T2N	470	471	463	462	439	467
BT1C	484	495	472	477	474	484
BT1N	452	464	444	439[a]	446	459
BT2C	505	511	484[a]	474	459[a]	495
BT2N	486	492	462	469	455	484
BTTN	455	464	439	440	442	457
BT4N	445	438	426	421	432	444
BT6N	484	484	412[a]	457	461	476
D6N	484	490	insoluble	470	460	481
D8N	484	493	449	461	450	485

Superimposed UV-vis spectra, recorded for **BT1C** in different solvents are shown in Figure 4. Spectra corresponding to all the other oligothiophenes are displayed in Figures A1-A13 (Electronic Supplementary Information).

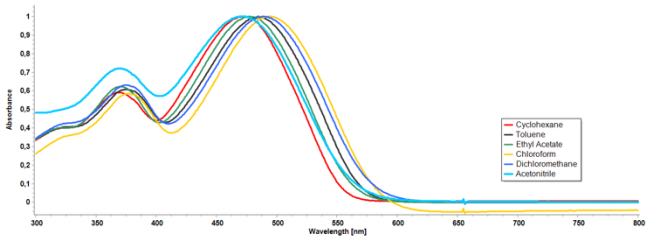


Figure 4. UV-Vis spectra of **BT1C** in different solvents

Analysis of the above spectra sheds light on the significant effect that solvent nature exerts on the position of the main absorption band. In particular, it was firstly bathochromically shifted going from cyclohexane to $CHCl_3$, but it exhibited a hypsochromic shift with the further increase in solvent polarity. With the only exception of **T2T**, a similar behaviour was detected for all the other oligothiophenes studied in this work.

In the attempt to correlate the above trend to solvent polarity, we plotted the position of the main absorption band (λ_{abs}) as a function of $E_T(30)$ values (Figure 5 for **BT1C** and Figures A14-A20 for all other oligothiophenes). This parameter accounts for solvent polarity, measuring the effect on the transition energy for the longest-wavelength solvatochromic absorption band of the pyridinium N-phenoxide betaine dye.[20]

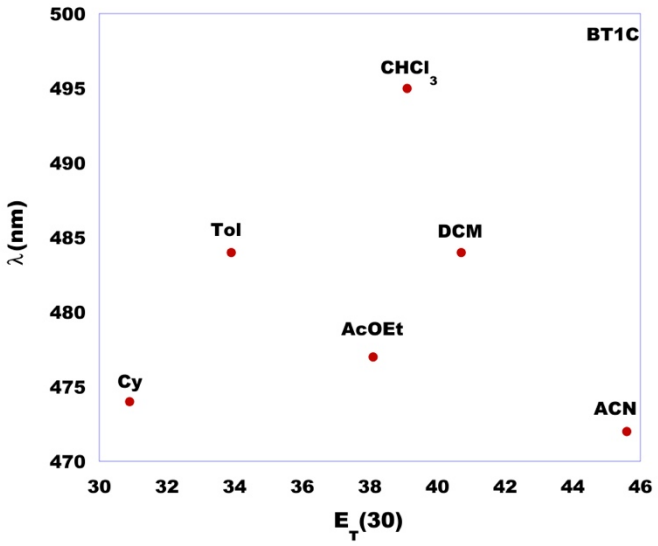


Figure 5. Trend of λ_{abs} of **BT1C** as a function of solvent polarity, $E_T(30)$.

In almost all cases considered, we obtained bell shaped curves showing the maximum value in correspondence of $CHCl_3$ solution. Only in the case of **T2T**, λ_{abs} was bathochromic alley shifted, going from Cy to Tol, but it remained unchanged with the further increase in solvent polarity (Figure A1).

Among all tested solvents, only in solution of AcOEt, we obtained λ_{abs} values lower than the ones detected in solvents having comparable polarity.

Analysis of data previously reported in literature allows stating that the above behaviour can be ascribed to the occurrence of a solvatochromism inversion process.[21-23]

The mechanism of this process is not fully understood. The most corroborated hypothesis suggests the presence of degenerated electronic states with different electronic distribution, that gives the same absorption band as a result of a superimposition process. The solvatochromism inversion is detected only if two bands exhibit different solvatochromic shift and absorption coefficients are differently affected by solvent polarity.[23] Effects of solvatochromism inversion are classified as weak or strong, if shifts lower than 20 nm or higher than 100 nm are detected, respectively.

In the majority of cases analysed in this work, solvatochromic effects detected for oligothiophenes proved weak and the weakest ones were obtained for **T2T**, **BT2T** and **BT4N**.

In the attempt to better analyse obtained results, we discerned the positive solvatochromism effect (bathochromic shift) from the negative ones (hypsochromic shift) (Figure 6).

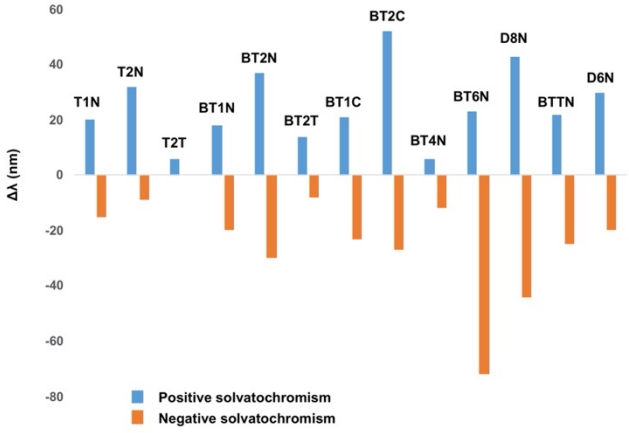


Figure 6. Positive and negative solvatochromism effects for different oligothiophenes.

We observed moderate positive effects for **T2N** and **BT2N**, and more pronounced effects for **BT2C** and **D8N**. Differently, negative solvatochromic effects were less significant than the corresponding positive ones, and only in the cases of **BT6N** and **D8N**, we observed shifts higher than 30 nm. In general, the most significant solvatochromic effects were detected for symmetrically substituted oligothiophenes (**BT2N** and **BT2C**), with the higher shift measured when the π-conjugated system ended with the heterocyclic unit (**BT2C**>**BT2N**).

As far as the central unit is concerned, analysis of collected data shows that the elongation of the π-conjugated system firstly weakens the effect and subsequently strengths it, as accounted for the observed trend in positive solvatochromism (**BT2N**>**BT4N**<**BT6N**). The above hypothesis is perfectly supported as far as data for **BT2N** and **D8N** are compared. Indeed, in the above cases, the elongation of π-conjugated systems exerts a significant increase in both positive and negative solvatochromism.

Solvatochromic effects were also investigated recording emission spectra (Figures A21-A33). The emission peak data are summarized in Table 2.

Table 2. Fluorescence emission data of compounds in all studied solvents. C=1×10^{-5} M. λ_{max} emission (nm). Low peak intensity is indicated with "low".

	DCM	$CHCl_3$	ACN	AcOEt	Cy	Tol
T2T	436	435	428	431	435	435
BT2T	457-484	456-487	455-479	452-480	453-480	456-485
T1N	582	576	602	566	513-542	545
T2N	571	569	576	561	538-575	545
BT1C	648	643	657	619	559	595
BT1N	626	614	643	low	542	585
BT2C	640	638	low	623	low	609
BT2N	609	601	621	594	559	585
BTTN	624	620	647	610	548-577	587
BT4N	592	597	577	587	570	588
BT6N	640	640	low	631	589	619
D6N	655	645	low	627	585	611
D8N	655	654	low	635	582	609

In general, the emission behaviour was more significantly affected by solvent nature than absorption one. In some cases, it was not possible to obtain the emission data, due to the poor solubility of the oligothiophenes in some solvents used for emission spectroscopy compared to absorption one. In Figure 7 the **BTTN** emission spectra, recorded in all studied solvents, are reported as example.

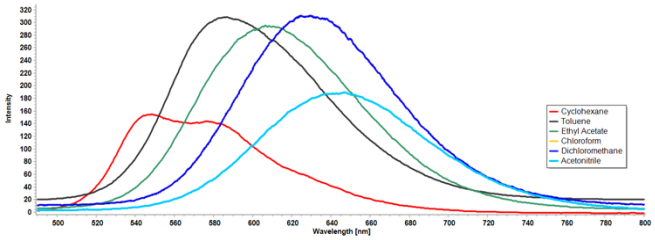


Figure 7. Emission spectra of **BTTN** in all studied solvents

Also in this case, we analysed the position of the main emission band as a function of solvent polarity, evidencing the occurrence of solvatochromism inversion only in the case of **BT4N**, differently from the UV-Vis investigation, which did not show solvatochromism inversion for **BT4N** (Figure 8).

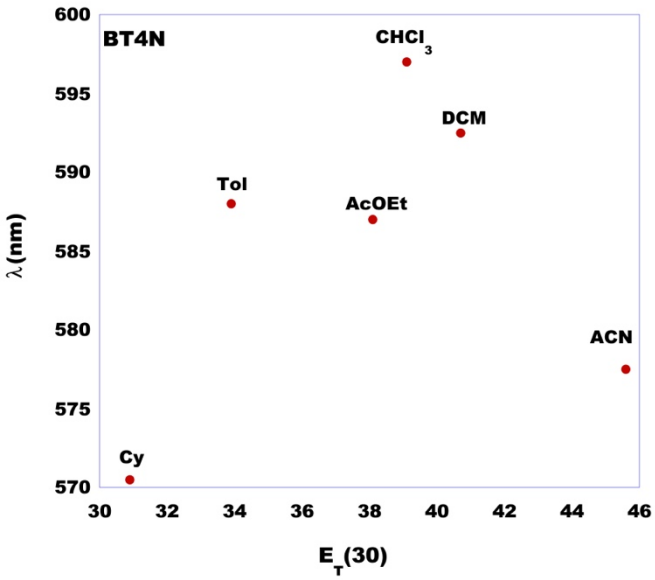


Figure 8. Trend of λem of BT4N as a function of solvent polarity, ET(30).

All other oligothiophenes exhibited positive solvatochromism effects (Figures A34-A40). The **BTTN** trend of λ_{em} is reported in Figure 9, taken as an example to illustrate the general emission trend of all oligothiophenes.

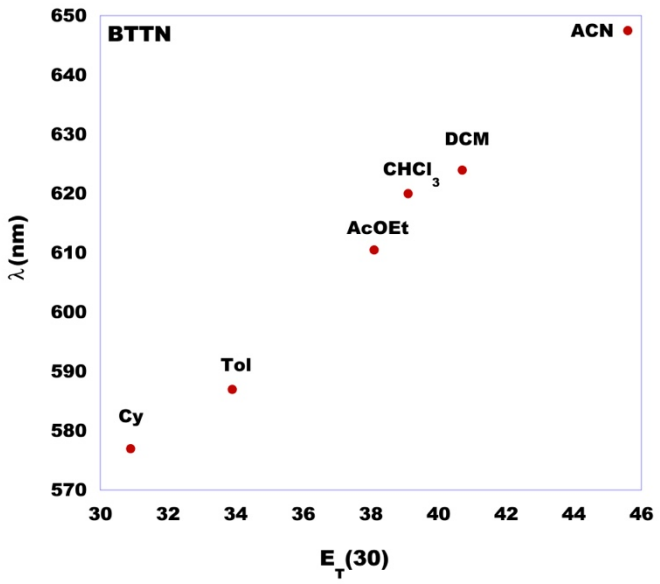


Figure 9. Trend of λ_{em} of **BTTN** as a function of solvent polarity, $E_T(30)$.

It is possible to observe a linear bathochromic shift that occurs increasing the polarity of the solvent. With only a few exceptions, in the case of the emission spectroscopy, the solvatochromic effects were significant with bathochromic shift going from 40 up to 100 nm (Figure 10).

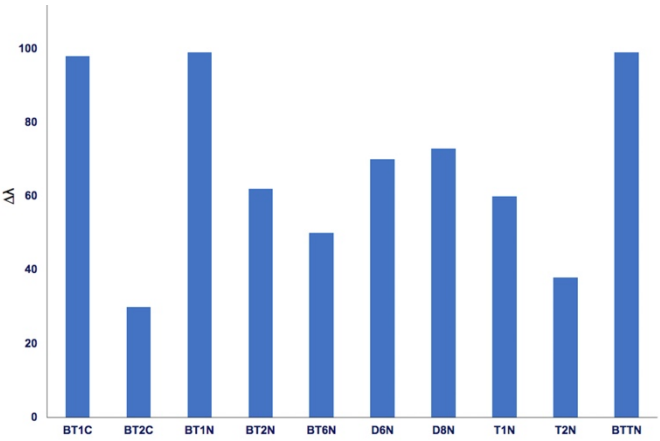


Figure 10. Positive solvatochromism effect for different oligothiophenes.

A deep analysis of above data, evidence that extending the π-conjugated system has a different effect depending on the elongation nucleus. Indeed, it induces a drop in the effect as far as the 3-octylthiophene nucleus is concerned (**BT2N** and **BT6N**); whereas the measured effect remains unchanged if the elongation nucleus is the thiophene ring (**D6N** and **D8N**). Furthermore, the entity of the effect depends on the symmetrical or unsymmetrical oligothiophene substitution, proving more significant in the latter than in the first case, as accounted for by the comparison between **BT1C** and **BT2C**,

BT1N and **BT2N**, **T1N** and **T2N**, with the more significant difference detected in the first case.

Data collected were also analysed by using the Lippert-Mataga equation,[24] to assess the sensitivity of the studied oligothiophenes to changes in solvent polarity. In particular, the Lippert-Mataga equation accounts for the correlation between the Stokes shift ($\Delta\nu_f$) and orientation polarizability (Δf), according to eqs (1) and (2):

$$\Delta\nu_f = 2\,(\mu_e - \mu_g)^2\,\Delta f\,hca^3 + C \qquad (1)$$

where μ_e and μ_g are the dipole moment corresponding to the excited and ground state, h is Planck's constant, c is the speed of light in vacuum, a is the radius of the cavity containing the fluorophore and Δf is given by eq. (2):

$$\Delta f = [(\varepsilon-1)/(2\varepsilon+1)] - [(n^2-1)/[(2n^2+1)] \qquad (2)$$

where n and ε represent the refraction index and dielectric constant of the solvent.

The occurrence of a linear correlation allows stating that the solvatochromic behaviour can be only ascribed to changes in solvent polarity and ruling out the occurrence of specific solute-solvent interactions.

In our case, good linear correlations were obtained only for **T2T**, **BT1C**, **BT1N, BT2N** and **T2N** (Figures A41-A47). With the only exception of **T2T** in all the other cases the slope of the linear correlation was positive, indicating that the increase in solvent polarity induces a more significant stabilization of the excited state with respect to the ground state.

Slopes of the linear correlations change along the following trend: **T2T**<**T2N**<**BT1C**≈**BT1N** (Table A1). Analysis of the above trend shows that the increase in the π-conjugated system, going from **T2T** to **BT1C** and **BT1N**, induces a significant increase in the chromophore sensitivity to the solvent polarity. On the other hand, comparison between data obtained for **BT1C** and **BT1N** evidence that, in the presence of an unsymmetrical substitution, the above parameter is not affected by the nature of the substituent.

Finally, according to the analysis of positive solvatochromism effects detected by recording emission spectra, the symmetrical substitution of the π-conjugated system induces a drop in sensitivity to solvent polarity, as accounted for by the comparison between slopes corresponding to **T1N** and **T2N**.

Conclusions

We synthesized a series of push-pull oligomers based on thiophene and bithiophene cores, both by chemicals and electrochemical syntheses and here we report a detailed analysis on the observed solvatochromic effects on solutions of these compounds realized with a number of solvents with different polarities. The solvatochromism study was carried on by the analysis of the UV-Vis absorption and fluorescence spectra of these solutions that are related, in a close relationship, with the polarity of the solvent, to several factors related to the studied compounds as their D-A or A-D-A structures, the number of thiophene units, the position (and number) of alkyl chains in the backbone, and, finally, the type of acceptor end-groups. Oligothiophenes synthesis has been improved by means of anodic dimerization of shorter precursors. Electrochemical synthesis of new donor-acceptor oligothiophenes are currently under development in our laboratory, with the dual purpose of obtaining compounds with increasingly better performances for applications in the field of organic electronics and to demonstrate how anodic electrodimerization can be an excellent tool for the synthesis of long-chain oligothiophenes in a cleaner and more efficient way.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors acknowledge Sapienza University of Rome for financial support and Mr. Marco Di Pilato for his help with the voltammetric analysis.

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