Synthesis and the electrochemical and fluorescence properties of new cyclophane-derivatized oligothiophenes

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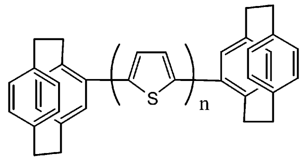
Several new oligothiophenes blocked by cyclophane end groups with 2, 3, 4 or 6 thiophene rings in the chain have been prepared and studied by electrochemistry and by UV-visible and fluorescence spectroscopy. Both radical cations and dications are stable, even for the bithiophene compound; besides the stabilization induced by the blocking of the reactive α positions, this strongly suggests electronic connection between the cyclophanes and the oligothiophene chains, especially for the shorter compounds. All the molecules are strongly fluorescent with increasing quantum yields up to 4 thiophene rings. The assumption of a conjugation between the cyclophane end groups and the oligothiophene main chain is also supported by the UV-visible and fluorescence results, since the spectroscopic data correlate well with $(n+2)^{-1}$ instead of n^{-1}, with n representing the number of thiophene rings in the oligomer.

Introduction

Building new end-blocked thiophene oligomers remains a particularly interesting challenge, motivated by the properties that such structures could posses.[1] Indeed, end-blocked oligothiophenes have been shown to display interesting electrochemical properties,[2] as well as very high charge carrier mobilities in field-effect transistors (FETs).[3] Interesting non-linear optical (NLO) properties like efficient two-photon absorption could be expected from compounds with electron-rich groups (*e.g.*, fluorene centers).[4] However, one of the most promising applications of such molecules is probably the fabrication of light-emitting devices (LEDs),[5] because of their intense fluorescence. Especially, attractive LED materials should display fluorescence in the solid state, which is not so easy to achieve, mainly because of quenching of the excited states by energy transfer between neighbouring molecules in a crystal, or even in the amorphous state. One way to overcome this problem can be to introduce bulky blocking groups to separate the fluorophores and thus diminish the quenching phenomena.

In the past, cyclophanes have attracted much interest due to their intriguing electronic properties, arising from the high steric compression of the neighbouring rings.[6] The orbital overlap between the two rings of [2.2]paracyclophane is quite important and could possibly lead to electronic interaction between substituents on both rings provided they have the appropriate energy levels. Recently, Bazan *et al.*[7] and some of us[8] have renewed the interest of these intriguing molecules in the field of electronic and optical materials. Cyclophanes like [2.2]paracyclophane acquire from the ring compression an electron-rich character, making them closer to a thiophene than to the parent benzene in terms of HOMO energies.[9] Therefore, the choice of cyclophanes as end-blocking groups appears very attractive, especially in the case of thiophene oligomers; for example, the production of highly stable cation radicals could be expected. Despite that this is not the only efficient blocking end group in view of such applications, it is likely that the bulkiness, associated with the weak reactivity of the cyclophane group, is likely to more efficiently separate the oligomers and decrease their reactivity. Meanwhile, given the comparable HOMO energy levels of the thiophene and cyclophane rings, one would expect to retain physicochemical properties very close to that of the unsubstituted oligothiophenes in the isolated molecule or in a dilute solution. Besides, bis-substituted cyclophanes exist as a couple of diastereoisomers; although of very similar energies, they may enhance the formation of noncrystalline structures like organic glasses.

We have prepared a series of cyclophane end-blocked oligothiophenes (see structure below) and we report here their synthesis and electrochemical and fluorescence properties (in solution). The α,ω-biscyclophanyloligothiophenes, with $n =$ 2, 3, 4, and 6 thiophene rings, will be referred to as B2, B3, B4 and B6, respectively.



n = 2, 3, 4, 6

Experimental

Synthesis

^{1}H spectra were recorded on a Bruker–Spectrospin AC 200 Spectrometer. [2.2]Paracyclophane, 2,2′-bithiophene, trimethyltin chloride and tetraphenylphosphinepalladium are commercial products and were used without further purification.

Due to the colouration of the molecules, their purity has been checked using concentrated TLC spots. All experiments were performed under nitrogen atmosphere and solvents were freshly distilled prior to use.

The reported procedures for the dibromation of cyclophane[10] were not found to work satisfactorily. Therefore, we report here our own method.

Monobromination of cyclophane. [2.2]Paracyclophane (19 mmol) is stirred with 20 mL of methylene chloride under an N_2 atmosphere. Bromine (20 mmol) is added in several portions. The coloured solution is stirred 72 h at room temperature and then hydrolyzed. The aqueous layer is extracted with methylene chloride. The combined organic layers are washed with water, dried and the solvent is removed. The crude solid obtained is recrystallized with light petroleum. (NMR and mass data have been published elsewhere.[8a])

Procedure for the synthesis of α,ω-bis([2.2]paracyclophanyl)-2,2′-oligothiophenes. As a typical example, the synthesis of 5,5′-bis([2.2]paracyclophanyl)-2,2′-bithiophene is given here; a similar procedure is used for other the oligothiophenes ($n = 1$ and 3). Bromoparacyclophane (500 mg, 1.75 mmol) is transferred in a Schlenck tube under nitrogen with 573 mg of bromocyclophane (1.75 mmol). The mixture is dissolved in 5 mL of toluene and 5 mL of K_2CO_3 (1 mol L^{-1}). The catalyst $Pd(PPh_3)_4$ (2% in mol) is added to the solution and the mixture is heated for 2 days at 90 °C. The mixture is then hydrolyzed and extracted with CH_2Cl_2. The organic layer is dried over sodium sulfate and the residue is purified by column chromatography with light petroleum–CH_2Cl_2 (9:1) as the eluent.

5-([2.2]Paracyclophanyl)-2,2′-bithiophene. ^{1}H NMR ($CDCl_3$) δ: 7.25 (m, β-thiophene), 7.20 (d, 1H, $J = 3.8$ Hz, α-thiophene), 7.06 (dd, 1H, $J = 3.6$ Hz and $J = 5.1$ Hz, proton on the carbon adjacent to the thiophene substitution), 7.01 (d, 1H, $J = 3.8$ Hz, cyclophane), 6.80 (dd, 1H, $J = 7.7$ Hz and $J = 1.7$ Hz, cyclophane), 6.56 (m, 6 H, cyclophane), 2.90–3.3 (m, 8 H, –CH_2–). HRMS (m/z): $M^{\bullet+} = 372$. Yield 60%.

5-([2.2]Paracyclophanyl)-2,2′-terthiophene†. ^{1}H NMR ($CDCl_3$) δ: 7.32–7.24 (m, β-thiophene), 7.21 (dd, 1H, $J = 9.9$ Hz and $J = 3.8$ Hz, β-thiophene), 7.10 (dd, 1H, $J = 3.6$ Hz and $J = 5.1$ Hz, α-thiophene) 6.89 (dd, 1H, $J = 7.7$ Hz and $J = 1.4$ Hz, cyclophane, proton on the carbon adjacent to the thiophene substitution), 6.80 (dd, 1H, $J = 7.7$ Hz and $J = 1.7$ Hz, cyclophane), 6.56 (m, 6H, cyclophane), 3.8–3.9, m, 2H (cyclophane bridge), 2.90, 3.3 (m, 8H, –CH_2–). HRMS (m/z): $M^{\bullet+} = 454$. Yield 70%.

1,1′-Biscyclophanyl-2,2′-terthiophene. ^{1}H NMR ($CDCl_3$) δ: 7.30 (s, 2H), 7.22 (2H, dd, β-thiophene), 7.15 (dd, 1H, β-thiophene), 6.89 (d, 1H, $J = 3.8$ Hz cyclophane, proton on the carbon adjacent to the thiophene substitution), 6.80 (dd, 1H, $J = 7.7$ Hz and $J = 1.7$ Hz, cyclophane), 6.56 (m, 6H, cyclophane), 2.90–3.3 (m, 8H, –CH_2–). HRMS (m/z): $M^{\bullet+} = 660$. Yield 50%.

Synthesis of 5,5′-bis([2.2]paracyclophanyl)-2,2′-bithiophene (B2). *Procedure for the synthesis of 2-[2.2]paracyclophanyl-5-bromothiophene.* 2-([2.2]Paracyclophanyl)thiophene (400 mg, 1.4 mmol) is dissolved with stirring in 10 mL of chloroform in a Schlenck tube under nitrogen. The mixture is cooled to 0 °C and 1 eq. *N*-bromosuccinimide is added in small portions. After 2 h of stirring, the mixture is hydrolyzed and extracted with chloroform. The organic layer is washed twice with a carbonate solution and water. This layer is dried over anhydrous sodium sulfate and the solvent is removed under reduced pressure. The residue is used without further purification. Quantitative yield. ^{1}H NMR ($CDCl_3$) δ: 7.10 (d, 1H, $J = 3.8$ Hz), 6.87 (d, 1H, $J = 3.8$ Hz), 6.80–6.40 (m, 7H, H aromatic), 3.80–2.80 (m, 8H,–CH_2).

Synthesis of 2-[2.2]paracyclophanyl-5-trimethyltinthiophene. 2-([2.2]Paracyclophanyl)thiophene (230 mg, 0.79 mmol) is dissolved under nitrogen in 5 mL of THF. Butyllithium [0.5 mL (0.79 mmol) as 1.6 mol L^{-1} in hexane] is added to the solution at 0 °C. After 1 h of stirring, 0.80 mL (0.79 mmol) of trimethyltin chloride (1 mol L^{-1} in THF) is added to the mixture at 0 °C. The solution is stirred at room temperature for 2 h. The solvent is evaporated and the residue is hydrolyzed with 20 mL of water. The aqueous layer is extracted with methylene chloride. The organic layer is then dried over anhydrous sodium sulfate and the solvent is removed under reduced pressure. The residue is used without further purification, because 2-([2.2]paracyclophanyl)-5-trimethyltinthiophene is very sensitive to acidic conditions. ^{1}H NMR ($CDCl_3$) δ: 7.50 (d, 1H, $J = 3.2$ Hz), 7.30 (d, 1H, $J = 3.2$ Hz), 6.80–6.40 (m, 7H, H aromatic), 3.60–2.80 (m, 8H, –CH_2–), 0.44 (s, 9H, –$C(CH_3)_3$).

Synthesis of 5,5′-bis([2.2]paracyclophanyl)-2,2′-bithiophene. Unpurified 2-([2.2]paracyclophanyl)-5-trimethyltinthiophene is mixed with unpurified 2-([2.2]paracyclophanyl)-5-bromothiophene in a Schlenck tube with 20 mL of THF and 20 mL of potassium carbonate (1 mol L^{-1}). The catalyst $Pd(PPh_3)_4$ (2% in mol) is added to the solution and the mixture is heated at 70 °C. After 2 days, the mixture is hydrolyzsed and extracted with methylene chloride. The organic layer is then dried over anhydrous sodium sulfate and the solvent is removed under reduced pressure. The residue is purified by column chromatography with light petroleum–CH_2Cl_2 (9:1) as the eluent. ^{1}H NMR ($CDCl_3$) δ: 7.31 (d, 2H, $J = 3.75$ Hz), 7.08 (d, 2H, $J = 3.75$ Hz), 6.85–6.45 (m, 14H, cyclophane), 4.80–2.80 (m, 16H, –CH_2–). HRMS (m/z): $M^{\bullet+} = 578$.

Dimerization of 5-([2.2]paracyclophanyl)-2,2′-bithiophene and terthiophene. A given 5-([2.2] paracyclophanyl)-2,2′-oligothiophene (50–100 mg) is dissolved in 20 mL of methylene chloride in a Schlenck tube under a nitrogen atmosphere. A methylene chloride solution of 2.1 molar equiv. of $FeCl_3$ is added at once to the solution. After 15 min of stirring, an excess of zinc powder is added. The crude mixture is then filtered to eliminate the inorganic impurities and the solvent is evaporated under vacuum. The residue is purified by column chromatography with light petroleum ether–CH_2Cl_2 (9:1) as the eluent.

5,5′-Bis([2.2]paracyclophanyl)quaterthiophene (B4). ^{1}H NMR ($CDCl_3$) δ: 7.22 (d, 2H, $J = 3.75$ Hz), 7.18 (d, 2H, $J = 3.75$ Hz), 7.15 (d, 2H, $J = 3.75$ Hz), 7.04 (d, 2H, $J = 3.75$ Hz) (all β thiophene); 6.82 (dd, 2H, $J = 7.8$ Hz and $J = 1.6$ Hz, cyclophane, 2H adjacent to the thiophene chain), 6.56 (m, 12H, cyclophane), 3.8–2.80 (m, 16H, CH_2). HRMS (m/z): $M^{\bullet+} = 742$.

5,5′-Bis([2.2] paracyclophanyl)sexithiophene (B6). ^{1}H NMR ($CDCl_3$) δ: 7.28 (d, 2H, $J = 3.75$ Hz), 7.22 (d, 2H, $J = 3.75$ Hz), 7.18 (d, 2H, $J = 3.75$ Hz), 7.15 (d, 2H, $J = 3.75$ Hz), 7.04 (d, 2H, $J = 3.75$ Hz) (all β thiophene); 6.82 (dd, 2H, $J = 7.8$ Hz and J = 1.6 Hz, cyclophane, proton adjacent to the thiophene chain), 6.56 (m, 12H, cyclophane), 3.8–2.80 (m, 16H, –CH_2–). HRMS (m/z): $M^{+} = 906$

Electrochemical set-up

Analytical experiments were performed in a three-compartment cell fitted with a silver nitrate (10^{-2} mol·L^{-1} in acetonitrile)|silver reference electrode, a glassy carbon (1.2 mm diameter) or a platinum disk (1.0 mm diameter) electrode and a platinum wire counter electrode. The potential of the reference electrode was checked *vs.* the ferrocene/ferricinium couple after each set of experiments. The electrochemical apparatus was a home-made potentiostat (equipped with an ohmic drop compensation system), designed according to ref.

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† THF is used as a solvent for the preparation of the terthiophene derivative. In addition, about 10% of 1,1′-bisparacyclophanyl-2,2′-terthiophene is formed, due to proton abstraction on 5-([2.2]paracyclophanyl)-2,2′-terthiophene and further coupling with bromoparacyclophane.

11. The solvent was spectroscopic grade dichloromethane (SDS) with tetrabutylammonium hexafluorophosphate (Fluka, puriss.) as the supporting electrolyte. The concentration of the oligothiophene derivatives was 10^{-3} mol L^{-1}, unless stated in the text. The solution was purged by argon bubbling prior to each cyclic voltammetry measurement.

Fluorescence and absorption experiments

All spectra were measured in dichloromethane of spectrometric grade from Sigma Aldrich; the substrate concentration was about 10^{-6} mol L^{-1}. The UV-vis spectra were recorded on a Varian Cary 500 double beam spectrometer, using a 1 cm path quartz cell. The fluorescence spectra were recorded on a Jobin Yvon Fluorolog-3 fluorimeter, with excitation wavelength at the absorption maximum for each sample. The optical density (O.D.) was adjusted to be lower than 0.1 to avoid reabsorption phenomena. Spectra were corrected for the apparatus function.

Quantum yield measurements were performed using either an aqueous basic fluoresceine solution or a quinine sulfate sulfuric acid solution as the reference.

The fluorescence decay curves were obtained with a time-correlated single-photon-counting method using a titanium-sapphire laser (82 MHz, repetition rate lowered to 4 MHz thanks to a pulse-peaker, 1 ps pulse width, doubling crystals to reach 495 nm excitation) pumped by an ionized argon laser. The Levenberg–Marquardt algorithm was used for nonlinear least square fits. The crystal decays were measured under a confocal set-up (microscope Nikon Diaphot 200).

Results and discussion

We have examined the electrochemical and fluorescence properties of the bis-α, ω-cyclophanyloligothiophenes having n = 2, 3, 4, and 6 thiophene rings (B2, B3, B4 and B6, respectively). It should be noted that the synthetic routes to these compounds vary, since the convenient oxidative dimerization reaction leading to the longest oligomers B4 and B6, fails with B2, because of the high oxidation potential of the cyclophanethiophene; therefore, a separate Stille synthesis had to be done (this compound has been prepared very recently by Collard *et al.*[12] by Kumada coupling). In addition, B3 is a by-product of the synthesis of cyclophanylterthiophene.

Electrochemical properties of the B*n* compounds

All the thiophene oligomers give well-defined cyclic voltammograms (Fig. 1), with stable formation of both the radical cation and the dication, indicating as expected that the cyclophane ring blocks the reactivity of the thiophene moieties. This is particularly noticeable for B2, since in the case of bithiophene (as also for thiophene), only a tertiobutyl,[13] methoxy[14] or thioalkylacetate[15] group had been proved to induce stability of the radical cation at rather low scan rates. It is surprising that formation of both the radical cation and the dication are possible in the case of B2, while in the case of ditertiobutylbithiophene or dimethoxybithiophene, only the reversible radical cation formation was discernible. This likely indicates that some charge must be stabilized on the cyclophane rings, especially in the case of the dicationic species.

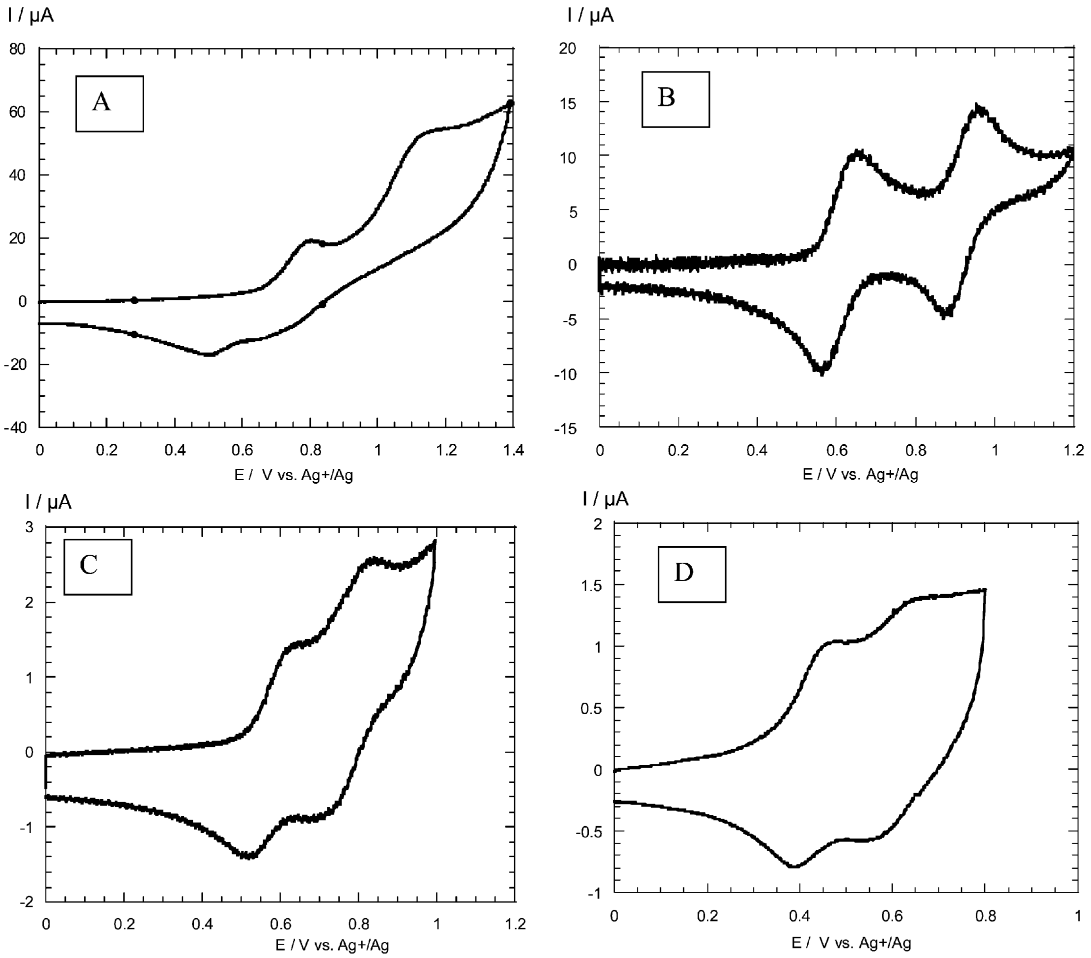

Fig. 1 Cyclic voltammograms of B*n* (*ca.* 1 mM) in dichloromethane + $TBAPF_6$ at 1 V s^{-1} on platinum [except (D) at 0.2 V s^{-1}]: n = 2 (A), 3 (B), 4 (C), 6 (D).

Table 1 Standard potentials for the monomer/radical cation ($E°_1$) and radical cation/dication ($E°_2$) redox couples in dichloromethane (*vs.* the ferrocene/ferricinium redox couple) deduced from cyclic voltammetry measurements

Compound	$E°_1$/mV *vs.* Fc	$E°_2$/mV *vs.* Fc
B2	540	790[a]
B3	435	754
B4	379	583
B6	331	511

[a] Ill-defined return peak.

The electrochemical potentials of the four compounds are listed in Table 1. As for classical oligothiophenes, the standard potentials of the monomer/radical cation couples correlate well with the inverse of the number of thiophene rings *n* (Fig. 2), and not so well with the inverse of the total number of rings ($n+2$), which includes the cyclophane end groups. This is a little bit surprising, in view of the results on the stability of the oxidized species coming from B2, and therefore it should be assumed that the participation of the cyclophanes in the charge delocalization becomes less important as the number of thiophene rings increases. However, the clear influence of the cyclophane moiety in the case of the shorter compounds shows up again: when one compares the standard potential for the first oxidation of B2 and ditertiobutylbithiophene,[13] there is a difference of close to −200 mV, which should be explained by the possibility of charge and/or spin delocalization on the cyclophane rings. Compared to dimethoxythiophene,[14b] the same difference is now *ca.* +160 mV, due to the stronger donor effect of the methoxy substituents. Nevertheless, the chemical stability of the radical cations is similar for both compounds, indicating an effective conjugation of the radical to the cyclophane rings. When the number of rings increases, the monomer/radical cation standard potential comes closer to the one of the parent oligothiophene; thus, the influence of the cyclophane is weaker in that case (including the donor mesomeric effect, which becomes less efficient), except for what is related to the blocking of the reactive α positions and the increased solubility of the B*n* compound.

Concerning the electron transfer kinetics, all the monomer/radical cation couples exhibit quasi-reversible behaviour. We have recorded the variations of peak potentials associated with the first redox system for B3 and B4, which exhibit well-defined voltammetric peaks over a rather large scan rate range (Fig. 3). The results are displayed in a potential *vs.* logarithm of the scan rate plot for each compound (Fig. 4). A classical quasi-reversible behaviour according to Butler–Volmer kinetics is clearly evidenced and the apparent heterogeneous rate constant appears to lie in the range of 0.01–0.1 cm s^{-1} and to be higher for B3 than for B4. This could be in relation with a greater delocalization of the charge in the radical cation form of B3, leading to a lower reorganization of the solvent associated with the electron transfer.[13] This would corroborate the fading influence of the cyclophane moieties as the number of thiophene rings increases.

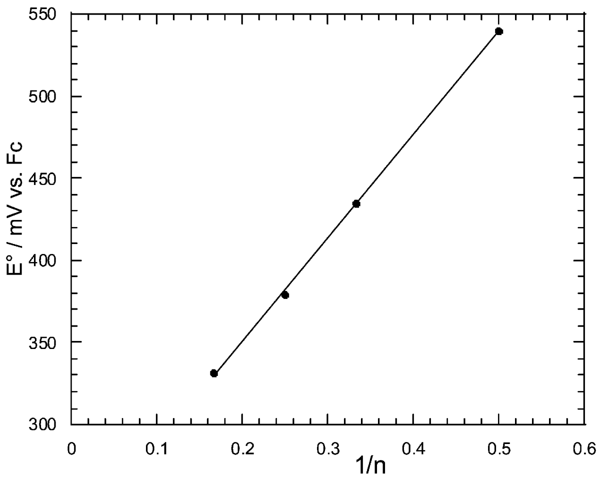

Fig. 2 Standard potentials of the monomer/radical cation couples of B*n* as a function of 1/*n*.

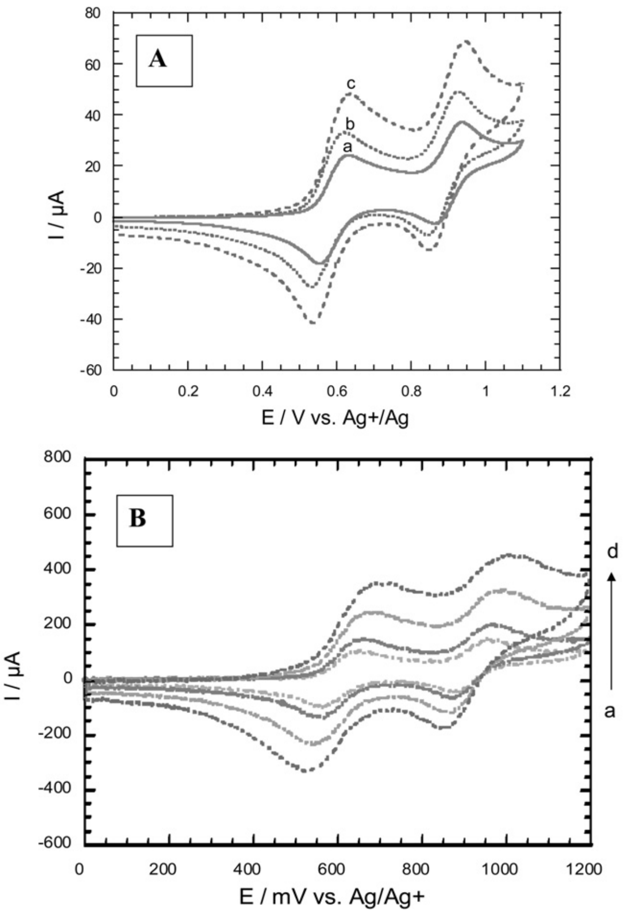

Fig. 3 Cyclic voltammograms of B_3 (*ca.* 10 mM) in dichloromethane + $TBAPF_6$ at various scan rates: (A) 0.05 (a), 0.1 (b), 0.2 (c); (B) 1 (a), 2 (b), 5 (c), 10 (d) V s^{-1}.

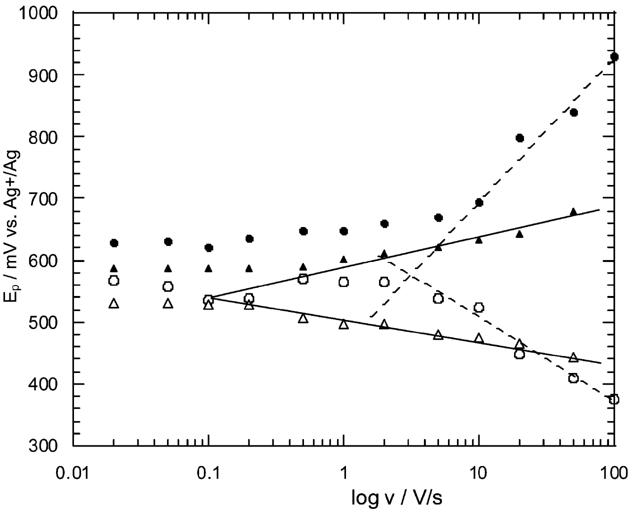

Fig. 4 Variation of the peak potential as a function of the logarithm of the scan rate for B3 (circles) and B4 (triangles).

The dications are commonly found to be stable in the B-family compounds, while this is not true with the short end-capped oligothiophenes; besides, the difference between the standard potentials of both redox couples (radical cation and dication) is rather low (typically 300 mV, see Table 1). Such a behaviour is similar to the one of α,ω-bromomethoxyter- and quaterthiophenes;[14] hence, since the donor effect of the cyclophane end groups is much less than the one of methoxy groups, these features suggest again an effective charge and spin delocalization on the cyclophane moieties. This is especially the case in the shorter compounds, because so far no end-substituted bithiophene compounds have ever exhibited stable dication species at such a low scan rate.

Fluorescence properties of the B*n* compounds

Typical absorption and fluorescence spectra are shown in Figs. 5 and 6, respectively, while Table 2 summarizes the main features of the new α,ω-cyclophanyl oligothiophenes B2 to B6 and compares them with the spectral data obtained in dioxane by Becker *et al.*[16] for unfunctionalized oligothiophenes.

In particular, we report the maximum absorption wavelengths (Abs. max.) and maximum emission wavelengths (Em. max.) in Table 2. The absorption spectra are devoid of any fine structure, whereas the vibronic structure can be seen in the fluorescence spectra at ambient temperature. This is due to the planarization of the conjugated system, following excitation. The ground state is twisted while the excited state is more planar, having more or less a quinoid structure. The periodicity (V_{em}) was calculated after Gaussian deconvolution. It is usually attributed to the C=C stretching mode of the oligothiophene. As the oligothiophene chain length increases, the stretching decreases as expected, because the increasing conjugation decreases the stretching strength.[17]

Fig. 7 displays the fluorescence excitation spectrum of B2, as well as its absorption spectrum; the accurate correspondence of the two spectra is indicative of the existence of a single species in the fundamental state. This is the case for the shorter B-oligomers while it is less obvious for B6. The fluorescence spectra are red-shifted with respect to the oligothiophene analogues (see Table 2). This shift indicates a coupling between the cyclophane and the sexithiophene orbitals. This is also confirmed by the increase of the absorption maximum wavelength with the number of thiophene rings. The Stokes shift measured in dichloromethane is relatively large. This indicates a noticeable change in the position of the atoms of the molecule between the ground and the excited states. This again indicates the existence of a twist in the ground state structure, whereas the excited state is more planar.

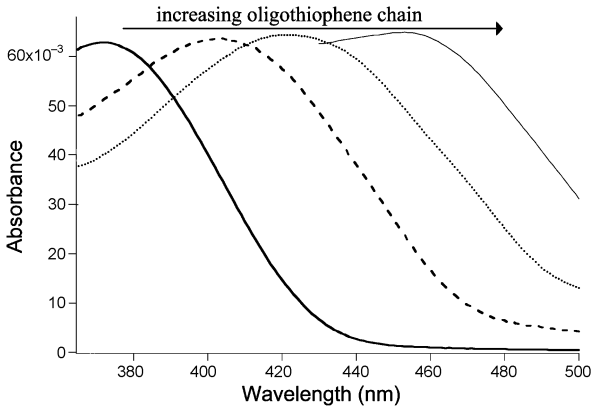

Fig. 5 Absorption spectra of B2, B3, B4 and B6 in dichloromethane: (bold line) B2, (dashed line) B3, (dotted line) B4, (thin line) B6. Note that the vibronic structure is not seen.

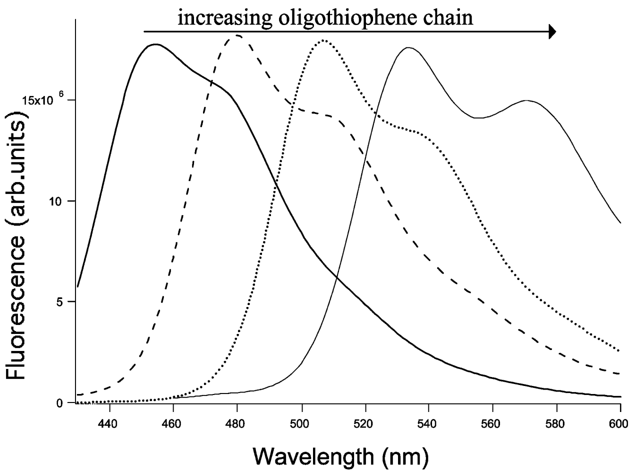

Fig. 6 Fluorescence spectra of B2, B3, B4 and B6 in dichloromethane: (bold line) B2, (dashed line) B3, (dotted line) B4, (thin line) B6. Note that the vibronic structure appears on these spectra.

The fluorescence quantum yield increases with the thiophene number n up to $n = 4$ and then decreases for $n = 6$ (see Table 2). Such a behaviour is different from that of the unfunctionalized oligothiophene series, where the yield was shown to increase up to 6 rings and then remains stable or even decreases.[16] However, if we consider the chain length as $n' = (n+2)$ rather than n, that is by including the cyclophane moieties, the fluorescence quantum yields continuously increase with n' up to $n' = 6$, as reported previously for the β-alkylated-oligothiophene series.[18] Then, from B4 to B6 (*i.e.*, from $n' = 6$ to $n' = 8$) the fluorescence quantum yield decreases, similarly to what was reported previously for the oligothiophene series.[16] The fact that evolution in the series correlates better with n' than n tends to show that the cyclophane rings play a similar role to thiophene units, rather than simple substituents, as far as the fluorescence properties are concerned.

In addition, it is worthwhile to stress that there is a linear correlation between the maximum energy of the first transition, as well as the 0–0 energy, and $(n+2)^{-1}$ (Fig. 8), whereas no good linear correlation between these energies and n^{-1} can be found. This is again strongly in favour of the participation of cyclophanes in the electronic conjugation of the oligomer chain, particularly in the planar excited state. Such a conclusion is not unexpected since it was previously reported that naphthalene moieties participate in the conjugation in α-naphthalenyl oligothiophenes.[19] This behaviour could not be predicted from the electrochemical measurements since the redox potential is correlated to the ionization energy of the neutral form, which is also sensitive to steric effects.

Table 2 Main features of the spectra of the new cyclophane-derivatized oligothiophenes B*n* at 293 K in dichloromethane

	Abs. max./ nm	Em. max./ nm	V_{em}/ cm^{-1}	Stokes shift/ cm^{-1}	Quantum yield
2T[a]	303	362	–	–	0.017
3T[a]	354	426	–	–	0.066
4T[a]	392	478	–	–	0.18
6T[a]	436	502	–	–	0.41
7T[a]	441	522	–	–	0.34
B2	374	457	1390	4783	0.1
B3	404	480	1380	3919	0.2
B4	421	507	1375	4029	0.6
B6	453	545	1361	3726	0.4

[a] Data from ref. 16 for the unsubstituted oligothiophenes in dioxane at room temperature.

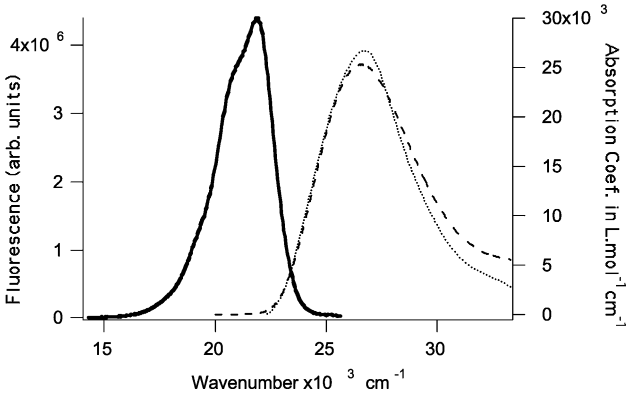

Fig. 7 Absorption (---), fluorescence (—) and fluorescence excitation (···) spectra of B2 in dichloromethane. Note the strong Stokes shift.

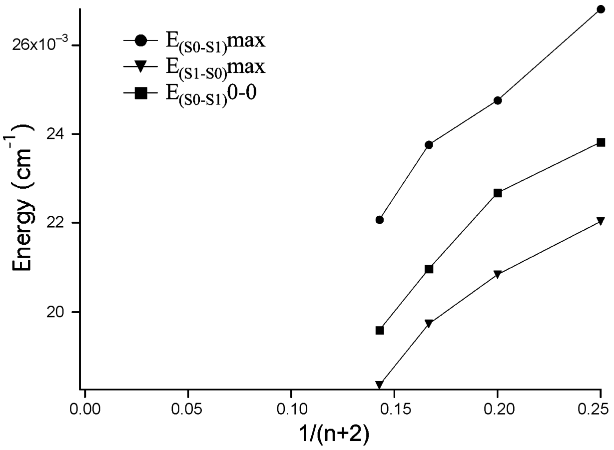

Fig. 8 Correlation between $1/(n+2)$ and the absorption maxima (round dots), the fluorescence maxima (triangles) and $E_{0\text{-}0}$ intercept (squares). Note the good correlation of the $E_{0\text{-}0}$ values.

The B6 fluorescence lifetime has a value of 0.8 ns (Fig. 9). The fluorescence anisotropy relaxes in 450 ps. This is faster than the 300 ps expected for a molecule approximately 3.2 nm long. This is probably due to the shape of the B6 molecule with two bulky groups at the end. The time zero anisotropy has a value of 0.3. This is less than the 0.4 expected for a molecule where absorption and emission dipoles are parallel. This again agrees with the change in the positions of the atoms of the molecule between the ground and excited states. The fluorescence lifetime of the dye powder decreases up to 610 ps with a slow component at 1.4 ns. The small reduction of the fluorescence lifetime of the main component in the powder illustrates the purity of the sample and makes B6 a promising material for organic light-emitting diodes.

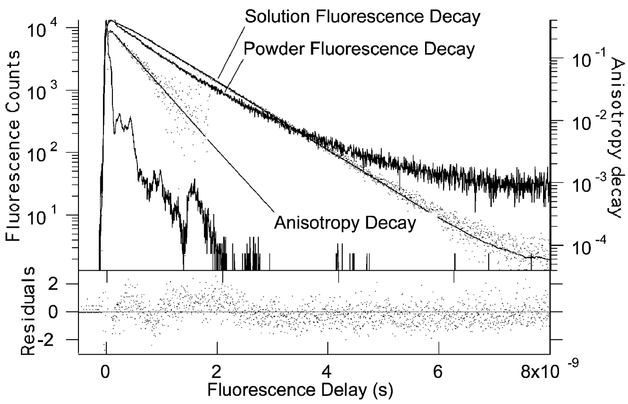

Fig. 9 Intensity and anisotropy decay of the fluorescence of B6 in dichloromethane. The excitation wavelength was 494 nm and the emission was collected at 580 ± 4 nm. The spectra (dots) have been overwritten with their fits by exponential functions.

Conclusion

We have presented herein the synthesis and the electrochemical and fluorescence properties, as well as some spectroscopic features, of several new oligothiophenes blocked by cyclophane rings. Electrochemical and optical data tend to show that effective conjugation takes place between the oligothiophene main chain and the cyclophane substituents. This results in stable radical cations and dications on the time scale of conventional cyclic voltammetry measurements, and in highly fluorescent excited states of the neutral molecules. In particular, the two longest molecules of the series, B4 and B6, display a strong fluorescence and should be promising compounds for LED devices. Their potential in view of such applications is currently being investigated.

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