New conjugated polymerizable pyrrole and 2,5-dithienylpyrrole azobenzene dyes: synthesis and spectroelectrochemical properties

Pierre Audebert,*[a] Saïd Sadki,[a] Fabien Miomandre,[a] Philippe Hapiot[b] and Kathleen Chane-Ching[c]

[a] *Laboratoire de Photophysique et Photochimie Supramoléculaires et Macromoléculaires (CNRS UMR 8531), Ecole Normale Supérieure de Cachan, 61 Av. du Pt Wilson, 94235, Cachan, France. E-mail: audebert@ppsm.ens-cachan.fr*

[b] *Laboratoire d'Electrochimie Moléculaire et Macromoléculaire, Synthèse et Electrosynthèse Organiques (CNRS UMR 6510), Université de Rennes 1, Bat. 10C, 35042, Rennes cedex, France*

[c] *Institut de Topologie et Dynamique des Systèmes, Université Denis Diderot (Paris 7), 1, rue Guy de la Brosse, 75005, Paris, France*

Received (in Montpellier, France) 5th November 2002, Accepted 20th January 2003
First published as an Advance Article on the web 9th April 2003

We describe the first easy syntheses of new fully conjugated monomers and their derived polymers containing a photoisomerizable azobenzene group, along with their electrochemical properties. Two classes of compounds have been studied differing in the nature of the polymerizable unit: pyrrole or 2, 5-dithienylpyrrole. A rather effective electronic interaction between the pyrrole and azo moieties has been demonstrated, while the conjugation is much less pronounced in the case of the terheterocycle. This behavior has been ascribed to a twisted conformation of the 2,5-dithienylpyrrole compounds in the neutral form, as demonstrated by theoretical modeling. All these molecules are electropolymerizable monomers, although the 2,5-dithienylpyrrole compounds lead only to thin films of conducting polymers when compared to their pyrrole analogs.

1. Introduction

The search for new superstructured conjugated organic polymers[1–7] continues to be of interest, in particular as these systems are expected to show NLO properties,[1,2] entrap metals,[4–6] as well as exhibit adjustable conductivities.[7,8] With regard to these properties, electrodeposited polymers with photoisomerizable azobenzene moieties appear to be useful candidates, in particular as concerns the electronic conjugation between the chains and the functional group. This conjugation may lead to mutual cooperativity such that the intrinsic properties of the polymer chain (like conductivity) could be tuned by the state of the azo pendant group, for example, by UV light irradiation. Conversely, the tuning of the functional group properties through the redox state of the chain could also be envisaged. Although electroactive polythiophenes and polypyrroles bearing azo pendant groups have been previously described,[9–12] this is the first time that conjugated electroactive polymers based on an azo dye are presented.

Moreover, it is interesting to try to prepare "ladder" polymers, connecting the conducting chains with the functional group as a "bar" between the chains. This way, enhanced effects could be expected due to the tighter link between the chains and the functional group. Up to now, almost all of the ladder conjugated polymers described in the literature exploit the "bar" of the ladder, focusing only on the conjugated or nonconjugated character. The aim here is to investigate the influence on the polymer of the existence or absence of additional electronic connectivity between the chains[7,8] through the conjugated linker. Following these ideas, we found it interesting to synthesize fully conjugated "one head" and "two head" monomers containing an azo moiety. Hence we have prepared five new heterocyclic azo dyes: 4-(1-pyrrolyl)azobenzene (**1**), 4-(1-pyrrolyl)-4′-nitroazobenzene (**2**), bis-4,4′-(1-pyrrolyl)azobenzene (**3**), 4-[(2,2′-bis thienyl)-*N*-pyrrolyl]azobenzene (**4**) and bis-4,4′-[(2,2′-bisthienyl)-*N*-pyrrolyl]azobenzene (**5**), which are all represented in Scheme 1. We describe here the synthesis of the monomers and their derived polymers prepared by electrooxidation, as well as their electrochemical and spectroscopic properties.

2. Experimental

2.1 Synthesis of the monomers

The pyrrole derived azobenzene compounds were prepared by a classical Paal–Knorr procedure. Typically, a stoichiometric mixture of the starting compounds is heated to reflux in acetic acid, after which the heating is immediately stopped and the solution is poured into iced water, neutralized with alkali, and extracted with dichloromethane. Chromatography (dichloromethane–petroleum ether 50:50) afforded the desired product (first eluted) with 40–60% yields.

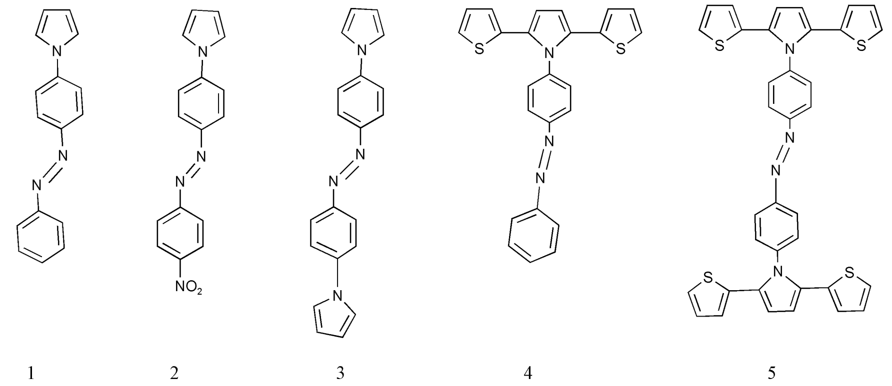
1. ^{1}H NMR (300 MHz): 6.45, t, 4H (α-py); 7.20, t, 4H (β-py); 7.60, m, azo; 7.95, m, azo; 8.05, m, azo. Anal. calcd: C: 77.71, N: 16.99, H: 5.30; found: C: 77.70, N: 16.88, H: 5.19%.

2: ^{1}H NMR: 6.47, t, 4H (α-py); 7.22, t, 4H (β-py); 7.55, d(t), azo; 8.34, d(t), azo. Anal. calcd: C: 65.75 N: 19.17, H: 4.11; found: C: 65.66, N: 19.21, H: 4.14%.

3: ^{1}H NMR: 6.42, t, 4H (α-py); 7.22, t, 4H (β-py); 7.55, d(t), azo, 8.05; m, 8H, azo; 8.40, d(t), azo. Anal. calcd: C: 76.92, N: 17.95, H: 5.13 found: C: 76.70, N: 17.89, H: 5.10%.

IR (KBr) data for **1** and **3** (very similar spectra): 3065, 1600, 1330.

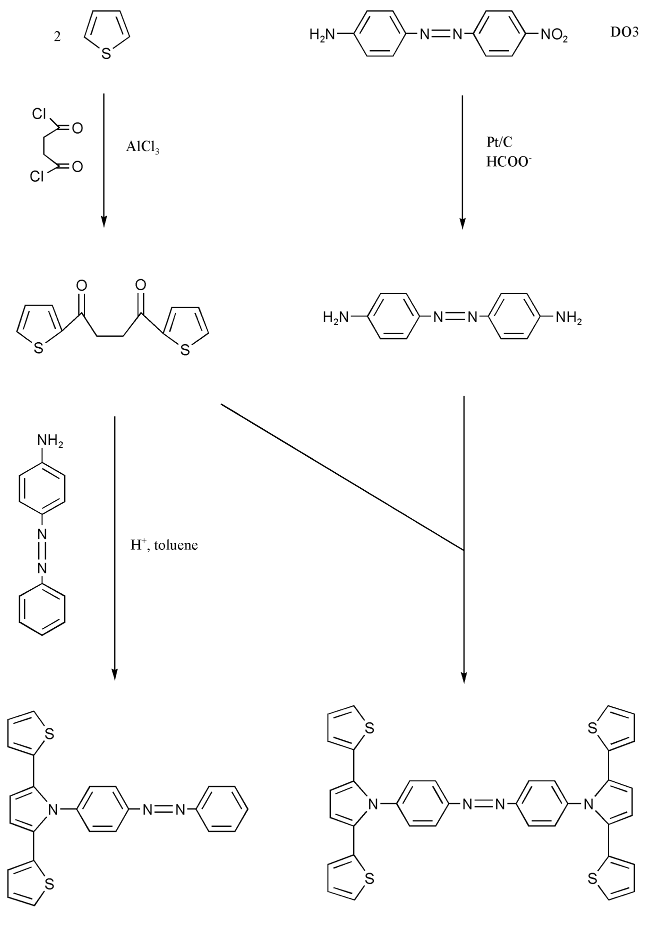
IR (KBr) data for **2** (very similar spectra): 3000, 1600, 1514, 1330.



Scheme 1

2,5-Dithienylpyrrole derivatives were synthesized according to a modified Paal–Knorr procedure as shown in Scheme 2. Standard synthetic procedures[8] have been used for all the steps, with only a modification of the purification procedure in the last one. A typical procedure for the synthesis of **5** is as follows: 4,4′-azodianiline (1.06 g, 5 mmol) and bis(2-thienyl)-1,4-butanedione (3 g, 10 mmol) are refluxed for 12 h in anhydrous toluene (20 mL) with 200 mg of paratoluenesulfonic acid. After reaction, excess toluene is evaporated, 5 mL of dichloromethane are added, and the crude mixture is poured on a silica gel column. After elution with 20% dichloromethane and 80% petroleum ether, **5** is collected and recrystallized from the elution solvent, with 60% yield.

4: ^{1}H NMR: 8.0, m (4H, α azo); 7.55, m (3H azo); 7.48, d (2H, azo); 7.12, d (2H, α thioph.); 6.85, t (2H, β pyr.); 6.58, s(m) (4H, β thioph.). Anal. calcd: C: 70.05, N: 10.21, H: 4.16; found: C: 69.78, N: 9.86, H: 4.11%.



Scheme 2

5: ^{1}H NMR: 8.25, d (4H, α azo); 7.44, d (4H β azo); 7.17, d (4H, α thioph.); 6.90, t (4H, β pyr.); 6.58, s (m) (16H, β thioph.). ^{13}C NMR: 9 aromatic C, 147.3, 144.0, 133.8, 130.4, 129.6, 127.0, 125.6, 125.1, 124.2. Anal. calcd: C: 67.50, N: 8.75, H: 3.75; found: C: 67.32, N: 8.65, H: 3.62%.

IR (KBr) data for **4** and **5** (very similar spectra): 2980, 1590, 1505, 1405.

Although the intermediate 4,4′-azodianiline is a commercial compound, because of its high price we found it more convenient to prepare it by reduction of the very classical "DO3" dye: reduction is achieved by using ammonium formiate in the presence of Pt/C (70% yield), according to an elegant method recently described.[13]

2.2 Electrochemistry and spectroscopic measurements

The electropolymerization and subsequent study of the polymer films were performed using an EG&G PAR 273 potentiostat, interfaced to a PC computer. The high speed cyclic voltammetry experiments were performed using a homemade potentiostat,[14] equipped with an ohmic drop compensation system.

The reference electrode used is an Ag^+/Ag electrode filled with 0.01 M $AgNO_3$. This reference electrode was checked *vs.* ferrocene as recommended by IUPAC. In our case, $E°(Fc^+/Fc) = 0.114$ V in toluene–ACN with 0.1 M TEAP, and 0.045 V in acetonitrile with 0.1 M TEAP. The reference electrode used for the spectroelectrochemistry is an Ag wire. In our conditions, we measured $E°(Fc^+/Fc) = -0.423$ V in toluene–acetonitrile with 0.1 M TEAP. The working electrode is either a platinum disc with 0.785 mm^2 area, or an ITO coated glass electrode with *ca.* 2 mm^2 immersed area, as stated in the text.

Tetrabutylammonium perchlorate was purchased from Fluka (puriss). Acetonitrile (Aldrich, 99.8%), dichloromethane (SDS, 99.9%) and toluene (Aldrich, 99.5%) were used as received. All solutions were deaerated by bubbling through argon gas for a few minutes prior to electropolymerization and electrochemical measurements.

UV-visible characterization of monomers was performed using a quartz cell (1 cm optical path) and a Cary500 (Varian) spectrophotometer. Spectra were recorded between 200 and 800 nm. UV-visible spectroelectrochemistry of polymers was performed using a homemade cell: the working electrode was made of ITO covered glass. Platinum and silver wires were used respectively as counter and reference electrodes and located on the cell sides in order not to disturb the beam. A double beam UVIKON 923 (Bio-Tek Kentron) spectrophotometer was used for spectra acquisition: a spectrum was recorded every 100 mV, after which the film was equilibrated in the given redox state for about 2 min.

2.3 Theoretical modeling

The calculations were performed using the Gaussian 98 package[15] for density functional theory. Gas phase geometries and electronic energies were calculated by full optimization without imposed symmetry of the conformations, using the B3LYP[16] density functional with the 6-31G* basis set.[17,18] Spin contamination was low for all calculations (s^2 lower than 0.76).

3. Results and discussion

3.1 Synthesis and spectroscopic features of the monomers

It should be noticed that the synthesis of the monomers is quite easy with the Paal–Knorr procedure (or its modified version for the substituted thiophene rings, see Scheme 2), despite the usually alleged sensitivity of the azobenzene group to acids. In addition, either in the case of the pyrrole or the 2,5-dithienylpyrrole derivatives, the synthesis is straightforward in one or two steps, with overall yields in the 50% range, which is quite significant in view of further applications, especially with regard to the ever increasing complexity of the syntheses of recent molecular materials. This allows gram quantities to be obtained from the relatively cheap precursors dimethoxytetrahydrofuran, thiophene, succinyl chloride and classical "DO" type dyes.

All the monomers are new dyes. Their UV-vis spectra are represented in Fig. 1 and the parameters listed in Table 1. It can be seen that all the absorption coefficients at the maximum wavelength are at the 10^4 mol^{-1}·L·cm^{-1} level, which is characteristic of π-π* transitions in the azo chromophore. A bathochromic shift of the absorption maximum is observed for monosubstituted azo compounds (**1**, **2**, **4**) relative to azobenzene (for the latter $\lambda_{\max} = 313$ nm[19]): this can be explained by an extended conjugation with the polymerizable moiety; the shift is very significant in the case of **2**, which must exhibit a strong "push-pull" character. Another noticeable effect is evidenced by the hypsochromic shift in the absorption maxima of symmetric compounds relative to their asymmetric counterparts (**1** and **4** *vs.* **3** and **5**). This tends to demonstrate a lower conjugation for symmetrically substituted azobenzene derivatives. Since the donor effects of the substituents should lead to the inverse behavior, one must invoke geometrical aspects like a twisted conformation of the molecule in the fundamental state to explain this absorption shift. In agreement with this, the absorption coefficients are all smaller for the symmetrically substituted azobenzenes, probably due to differences in the molecular conformation between fundamental and excited states.

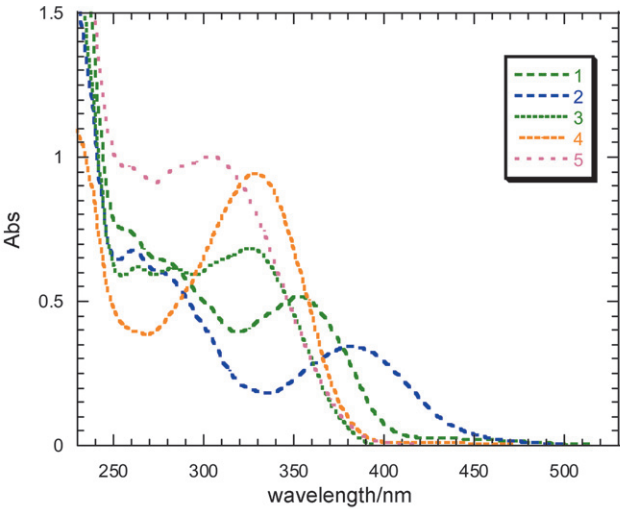


Fig. 1 Absorption spectra of **1**–**5** in dichloromethane (conc. 2.5×10^{-5} mol L^{-1}). Maximum absorption wavelengths and corresponding molar absorption coefficients are listed in Table 1.

Table 1 Spectroscopic features of azo compounds **1**–**5** in dichloromethane (conc. 2.5×10^{-5} mol L^{-1})

Compound	$\lambda_{\max}$/nm	$\varepsilon/10^4$ mol^{-1}·L·cm^{-1}
1	353	2.07
2	382	1.37
3	325	2.73
4	328	3.77
5	304	4.02

3.2 Electrochemical behavior of the pyrrole derivatives

The electrochemistry of pyrrole compounds, substituted on the nitrogen atom by phenyl rings, themselves bearing electron-donor or -attracting groups, has been described a long time ago by Diaz, Salmon and coworkers[20] The authors found some correlation between the oxidation potential and the substituent nature, and in addition polymerization was quite less efficient when an attracting group was located at the para position of the phenyl ring. In the case of our molecules, the electron-attracting power of the azo group, although not very high, is however quite obvious, with unavoidable consequences on the polymerization ability of compounds **1**–**3**.

In fact, **1** and **2** give rise to conducting polymers upon electrooxidation, while **3** does not polymerize when alone in solution. Electropolymerization of **2** is difficult and requires high anodic potential (*ca.* 2 V *vs.* Ag), due to the strong withdrawing power of the nitro substituent. The reason why **3** does not polymerize seems more obscure at first sight, even if a strong stabilization of the radical cation is likely to be achieved through extended conjugation (see §3.4 below). Copolymerization with pyrrole is actually possible, but the incorporation of azobenzene is difficult to check by UV spectroscopy or related methods. Fig. 2(a) features the electrochemical behavior of **1** in dichloromethane. It is clear that in this case a classical conducting polymer is obtained, whose cyclic voltammogram in a solution free of monomer is shown in Fig. 2(b). The standard potential of the polymer is found at −0.13 V *vs.* Ag$^+$/Ag, which is about 0.1 V higher than for classical polypyrrole due to the slight electron-attracting power of the azo linker.

3.3 Electrochemical behavior of the 2,5-dithienylpyrrole derivatives

Both **4** and **5** are very soluble in dichloromethane but in this solvent, the polymer electrogenerated from **5** is unfortunately quite soluble. Therefore, we have chosen for this compound a mixture of toluene–acetonitrile (50:50, v/v) with 0.1 M TBAP as the electropolymerization medium. It had been previously shown to be very convenient for the electrochemical study of thiophene oligomers.[21] The oxidation of monomers **4** and **5** occurs at around +0.6 V (*vs.* Ag/Ag$^+$) on a platinum disc electrode (Fig. 3). Electrochemical polymer growth can be obtained by repeated cycling and an adherent film is deposited on the working electrode after ten cycles. Nevertheless, it seems difficult to obtain thick films, since the growth nearly stops after a few cycles. Polymers can also be potentiostatically synthesized in the same electrolyte. The optimum polymerization potential of **4** is +0.65 V (*vs.* Ag/Ag$^+$), either on a platinum disc or an ITO glass electrode.

Fast scan rate electrochemistry of **4** and **5** has been performed under the same conditions as stated above and the resulting voltammograms are given in Fig. 4. It is clear, especially in the case of **5**, that radical cation formation is chemically irreversible up to 20 V s^{-1} and becomes rather reversible above 50 V s^{-1}, showing that this radical cation is

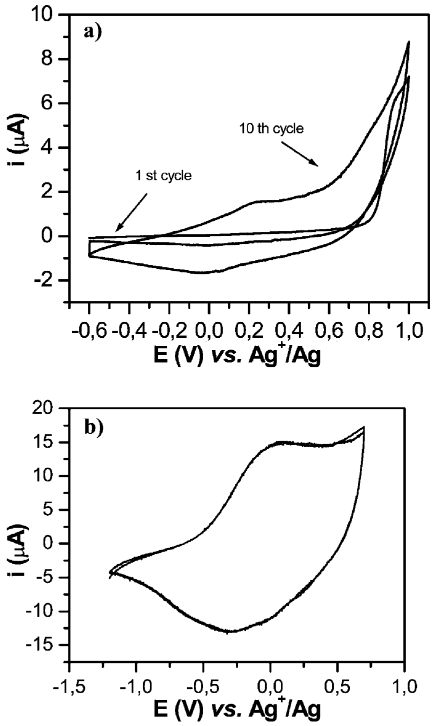


Fig. 2 (a) Electrochemical polymerization of **1** by cyclic voltammetry ($v = 50$ mV s^{-1}) on a platinum working electrode (Ag/10^{-2} M Ag^+ reference). First and tenth cycles in 0.1 M TEAP in dichlomethane. (b) Cyclic voltammogram of poly(**1**) in 0.1 M TEAP in ACN at 10 mV s^{-1} (Ag/10^{-2} M Ag^+ reference).

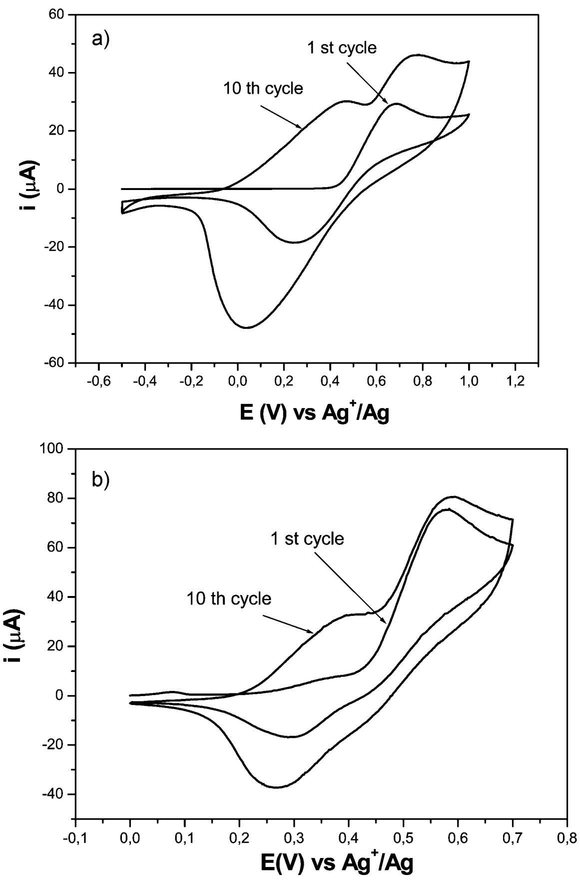


Fig. 3 Electrochemical polymerization of (a) **4** in 0.1 M TEAP in dichloromethane and of (b) **5** in 0.1 M TEAP in acetonitrile–toluene (v/v 50:50), on a platinum disc working electrode (reference Ag/10^{-2} M Ag^+); $v = 100$ mV s^{-1}. First and tenth cycles in each case.

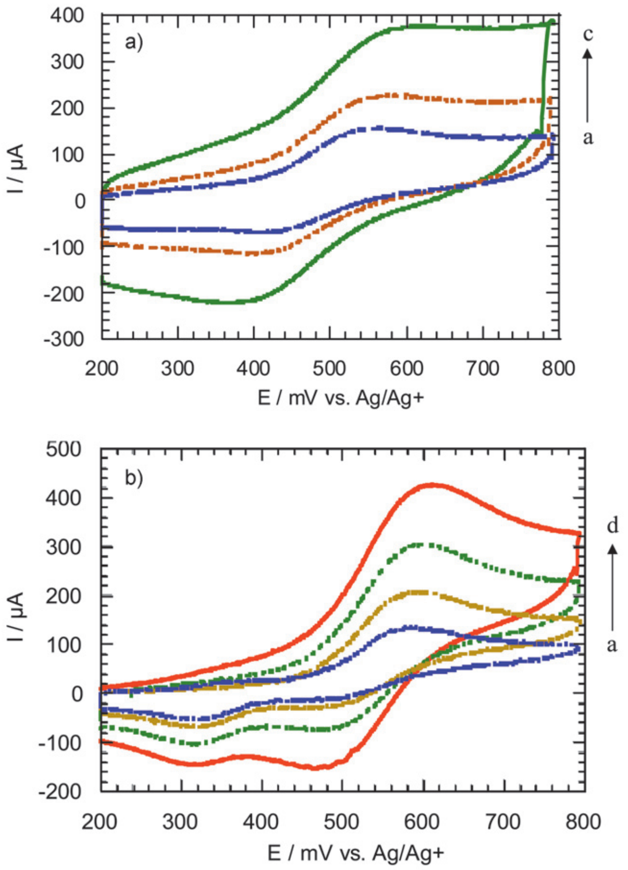


Fig. 4 Fast scan rate electrochemistry of (a) **4** and (b) **5** in 0.1 M TBAP, acetonitrile–toluene (v/v, 50:50), on a platinum disc electrode (reference Ag/10^{-2} M Ag^+) at the following scan rates: (a) 100, 200 and 500 V s^{-1} for curves a–c, respectively; (b) 10, 20, 50 and 100 V s^{-1} for curves a–d, respectively.

relatively stable (lifetime > 10 ms). This stability is actually similar to the one of unsubstituted 2,5-dithienylpyrrole and 2,5-dithienyl-*N*-methylpyrrole[22] radical cations, which seems to account for a weak stabilizing role through extended conjugation played by the azo moiety, which therefore increases the radical cation lifetime.

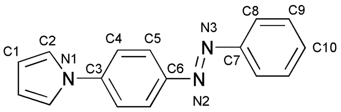
Comparison with ferrocene allows us to measure the standard potential of the radical cation/monomer redox couple, along with the number of exchanged electrons. Standard potentials of +350 and +390 mV *vs.* Fc^+/Fc are obtained respectively for **4** and **5** (compared to +290 mV for unsubstituted 2,5-dithienylpyrrole under the same conditions), while the numbers of exchanged electrons are respectively 0.9 and 1.8. These values confirm that there is no significant stability induced by the possible conjugation of the terheterocycle with the azo group and that the first oxidation process in **5** actually involves both polymerizable moieties.This latter point indicates that a "ladder" structure is likely to be obtained in the case of poly(**5**).

3.4 Theoretical modeling on pyrrole and 2,5-dithienylpyrrole derivatives

In order to explain the electrochemical results, we performed geometry optimizations using the density functional B3LYP for molecules **1**–**5** and their corresponding radical cations for **1**–**4**. This method was chosen as a compromise between acceptable calculation times and good accuracy.

For neutral pyrrole molecules (**1**–**3**), the "diphenyl azo" cores were found to be planar with a small dihedral angle with the pyrrole ring ($\theta = 32.5°$). In the radical cation, the dihedral

Table 2 Bond lengths in the neutral and oxidized forms of compounds **1**–**5** from B3LYP/6-31G* calculations[a]

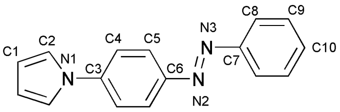


Compound	C1=C2	N1–C3	C4=C5	C6–N2	N2=N3	N3–C7	C8=C9
1	1.372	1.412	1.386	1.415	1.263	1.417	1.393
1$^+$	1.359	1.375	1.373	1.361	1.253	1.381	1.383
2	1.372	1.407	1.389	1.408	1.264	1.417	1.387
2$^+$	1.358	1.373	1.371	1.360	1.252	1.389	1.389
3	1.373	1.412	1.386	1.413	1.264	1.412	1.390
3$^+$	1.361	1.379	1.372	1.372	1.292	1.371	1.375
4	1.388	1.242	1.393	1.419	1.262	1.417	1.389
4$^+$	1.428	1.256	1.389	1.420	1.264	1.408	1.393
5	1.387	1.428	1.391	1.416	1.262	1.416	1.388
Reference	1.379[b]	1.465[c]	1.397[d]	1.465[c]	1.246[e]	1.465[c]	1.397[d]

[a] See structure above for atom numbering. [b] C=C in pyrrole. [c] N–C in H_2N–CH_3. [d] C=C in benzene. [e] N=N in HN=NH.

angle decreases ($\theta = 15.8°$), but the most considerable changes are located in the azo core, which becomes highly distorted. Similar behavior was observed for the radical cation of **2**, while the deformations of the azo core were much smaller in the radical cation of **3**. To get more quantitative data on the geometry changes, it is interesting to compare the bond length changes from the neutral to the cation state in the case of a few characteristic bond lengths (see Table 2). The results of the calculations demonstrate that bond lengths tend to equalize in the radical cation, with the largest modifications occurring in the "diphenyl azo" group, indicating a high degree of conjugation in all the molecules. Similarly, the spin densities in the radical cations are also consistent with extensive delocalization of the unpaired electron over the whole molecule with maxima around the azo moiety (Table 3). This delocalization of the unpaired electron seems to be better in the bispyrrole molecule **3** than in the two other substituted pyrroles, explaining the difficulties to polymerize it. Thus, we can conclude that electronic interactions actually exist between the pyrrole rings and the azo group in the neutral and even more in the radical cation forms, although remaining globally less important that what could have been expected.

Table 3 Mulliken spin densities in the radical cation forms of compounds **1**–**4** from B3LYP/6-31G* calculations



Atom[a]	**1**$^+$	**2**$^+$	**3**$^+$	**4**$^+$
C1	0.06	0.07	0.07	0.06
C2	−0.02	−0.03	−0.03	0.22
N1	0.09	0.11	0.10_5	−0.07
C3	0.07	0.06	0.10	0.00
C4	0.02	0.04	0.02	0.00
C5	0.02	0.00	0.02	0.00
C6	0.09	0.12	0.11	0.00
N3	0.19	0.17	0.03	0.00
N4	0.25	0.25	0.03	0.00
C7	0.00	−0.02	0.11	0.00
C8	0.07	0.07	0.02	0.00
C9	−0.04	−0.04	0.02	0.00
C10	0.11	0.10	0.10	0.00

[a] See structure above for atom numbering.

The situation is completely different with the terheterocycles. In the neutral and radical cation forms of **4** and **5**, the phenyl group is too large to be planar with the heterocycle. Due to the steric hindrance, the "diphenyl azo" core is almost perpendicular to the terheterocycle head (see Fig. 5). This results in a very weak conjugation between the polymerizable moiety and the azo group. This is confirmed by looking at the bond changes in the radical cation form of compound **4**: the bond lengths in the azo core remain almost unchanged when passing from the neutral to the cation state. Similarly, the spin density in the oxidized form of **4** is close to zero in the azo group. Because of limited calculation times, we calculated only the neutral form of **5**, but a similar nonplanar geometry was observed, indicating a very low electronic interaction between the two heterocycle moieties through the azo linker. All these results tend to evidence a much weaker conjugation for the 2,5-dithienylpyrrole derivatives than for the pyrroles, due to larger steric hindrance between the polymerizable moiety and the azo chromophore.

3.5 Spectroelectrochemical characterization of the polymers

Fig. 6 shows cyclic voltammograms of poly(**4**) in 0.1 M TEAP/acetonitrile. The polymer film exhibits the classical features observed with conducting polymers, especially the peak currents vary linearly with the scan rate. The oxidation peak E_{pa} of poly(**4**) is observed at 0.30 V and the reduction peak E_{pc} is at 0.22 V, corresponding to a standard potential equal to 0.26 V. Poly(**5**) shows analogous behavior, with the oxidation peak E_{pa} at 0.36 V and the reduction peak E_{pc} at 0.28 V, leading to a standard potential equal to 0.32 V. One can notice a minor shift between the standard potentials of the

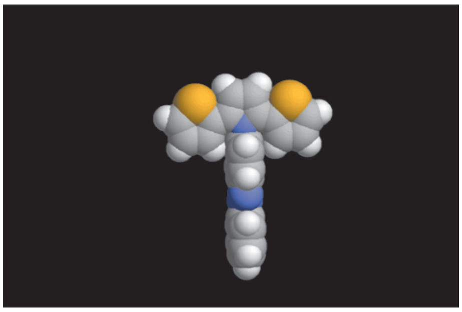


Fig. 5 Optimized geometry of the neutral form of **4** calculated at the B3LYP/6-31G* level, showing the position of the azo group perpendicular to the (2,5-dithienylpyrrole) plane.

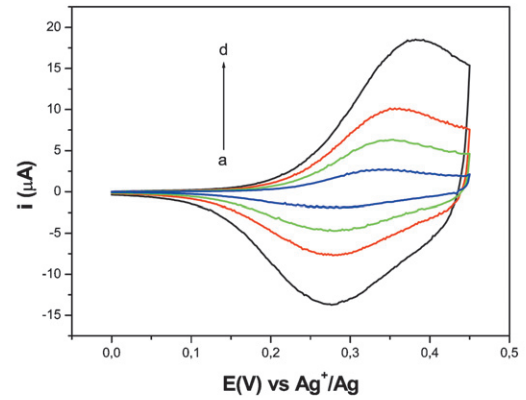


Fig. 6 Cyclic voltammograms of poly(**4**) in 0.1 M TEAP in acetonitrile on a platinum disc electrode (Ag/10^{-2} M Ag^+ reference) at scan rates of 20, 40, 60 and 100 mV s^{-1} for curves a–d, respectively.

monomers (deduced from high scan rate measurements) and those of their corresponding polymers: this is indicative of a low degree of polymerization or of short conjugation lengths due to a high number of structural defects.

Poly(**4**) and poly(**5**) films were deposited potentiostatically on ITO-coated glass plates, in their respective polymerization media, with 0.01 M monomer and 0.1 M TEAP, in order to perform spectroelectrochemical studies. The spectra were initially recorded in the fully reduced state of the polymers. For this state, an absorption peak is observed at $\lambda_{max} = 420$ nm, which is attributed mainly to the azo chromophore. The π-π* transition of the conjugated polymer is hidden behind the azo chromophore absorption, making it difficult to evaluate the band gap of the polymer. One can see clearly in Fig. 7 the strong increase of absorption in the red part of the spectrum when the applied potential becomes more anodic: this corresponds to the generation of charge carriers (polarons and bipolarons) in the polymer chains.[23] The analysis of the spectra for poly(**4**) tends to show a maximum contribution of radical cation species (polarons, $\lambda_{max} \approx 640$ nm) at 0.6 V, while at more anodic potentials, these species are converted into dications (bipolarons), as evidenced by the gradual absorption increase beyond 800 nm along with the stagnation of the absorption around 640 nm. In the case of poly(**5**), the amount of polarons increases regularly, while the contribution of bipolarons appears significantly only at 1.2 V. The difference between both polymer spectra is consistent with the participation of both 2,5-dithienylpyrrole moieties in the formation of polarons in poly(**5**), leading to a higher amount of polarons for approximately the same doping level.

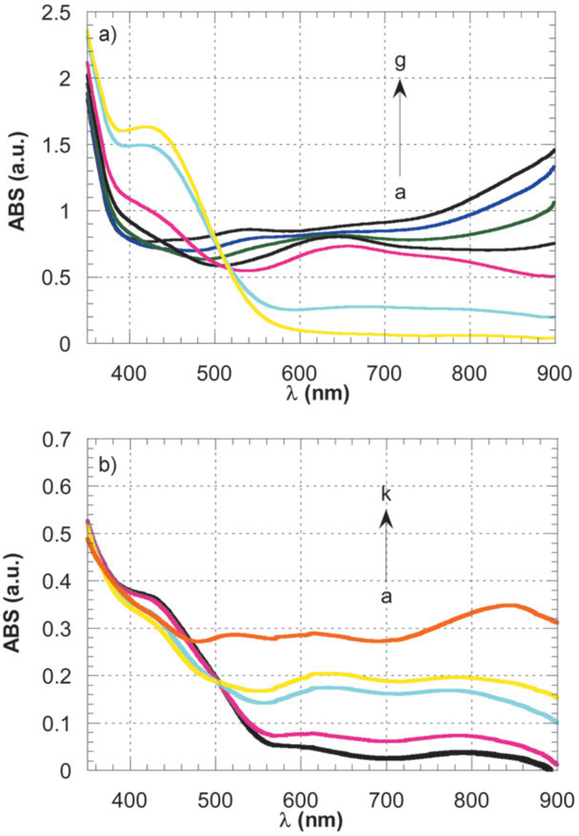


Fig. 7 Spectroelectrochemistry of a film of (a) poly(**4**) in CH_2Cl_2 and (b) poly(**5**) in acetonitrile–toluene (v/v, 50:50), on an ITO working electrode at various electrode potentials (Ag wire reference). Each film was obtained potentiostatically at $E = 1.0$ V (a) or 1.2 V (b) applied during 500 s ($Q \approx 100$ mC·cm^{-2}). Electrode potential: (a) −0.5, 0.3, 0.5, 0.6, 0.7, 0.8 and 0.9 V for curves a–g, respectively; (b) 0.1, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.85, 0.9, 1.0 and 1.2 V for curves a–k, respectively. *N.B.*: curves a–f in (b) are exactly the same and are represented as the bottom curve.

4. Conclusion

We have presented the synthesis and electrochemical study of new conjugated polymers with azo groups directly connected to the polymer chain. The synthesis procedure is quite straightforward and affords the target molecules with rather good yields. The first results obtained from spectroscopic and electrochemical measurements, as well as the theoretical calculations, have demonstrated an extended conjugation brought about by the azo moiety in the pyrrole derivatives. In the case of 2,5-dithienylpyrrole derivatives, no stabilizing effect through the conjugation with the azo group has been observed, leading to oxidation localized on the polymerizable units. Therefore, it seems unfortunately unlikely that in conjugated polymers of this kind, a high conjugation may be achieved between the main chain and the functional group. However, this feature remains to be confirmed by further studies.

References

1 C. S. Wang, *Trends Polym. Sci. (Regul. Ed.)*, 1997, **5**, 138.
2 B. Hauschel, P. Stihler and M. Hanack, *Trends Polym. Sci. (Regul. Ed.)*, 1996, **4**, 348.
3 J. D. Debad and A. J. Bard, *J. Am. Chem. Soc.*, 1998, **120**, 2476.
4 J. P. Lang, H. Kawaguchi and K. Tatsumi, *Inorg. Chem.*, 1997, **36**, 6447.
5 T. Shimidzu, H. Segawa, F. Wu and N. Nakayama, *J. Photochem. Photobiol., A*, 1995, **99**, 1.
6 H. Segawa, F.-P. Wu, N. Nakayama, H. Maruyama, S. Sagisaka, N. Higuchi, M. Fujitsuka and T. Shimidzu, *Synth. Met.*, 1995, **71**, 2151.
7 K. I. Chane-Ching, J. C. Lacroix, R. Baudry, M. Jouini, S. Aeiyach, C. Lion and P. C. Lacaze, *J. Electroanal. Chem.*, 1998, **453**, 139.
8 P. E. Just, K. I. Chane-Ching, J. C. Lacroix and P. C. Lacaze, *J. Electroanal. Chem.*, 1999, **479**, 3.
9 I. Lévesque and M. Leclerc, *Macromolecules*, 1997, **30**, 4347.
10 M. Zagorska, I. Kulszewics-Bajer, A. Pron, J. Sukiennik, P. Raimond, F. Kajzar, A.-J. Attias and M. Lapkowski, *Chem. Mater.*, 1998, **31**, 9146.
11 C. Della-Casa, A. Fraleoni, P. Costa-Bizzari and M. Lanzi, *Synth. Met.*, 2001, **124**, 467.
12 Y. Chen, W. T. A. Harrison, C. T. Imrie and K. S. Ryder, *J. Mater. Chem.*, 2002, **12**, 579.
13 D. Channe Gowda and B. Mahesh, *Synthetic Commun.*, 2000, **30**, 3639.
14 D. Garreau and J. M. Savéant, *J. Electroanal. Chem.*, 1975, **50**, 1.
15 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi,

V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian 98, rev. A.1, Gaussian, Inc., Pittsburgh, PA, USA, 1998.

16 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

17 P. C. Hariharan and J. A. Pople, *Chem. Phys. Lett.*, 1972, **16**, 217.

18 (*a*) Hybrid density functional methods with the 6-31G* base have been used previously for calculations on neutral and radical cation of heterocycles containing sulfur atoms[18b–d] and on extended TTF and have been found to give a good qualitative description of their properties; (*b*) V. Hernández, H. Muguruma, S. Hotta, J. Casado and J. T. López Navarrete, *J. Phys. Chem. A*, 2000, **104**, 735; (*c*) T. Keszthelyi, M. M.-L. Grage, J. F. Offersgaard, R. Wilbrandt, C. Svendsen, O. S. Mortensen, J. K. Pedersen and H. J. A. Jensen, *J. Phys. Chem. A*, 2000, **104**, 2808; (*d*) A. J. Moore, M. R. Bryce, A. S. Batsanov, A. Green, J. A. K. Howard, A. McKervey, P. McGuigan, I. Ledoux, E. Orti, R. Viruela, P. M. Viruela and B. Tarbit, *J. Mater. Chem.*, 1998, **8**, 1173.

19 H. Rau, in *Photochemistry and Photophysics*, ed. J. F. Rabek, CRC press, London, 1990, vol. II, ch. 4, p. 119.

20 (*a*) A. F. Diaz, J. Castillo, K. K. Kanazawa, J. A. Logan, M. Salmon and O. Fajardo, *J. Electroanal. Chem.*, 1982, **133**, 233; (*b*) M. Salmon, M. Aguikar and M. Saloma, *J. Chem. Soc., Chem. Commun.*, 1983, 570.

21 P. Audebert, P. Hapiot, P. Garcia, J. M. Pernaut and K. Monnier, *Chem. Mater.*, 1994, **6**, 1549.

22 P. Audebert, J. M. Catel, G. Le Coustumer, V. Duchenet and P. Hapiot, *J. Phys. Chem. B*, 1998, **102**, 8661.

23 D. J. Firmin, H. Teruel and B. R. Scharifker, *J. Electroanal. Chem.*, 1996, **401**, 207.