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Alternating Donor−Acceptor Substitutions in Conjugated Polythiophenes

F. Demanze, A. Yassar, and F. Garnier*

Laboratoire des Matériaux Moléculaires, CNRS, 2 rue Dunant, 94320 Thiais, France

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ABSTRACT: A series of bithiophenes, disubstituted with electron donor and electron acceptor groups, have been synthesized. The electronic effects exerted by these groups, on the electrochemical oxidation potential of bithiophenes, are additive, which allows us to control the overall substituent effect and make it compatible with the electropolymerization of these molecules. The electrochemical characterization of the resulting polymers has revealed unusual properties, in the case of unsymmetrical disubstitution with strong electron acceptor and donor groups. Charge confinement is observed for the first oxidated state of poly(3-cyano-3′-methoxybithiophene), which has been interpreted by the existence of multiple potential wells, created by these push−pull substituents alternating along the conjuated polythiophene chain.

The first attempts toward the functionalization of organic conjugated polymers has mainly aimed at the improvement of their very low solubility and has been realized for instance by the grafting of alkyl or alkoxyl chains on polythiophene, polyaniline, or poly(phenylenevinylene).[1,2] The potential interest of such functionalization for controlling the electronic properties of conducting polymers was then emphasized, and much work has clearly shown how electron donor or electron acceptor groups, when substituted on the conjugated polymer backbone, allow the control of the band level energies, together with the tuning of the band gap of these polymers.[3] This elegant approach has been recently successfully applied to the field of electroluminescent diodes, allowing a large variation of the emitted light wavelength, and also the building of efficient charge blocking layers.[4,5] Most of these polymer functionalizations have been up to now based on the use of only one type of substituent, either electron donor or electron acceptor. However, conjugated polymers are materials whose electronic properties can be designed at the molecular level of their monomer units, which means that multiple functionalization is in principle achievable.[6] By the appropriate multifunctionalization of the monomers, considered as the bricks of the molecular assembly, very elaborate polymer architectures can be constructed, in which new electronic properties can be expected from the use of substituents with different electronic effects. With this aim, we report here on the synthesis and characterization of conjugated polythiophenes, in which the adjacent thiophene units are alternatively substituted with donor and acceptor substituents. These polymers have been realized from disubstituted bithiophene, used as monomer building blocks. The synthesis and characterization of these disubstituted bithiophenes will be first described, followed by those of poly(disubstituted bithiophenes).

Synthesis

Various experimental routes have been proposed in the literature for synthesizing symmetrically disubstituted oligothiophene derivatives, A-*n*T-A[7] or D-*n*T-D,[8] or unsymmetrically disubstituted ones, A-*n*T-D,[8] where *n*T represents a short conjugated oligothiophene containing *n* thiophene units, and A and D represent acceptor and donor groups, respectively. In order to obtain regioselectively substituted derivatives, it has been shown that the most pertinent route involves the coupling between appropriately substituted aromatic subunits.

Bithiophene, symmetrically disubstituted with electron donating groups, can be obtained by direct homocoupling of the corresponding substituted thiophenes D-T. The higher acidity of the protons in the α-position in thiophene, as compared to the *β* one, allows the selective lithiation of the α-position, by the use of *n*-butyllithium, *n*-BuLi, at −70 °C, followed by a further coupling using $Fe(acac)_3$,[9] which leads to the desired D-2T-D compounds, as shown in the case of 3,3′-dimethoxybithiophene. This reaction is more difficult to perform when using an acceptor susbtituted thiophene, A-T. As a matter of fact, strong acceptor groups are sensitive to *n*-BuLi and mainly lead to the formation of byproducts. This problem can be overcome by using a milder lithiating agent, such as lithium diisopropylamide, LDA, which is less basic than *n*-BuLi, or alternatively by protecting the acceptor group. Thus, in the case of A = COOH, the carboxylic function has been first protected by esterification with ethanol in presence of $SOCl_2$. After lithiation by LDA and coupling with $CuCl_2$, the deprotection by acid hydrolysis is carried out on the final disubstituted bithiophene derivative. However, in the case of A = CN, the 2-lithio-3-cyanothiophene, which is obtained by using LDA in anhydrous diethyl ether at −70 °C, could not be coupled by the use of copper chloride.

For the synthesis of unsymmetrically disubstituted bithiophene, A-2T-D, the classical Ullmann[10] or Gomberg[11] coupling reactions cannot be employed, as secondary reactions with the functional A and D groups do not allow the required high selective coupling in the α-positions of the thiophene units. The most efficient synthetic route involves the coupling between an organozincic derivative and a 2-halogenated thiophene derivative, which allows the coupling between differently substituted thiophene moieties.[12] This coupling is catalyzed by a transition metal catalyst, which is chosen for its activity, its chimio and regioselectivity, and its very low sensitivity toward the functional groups. Complexes from $Pd^{(0)}$, such as tetrakis(triphenylphosphine)palladium, show lower sensitivity toward

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Chart 1. Structure of 3,3′-Disubstituted 2,2′-Bithiophenes

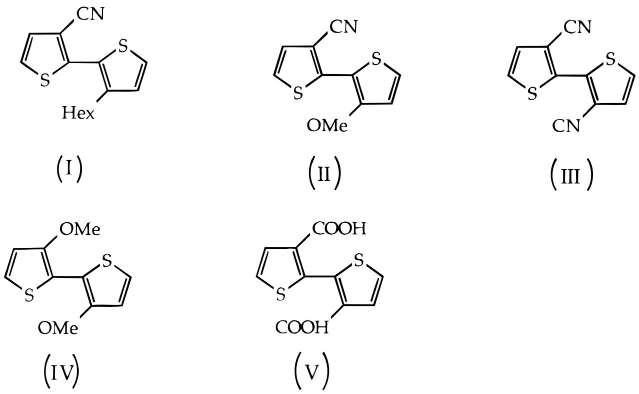

Table 1. Oxidation Potentials, E_{ox}, of 3,3′-Disubstituted 2,2′-Bithiophenes[a]

substituents: X,Y	E_{ox1}	E_{ox2}	E_{ox3}
X = Y = CN	1.86	2.19	2.36
X = CN, Y = hexyl	1.53	1.88	2.10
X = Y = COOH	1.50		
X = Y = H	1.26	1.62	1.78
X = CN, Y = OMe	1.23	1.62	2.06
X = Y = OMe	0.74	1.30	1.68

[a] Reference: SCE.

electron accepting groups than nickel-based catalysts.[13] The 2-halogenation of thiophenes, 3-substituted by electrodonating groups, is best carried out by the use of *N*-bromosuccinimide (NBS) in dimethylformamide as solvent, as recently proposed by P. Baüerle,[14] at a temperature of −20 °C for favoring mono- over dibromination. Thus, 3-methoxythiophene and 3-hexylthiophene were converted, by this way, into 2-bromo-3-methoxythiophene and 2-bromo-3-hexylthiophene. 2-Bromo-3-methoxythiophene and 2-bromo-3-hexylthiophene were coupled with the zincic derivative of 2-lithio 3-cyanothiophene, in anhydrous ether and in the presence of tetrakis(triphenylphosphine)Pd$^{(0)}$.

By the use of these synthetic routes, detailed at the end of the text, compounds **I**−**V**, as shown in Chart 1, were synthesized.

Results and Discussion

Electrochemical Characterization of Monomers. Unsubstituted bithiophene as well as disubstituted **I**−**V** bithiophenes show a comparable cyclic voltammogram, with a well-defined oxidation peak, E_{ox1}, followed by two shoulders, E_{ox2} and E_{ox3} (Figure 1). Electrochemical data are reported in Table 1. When using unsubstituted bithiophene as reference, with an oxidation peak at 1.26 V/SCE, these data show that symmetrical disubstitution by electron donating groups, such as methoxy ones in **IV**, leads to a significant decrease of the oxidation potential, of 520 mV for (3,3′-dimethoxybithiophene). Inversely, electron accepting groups induce an important increase of the oxidation potential, up to 600 mV for the dicyano-substituted bithiophene (**III**). Substituent effect allows thus an extraordinary large variation of 1.12 V in the oxidation potential of bithiophene, when passing from strong donor substituents, dimethoxy, to strong acceptor ones, dicyano.

These variations can be rationalized by the use of substituent parameters σ_p^+, proposed by Brown[15] for describing their electronic effects, in terms of a linear free energy relationship relating the oxidation potential E_{ox} to σ_p^+ (*16*), $E_{ox} = E_{ox}^H + \rho_p\sigma_p^+ + S$, where S is a parameter taking account for steric effects induced by the substituents and E_{ox}^H is the oxidation potential of unsubstituted bithiophene. In the case of low or comparable steric interactions originating from these substituents, linear relations are observed between E_{ox} and σ_p^+, as evidenced on Figure 1. The obtained slope $\rho_p = 0.382$ can be compared to that obtained in the case of 3-substituted thiophenes, already given in the literature, $\rho_p = 0.615$.[16] The much lower value of the slope for bithiophenes, as compared to that of thiophenes, can be attributed to the higher delocalization of the π-conjugated system in the bithiophene series.

When unsymmetrically disubstituted with an electron accepting group and an electron donating one, bithiophenes show an intermediate variation of their oxidation potential. It is noteworthy to mention that these substituent effects are strictly additive, as the E_{ox} values corresponding to **I** and **II** fit precisely with the linear relationship obtained previously. This correlation allows thus an interesting predictive approach for the determination of oxidation potentials of unsymmetrically substituted bithiophenes. As a matter of fact, the tuning of the monomer oxidation potential appears necessary, on one hand for achieving a sufficiently high oxidation potential value required for the electropolymerization to take place, without reaching on the other hand the overoxidation potential range, which leads to the degradation of polybithiophene.

Electropolymerization of Monomers. These disubstituted bithiophenes can be electropolymerized, as shown for example by the first cyclic potential scans carried out between −0.2 and 2.0 V/SCE for (3,3′-dimethoxybithiophene) 10^{-1} M in acetonitrile, with 0.1 M of tetrabutylammonium perchlorate, TBAP, as electrolyte. In addition to the already reported peaks at 0.42, 1.26, and 1.6 V/SCE, attributed to the monomer oxidation, new peaks appear at 0.40 and 1.38 V/SCE, which are associated to the growth of an electroactive species onto the platinium working electrode. When performing successive scans between −0.2 and +1.4 V/SCE, the polymer film obtained on the electrode is stable and electroactive, as characterized in an acetonitrile−$LiClO_4$ 10^{-1} M electrolytic medium. The polymer oxidizes at +0.4 V/SCE and reduces at 0.04 V/SCE, the peak intensity being proportional to the scan sweep rate, which indicates the presence of an electroactive species grafted onto the electrode. The polymer electroactivity is stable with time when electrochemical scans are carried out between −0.2 and +0.8 V/SCE. However, degradation of the polymer is observed when the electrode potential is driven to 1.4 V/SCE, which can be attributed to overoxidation of the polybithiophene, as generally observed for conjugated polymers.

All monomers could be polymerized, excepting those bearing strong acceptor groups, 3,3′-diacid carboxylic bithiophene (**V**) and 3,3′-dicyanobithiophene (**III**). This absence of polymerization can be attributed to the decrease of the electronic density on the α- and α′-positions of the disubstituted bithiophene, which increases its oxidation potential and hence its reactivity toward nucleophilic solvents. The electropolymerization of 3-hexyl-3′-cyanobithiophene (**I**) is accompanied by the apparence of a dark red coloration at the vicinity of the working electrode, indicating the formation of soluble oligomers.

Whereas electropolymerization reactions of these monomers can be performed in various media, including nitrobenzene or propylene carbonate, in the case of

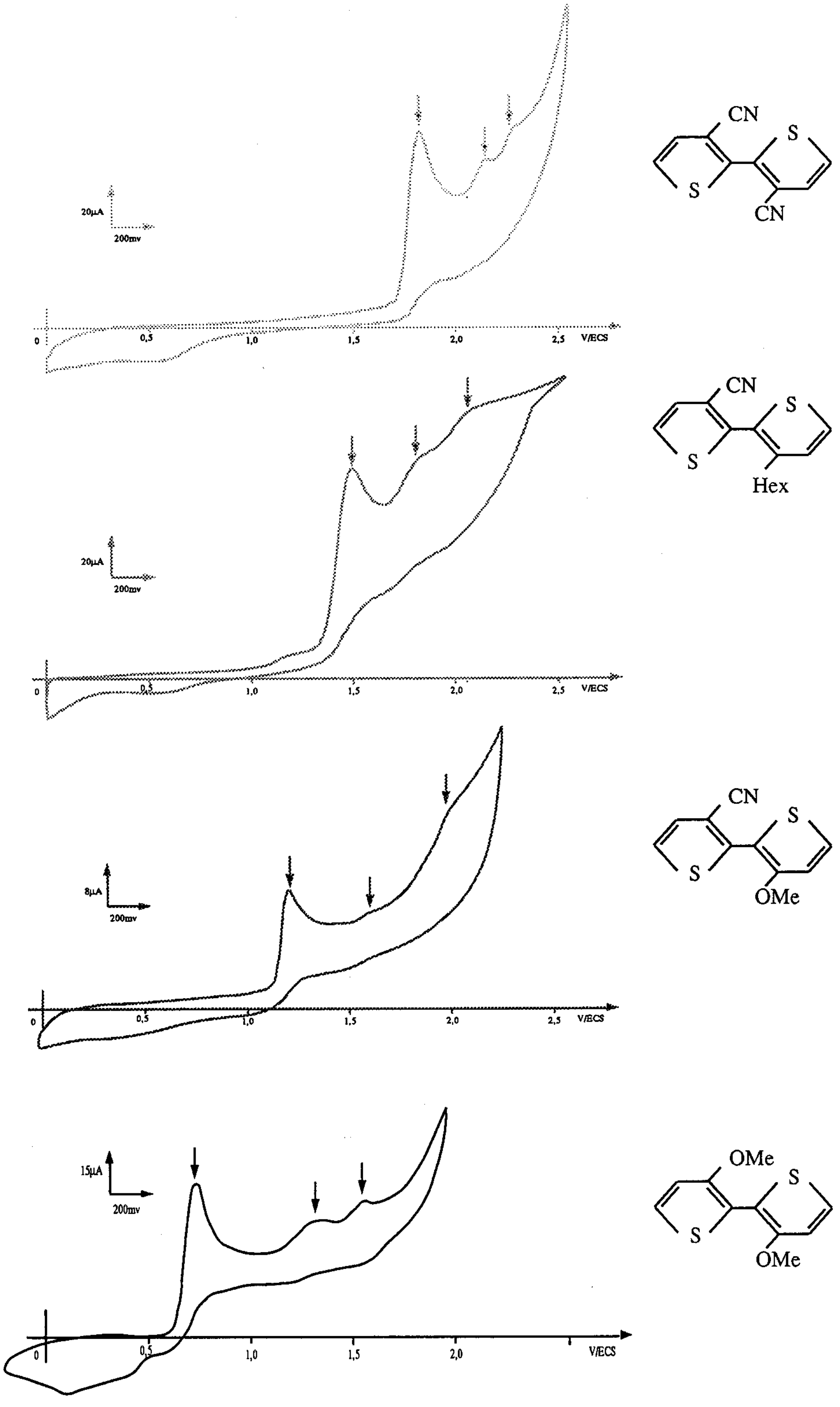

Figure 1. Cyclic voltammogram of 3,3′-disubstituted 2,2′-bithiophenes in 0.1 M $LiClO_4-CH_3CN$, scan rate 50 mV/s.

3-cyano-3′-methoxybithiophene) (**II**), self-standing films are only obtained when using acetonitrile as electropolymerization medium. The other solvents lead to thin powdery deposits, which do not adhere on the electrode and are released in the electrolytic medium during electrochemical cycling. Oligomers rather than polymers must have been formed in this last case. The structure which can be assigned for poly(**II**) relies on the orientation during coupling of monomer molecules during their polymerization, which can proceed either randomly or regioselectively. Whereas unsubstituted thiophenes show a same reactivity at their α-positions, it is known that substituents on the β-positions induce a dissymetry of reactivity of the α-, 2-, and 5-positions, which increases with the strength of electronic effect of the substituents, orienting the coupling toward higher regioselectivity. Thus, it has been recently shown that 3-alkyl-4-alkoxy disubstitutions lead to a 95% regioselectivity for the obtained polythiophene, even when using a strong coupling agent such as $FeCl_3$.[8] Owing to the stronger electronic effects of the CN and methoxy substituents present on monomer **II**, it can be assumed

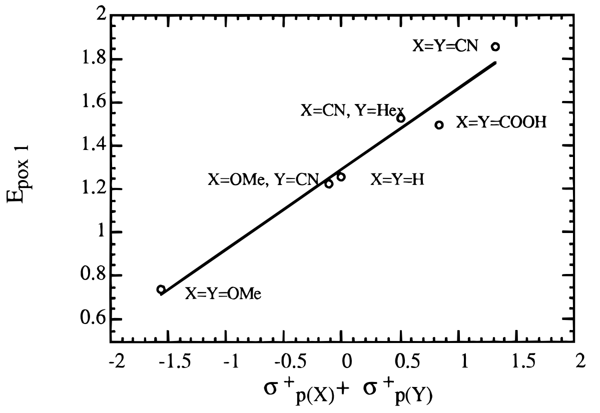

Figure 2. Free energy relationship between the oxidation potentials of bithiophenes, E_{ox}, and the substituent constant σ^+.

Table 2. Oxidation, $E_{ox,pol}$, and Reduction, $E_{red,pol}$, Potentials of Poly(3,3′-Disubstituted 2,2′-Bithiophenes)[a]

substituents: X, Y	$E_{ox1,pol}$	$E_{ox2,pol}$	$E_{ox3,pol}$	$E_{red1,pol}$	$E_{red2,pol}$
X = CN, Y = hexyl	1.10			0.92	
X = Y = H	0.95			0.57	0.85
X = OMe, Y = CN	0.84	1.10	1.30	0.70	1.10
X = Y = OMe	0.40		1.38	0.04	

[a] Reference: SCE.

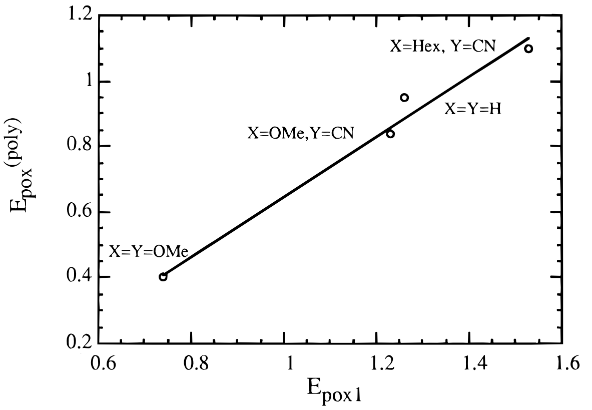

Figure 3. Relationship between the oxidation potentials of tthe polymer, $E_{ox,pol}$, and of the monomer, E_{ox}.

that the 2- and 5′-positions of **II** will show a large difference in reactivity, and that the monomer units **II** will be mostly regioselectively coupled in the resulting polymer poly(**II**). Thus, monomer **II** forms an intermediate case between the dicyano derivative **III** where the α-positions are completely deactivated, and the dimethoxy deriavtive **IV**, for which the large and symmetrical recativity of α-positions is observed.

Electrochemical Characterization of Polymers. The oxidation potentials of the obtained polymer films, $E_{ox,pol}$ (Table 2), are also very sensitive to substituent effects, electron donating and accepting groups leading to a decrease and to an increase of $E_{ox,pol}$, respectively. These variations can also be rationalized in terms of a linear free energy relationship, as in the case of monomers. Figure 3 shows that electronic effects of substituents have comparable effects on the polymer as on the monomers, in agreement with results obtained with substituted thiophenes.[16]

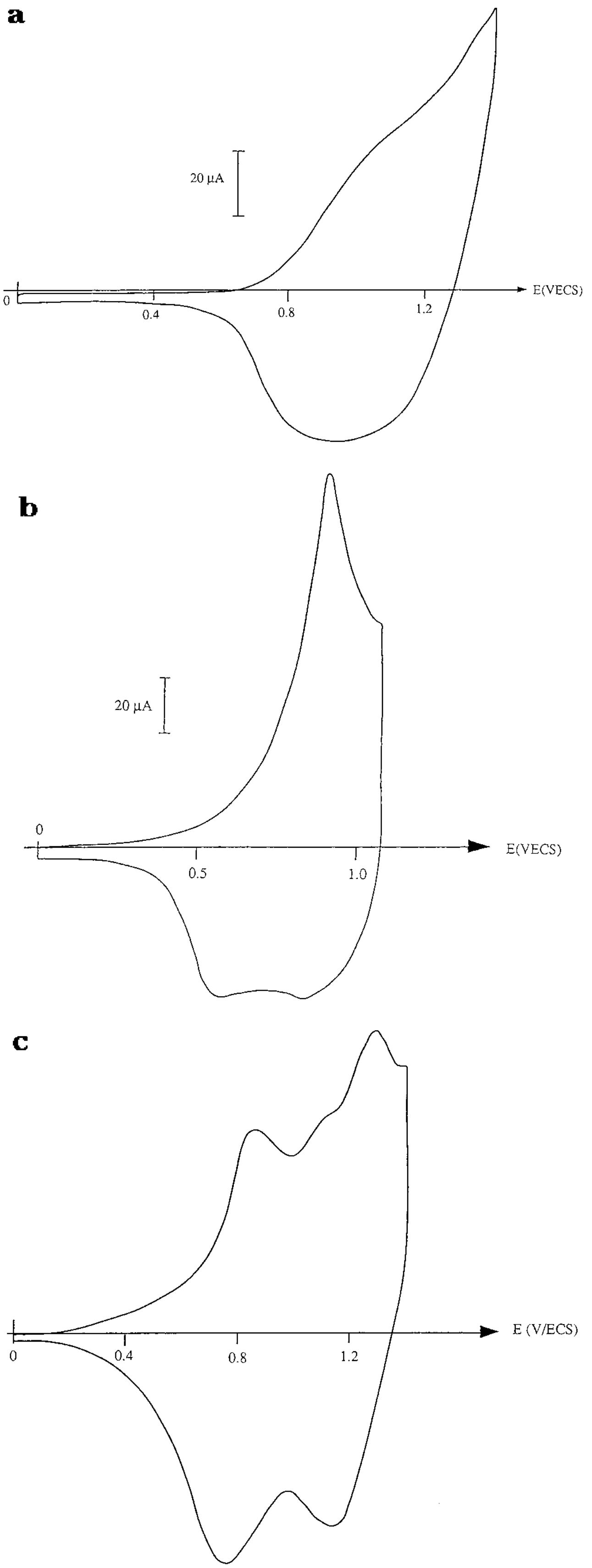

Figure 4. Cyclic voltammograms of (a) poly(3-hexyl-3′-cyano-2,2′-bithiophene); (b) poly(2,2′-bithiophene); (c) poly(3-cyano-3′-methoxy-2,2′-bithiophene), realized in 0.1 M n-Bu_4ClO_4–CH_3CN, scan rate 50 mV/s.

The electrochemical properties of poly(3-hexyl-3′-cyanobithiophene), poly(**I**), have been detailed by analyzing its voltammetric behavior. The cyclic voltammogram of poly(**I**), Figure 4a, shows a broad anodic wave at 1.1 V and a reduction wave at 0.92 V/SCE. When compared to unsubstituted polybithiophene, the higher E_{pa} value observed with poly(**I**) indicates a shorter effective conjugation length, which may result from the

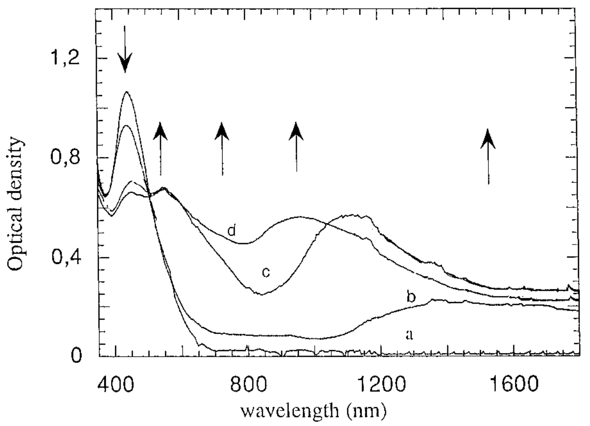

Figure 5. Spectroelectrochemical analysis of poly(3-methoxy-3′-cyano-2,2′-bithiophene). UV/visible/near-IR spectra were recorded at the following potentials (V/SCE): (a) 0.0; (b) 0.8; (c) 1.1; (d) 1.2.

overall withdrawing effect of both substituents. It is known that electron donating groups in the 3-position of thiophene decrease the oxidation potential of the monomer and increase the stability of its cation radical. On the other hand, electron withdrawing substituents exert an opposite effect, inducing a high oxidation potential of the monomer and a high reactivity of the corresponding radical cation, which can thus undergo rapid reactions with the solvent, to form soluble products rather than a stereoregular α−α′ polymer. An elegant way for neutralizing the strong electron accepting effect of the cyano group involves the use of a second strong electron donating group, such as methoxy one.

Poly(3-cyano-3′-methoxybithiophene), poly(**II**), shows interesting results, which have been compared to polybithiophene, Figure 4b. Instead of a wide oxidation peak observed with polythiophenes, poly(II) shows three very sharply defined oxidation peaks, located at 0.84, 1.1, and 1.3 V/SCE (Figure 4c. These electrochemical couples, and mainly the first one, show a high reversibility, as indicated by its peak shift value, $\Delta E = E_{\mathrm{ox}} - E_{\mathrm{red}}$, close to 60 mV. The stability and high electrochemical reversibility observed for the first, electrochemically independent, oxidated state, at 0.84 V/SCE, suggest that the positive charge is strongly localized, which means that the polaronic state extends over a very short conjugated segment of the polythiophene chain. The second redox system is compatible with a π-dimer, corresponding to the entanglement of two polarons, and, finally, the third oxidation state corresponds to the formation of a bipolaron, extended over a much longer conjugated segment, as observed in the case of classical oxidized polythiophenes, for which a precise length is difficult to assess.

Further characterization of these states has been carried out by means of spectroelectrochemistry, by imposing the appropriate potential on this polymer film deposited on ITO, and recording the absorption spectrum in the UV−visible and near-infrared range.[17] As shown in Figure 5, the absorption spectrum of the neutral polymer, Figure 5a, located at 435 nm, is associated to the $\pi-\pi^*$ transitions of the conjugated polymer chains. Upon first oxidation, new absorption bands appear at 735 and 1400 nm, Figure 5b, which agree with the formation of a polaronic state. By comparing the position of these absorption maxima with literature data on the spectral properties of radical cations derived from oligothiophenes, a short conjugation length can be inferred to this polaronic state, of some 3 thiophene units. Upon further oxidation, a new band appears near 557 nm, together with a slight blue shift of the lower energy absorption band, Figure 5c, which is attributed to the dimerization of the radical cations into π-dimers. Finally, at higher oxidation potential, a large band centred at 960 nm is created, Figure 5d, which corresponds to the formation of the stable bipolaronic state.

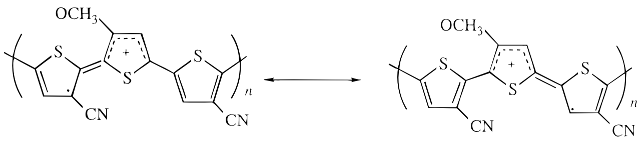

Figure 6. Structure proposed for the polaronic state, with confinement of charge in a molecular-based potential well.

The electrochemical and optical features observed for the first charged state suggest that the positive charges developed in the polaronic state are confined on short conjugated segments, of about three thiophene units, along the polythiophene chains. As the most reasonable interpretation, it can be proposed that the positive charges are located on the hole-attracting 3-methoxythiophene units of the polymer chain. These positive charges encounter on both adjacent 3-cyanothiophene units large potential barriers, due to the electron withdrawing and thus hole-repelling properties of the cyano groups, which explains the experimental fact that the positive charges are strongly localized along the polymer backbone. Such sequences of (3-cyanothiophene)−(3-methoxythiophene)−(3-cyanothiophene) represent thus the charge confinement units in the polymer chains and can be described as molecular potential wells, extending over three adjacent thiophene units, which determines the well thickness, Figure 6. Polymers derived from unsymmetrically substituted bithiophenes can thus be described as organic multiple potential well structures, which opens interesting perspectives. As a matter of fact, the characteristics of these organic-based potential wells can be easily tuned, through subtle chemical modifications of the monomer units, i.e., the building blocks of these materials. The well thickness can be designed by the length of the monomer unit, and the well depth is determined by the difference in the electronic effect between electron attracting and electron donating groups. These features open the possibility of molecular engineering of organic multiple potential well structures, which underlines the potential interest of these new materials.

Conclusion. A series of symmetrically and unsymmetrically disubstituted bithiophenes have been synthesized. Their electrochemical oxidation potential E_{ox} obeys a linear free energy relationship as a function of the electronic substituent effect σ_{p}^{+}. This $E_{\mathrm{ox}} - \sigma_{\mathrm{p}}^{+}$ relation allows the design of disubstituted bithiophene structures, for their compatibility with electrochemical polymerization. Electrochemical characterization of oxidized unsymmetrically disubstituted poly(bithiophenes) has shown that the positive charges are confined in small conjugated segments of the polymer chain. These polymers behave as multiple potential well structures, opening an interesting future for these conjugated materials.

Experimental Section

Electropolymerization and cyclic voltammetry were performed with a EGG PAR 273 potentiostat/galvanostat. UV−vis absoption spectra were recorded on a Varian-Cary 2415 spectrophotometer. Electropolymerizations and spectroelectrochemistry were carried out following the procedure previously described.[17]

Lithium diisopropylamide (LDA (1.5 M in hexane)), butyllithium (*n*-BuLi), zinc chloride (1 M in diethyl ether), *N*-bromosuccinimide (NBS), 3-methoxythiophene, 3-thiophenecarboxylic acid, bithiophene, and tetrakis (triphenylphosphine)palladium(0) were purchased from Aldrich. 2-Bromo-3-hexylthiophene is a gift from F. Deloffre. 3-Cyanothiophene was purchased from Landcaster.

2-Bromo-3-methoxythiophene. To a solution of 3-methoxythiophene (4.7 g (39.4 mmol) in dry DMF at 0 °C) was added in small portions NBS (7 g (39.4 mmol)). The mixture was stirred at room temperature for 15 h, hydrolyzed, and extracted with diethyl ether. The organic phase was washed with brine and dried over $MgSO_4$. The solvent was removed by rotary evaporation, and the residue was purified by distillation (T = 46 °C at 12 cmHg) to provide 2.3 g (54.6% yield) of 2-bromo 3-methoxythiophene. Purification of this compound can also be carried out by column chromatography, on silica gel, using heptane as eluent. M^+= 194 (63.6), 179 (21.71), 83 (31.78), 69 (33.07), 45 (100). UV−vis (hexane): 260 nm, 235 nm. ^{1}H-NMR ($(CD_3)_2CO$), ppm: 7.48 (d, 1H, J = 6.08 Hz, H5), 6.97 (d, 1H, J = 5.95 Hz, H4), 3.88 (s, 3H, OCH_3). It must be mentioned that this compound shows a very low stability at room temperature, and must be stored at −20 °C.

Ethyl Thiophene-3-carboxylate. Thionyl chloride, 5.61 cm^3, was added at −10 °C to 100 cm^3 of absolute ethanol. The solution was stirred for 10 min. Then 5 g of 3-thiophenecarboxylic acid was added, and the mixture was warmed up to room temperature and stirred for 1 h. Then the solvent and the excess of thionyl chloride were removed under vacuum. The crude product was distilled under 10 mmHg, leading to the desired compound (yield = 55%), mp = 90 °C. ^{1}H-NMR ($CDCl_3$), ppm: 8.03 (dd, 1H, J_1 = 3.06, J_2 = 1.06 Hz, H2), 7.4 (dd, 1H, J_1 = 4.99, J_2 = 0.97 Hz, H5), 7.2 (dd, 1H, J_1 = 5.05, J_2 = 3.03 Hz, H4), 4.2 (q, 2H, J = 7.24 Hz, CH_2), 1.2 (t, 3H, J = 7.12 Hz, CH_3).

Diethyl 2,2′-Bithiophene-3,3′-dicarboxylate. In a three-necked round bottom flask containing 50 mL of dry THF and 5 g (32 mmol) of ethyl thiophene-3-carboxylate at −70 °C, a solution of 21 cm^3 (32 mmol) of LDA[1] was added dropwise. After 30 min, 6.45 g (48 mmol) of $CuCl_2$ was added. The reaction mixture was allowed to warm up to room temperature and stirred overnight befor hydrolysis. The water phase was washed with CH_2Cl_2 (3 × 100 mL). The combined organic phase was washed with brine and dried over $MgSO_4$. After removal of the solvent, the residue was purified, using silica column chromatography and ethyl acetate/heptane mixture (10/90) as eluent. Yield: 58% ^{1}H-NMR ($CDCl_3$), ppm: 7.4 (d, 2H, J = 5.4 Hz, H5), 7.2 (d, 2H, J = 5.36 Hz, H4), 4 (q, 2H, J = 7.2 Hz, CH_2), 1 (t, 3H, J = 7.2 Hz, CH_3).

3-Hexyl-3′-cyano-2,2′-bithiophene (I). In a three-necked round bottom flask containing 30 mL of dry diethyl ether and 3-cyanothiophene (2 g, 13.3 mmol) at −70 °C, a solution of LDA (12.3 mL, 18.3 mmol) was added dropwise. After 45 min, $ZnCl_2$ (27.45 mL, 27.45 mmol) was added. The reaction mixture was allowed to warm up to room temperature and stirred for 1 h. Then tetrakis(triphenylphosphine)palladium(0) (1.13 g, 0.98 mmol) and 2.68 g (15.9 mmol) of 2-bromo-3-hexylthiophene in 10 mL of diethyl ether were added. The reaction mixture was refluxed overnight before hydrolysis. The water phase was washed with diethyl ether (3 × 100 mL). The combined organic phase was washed with brine and dried over $MgSO_4$. After removal of the solvent, the residue was purified, using silica column chromatography and toluene as eluent. The collected product (2.4 g, 66% yield) appears as pale yellow oil.

M^+ = 275. ^{1}H-NMR (200 MHz, $CDCl_3$), ppm: 0.76 (t, 3H, J = 6.2 Hz, CH_3), 1.16 (m, 8H, CH_2), 1.51 (t, 2H, J = 7.6 Hz, CH_2) 6.93 (d, 1H, J = 5.22 Hz, 4′H), 7.17 (d, 1H, J = 5.40 Hz, 5′H), 7.28 (d,1H, J = 5.4 Hz, 4H), 7.29 (d, 1H, J = 5.18 Hz, 5 H). IR (hexane): CN 2200 cm^{-1}; λ_{max} (hexane) = 302 nm (log ϵ = 3.89).

3-Methoxy-3′-cyano-2,2′-bithiophene (II). In a three-necked round bottom flask containing 30 mL of dry diethyl ether and 3-cyanothiophene (2 g, 13.3 mmol) at −70 °C, a solution of LDA (12.3 mL, 18.3 mmol) was added dropwise. After 45 min, $ZnCl_2$ (27.45 mL, 27.45 mmol) was added. The reaction mixture was allowed to warm up to room temperature and stirred for 1 h. Then tetrakis(triphenylphosphine)palladium(0) (1.13 g, 0.98 mmol) and 2-bromo-3-methoxythiophene in 10 mL of diethyl ether were added. The reaction mixture was refluxed overnight before hydrolysis. The water phase was washed with diethyl ether (3 × 100 mL). The combined organic phase was washed with brine and dried over $MgSO_4$. After removal of the solvent, the residue was purified, using silica column chromatography and toluene as eluent. The collected product, **II** (2.1 g, 52% yield), appears as pale orange crystals, mp = 99 °C. UV−vis (CH_2Cl_2): 339 nm, λ_{em} = 404 nm. M^+ = 221 (100), 206 (85.03), 178 (14.01), 152 (53.5), 134 (25.48), 94 (18.15), 69 (12.10), 45 (41.40). ^{1}H-NMR, (200 MHz, $CDCl_3$), ppm: 3.94 (s, 3H), 6.94 (d, 1H, J = 5.42 Hz, 4H), 7.11 (d, 1H, J = 5.42 Hz, 4′H), 7.23 (d, 1H, J = 5.50 Hz, 5H), 7.34 (d, 1H, J = 5.55 Hz, 5′H). IR (KBr pellets): CN, 2210 cm^{-1}. Anal. Calcd for $C_{10}H_7NOS_2$: C = 54.3, H = 3.17, N = 6.33, O = 7.24, S = 28.96; found: C = 54.31, H = 3.51, N = 6.21, O = 8.31, S = 28.05.

3,3′-Cyano-2,2′-bithiophene (III). This compound has been isolated as a byproduct from the synthesis of 3-methoxy-3′-cyano-2,2′-bithiophene (**II**) in 15% yield. This compound appears as a pale yellow solid, mp = 244 °C. UV−vis (CH_2Cl_2): λ_{abs} = 319 nm, λ_{em} = 408 nm. ^{1}H-NMR (200 MHz, $CDCl_3$), ppm: 7.46 (d, 2H, J = 5.374 Hz, H5, H5′), 7.28 (d, 2H, J = 5.381 Hz, H4, H4′). IR (KBr pellets): CN, 2211 cm^{-1}. Anal. Calcd for ($C_{10}H_4C_2S_2$): C = 55.55, H = 1.8, N = 12.96, S = 29.62; found: C = 55.07, H = 2.28, N = 12.46, S = 28.89.

3,3′-Dimethoxy-2,2′-bithiophene (IV). In a three-necked round bottom flask containing 50 mL of dry THF and 5 g (43.8 mmol) of 3-methoxythiophene at −70 °C, 29.2 cm^3 (43.8 mmol) of LDA was added dropwise. After 30 min, 25 g (65.7 mmol) of $Fe(acac)_3$ was added. The reaction mixture was allowed to warm up to room temperature and stirred overnight before hydrolysis. The water phase was washed with diethyl ether (3 × 100 mL). The combined organic phase was washed with brine and dried over $MgSO_4$. After removal of the solvent, the residue was purified, using silica column chromatography with heptane as eluent. The collected product, 3.8 g, appeared as a white solid. Yield: 70%. ^{1}H-NMR ($CDCl_3$), ppm: 7.30 (d, 2H, J = 5.58 Hz, H5), 7.06 (d, 2H, J = 5.54 Hz, H4), 4 (q, 2H, J = 7.2 Hz, CH_2), 1 (t, 3H, J = 7.2 Hz, CH_3), 3.94 (s, 3 H). UV−vis (CH_2Cl_2): λ_{abs} = 321 nm, λ_{em} = 370 nm. Anal. Calcd for $C_{10}H_{10}O_2S_2$: C = 53.09, H = 4.42, O = 14.16, S = 28.32; found: C = 51.62, H = 4.41, O = 15.88, S = 27.95.

2,2′-Bithiophene-3,3′-dicarboxylic Acid (V). A total of 2 g of diethyl 2,2′-bithiophene-3,3′-dicarboxylate was dissolved in methanol and added to a 20% aqueous sodium hydroxide solution (300 mL). The mixture was refluxed for 4 h. After concentration, the aqueous solution was washed with CH_2Cl_2, acidified with concentrated HCl to pH 1, and extracted with CH_2Cl_2. The CH_2Cl_2 solution was washed up to pH 7, and evaporation of the solvent yielded compound **V** in 87% yield. ^{1}H-NMR ($CDCl_3$), ppm: 7.45 (d, 2H, J = 5.41 Hz, H5), 7.54 (d, 2H, J = 5.40 Hz, H4). The acidic H of COOH could not be observed. UV−vis (CH_3CN): λ_{abs} = 340 nm, λ_{em} = 434 nm.

References and Notes

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