Ionochromic and Potentiometric Properties of the Novel Polyconjugated Polymer from Anodic Coupling of 5,5′-Bis(3,4-(ethylenedioxy)thien-2-yl)-2,2′-bipyridine

Gianni Zotti,* Sandro Zecchin, and Gilberto Schiavon

Istituto CNR Polarografia ed Elettrochimica Preparativa, c.o. Stati Uniti 4,
35020 Padova, Italy

Anna Berlin* and Michele Penso

Centro CNR Sintesi e Stereochimica di Speciali Sistemi Organici, via C.Golgi 19,
20133 Milano, Italy

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Anodic coupling of 5,5′-bis(3,4-(ethylenedioxy)thien-2-yl)-2,2′-bipyridine has produced a new ion-coordinating polyconjugated polymer as thin films on electrodes. The polymer has been characterized by cyclic voltammetry, FTIR reflection−absorption, UV−vis spectroscopy, electrochemical quartz crystal microbalance, in situ ESR, and in situ conductivity. The as-prepared polymer, which bears protonated bipyridine units, is reversibly oxidized with one electron every other bithiophene moiety and reduced in two complex steps to the neutral material. Deprotonation of the polymer films produces substrates able to coordinate protons and divalent transition metal ions (Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+}) with corresponding spectral and redox changes. The ionochromic and potentiometric properties of the polymer films as prototype sensor materials are reported.

Introduction

Among the most investigated modifications of polyconjugated polymers is their functionalization with redox groups, useful for applications in several fields. In particular, polyconjugated polymers bearing 2,2′-bipyridyl (bipy) complexes are produced from pyrrole-substituted bipy ligands coordinated with iron, ruthenium, copper, and cobalt.[1−4] In all these cases the bipy complex is pendant from the polyconjugated polymer chain.

In recent investigations the bipy moiety has been inserted in the polyconjugated chain. In this case, the conjugative properties of the polymer are directly influenced by the ligand and by its ion coordination with consequent changes in optical, redox, and conductive properties. Thus 5,5′-bipy-phenylene-vinylene-[5] and 2,5-pyridine-phenylene-vinylene-based[6] polymers have been produced as materials for ionochromic and optoelectronic devices. A benzimidazole-based polymer has been used as the support for a ruthenium complex via its bipy-like units to assess the conductive properties of a redox center in the main chain.[7] With analogous purposes poly(2,5-pyridine) films have been produced and coordinated to nickel ions.[8] With the same scope of investigating the interplay of redox and bipolaron conductive properties the bipy moiety has been inserted between dithiophene groups and the resulting linear polyconjugated monomer has been anodically coupled to polymer.[9] A subsequent investigation has attempted the polymerization of a series of dithienyl-bipy isomers.[10] The influence of a ruthenium-bipy complex in the main chain of a phenylene-vinylene regular copolymer[11] was expected to sensitize the material for photorefractive effects.

In this class of polymers, the ionochromic responses are expected to be associated with electrochemical changes of the polyconjugated backbone but this aspect has not been investigated. We addressed this point by producing ion-sensing polymers of this type on electrode surfaces, which procedure allows electrochemical modulation of their properties. To this end, we selected compounds in which the bipy moiety is 5,5′-functionalized with 3,4-(ethylenedioxy)thiophene (EDOT) as polymerogenic unit. EDOT shows an oxidation potential lower than that of thiophene and is capped at the 3 and 4 positions in the ring, therefore allowing the production of polymer films without overoxidation problems. The

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* Correspondence should be addressed to gzotti@pdadr1.pd.cnr.it.

[1] Eaves, J. G.; Munro, M. S.; Parker, D. *J. Chem. Soc., Chem. Commun.* **1985**, 684.

[2] Cosnier, S.; Deronzier, A.; Moutet, J. C. *J. Electroanal. Chem.* **1985**, *193*, 193.

[3] Daire, F.; Bedioui, F.; Dewynck, J.; Bied-Charreton, C. *J. Electroanal. Chem.* **1986**, *205*, 309.

[4] Daire, F.; Bedioui, F.; Dewynck, J.; Bied-Charreton, C. *J. Electroanal. Chem.* **1987**, *224*, 95.

[5] Wang, B.; Wasieleski, M. R. *J. Am. Chem. Soc.* **1997**, *119*, 12.

[6] Fu, D. K.; Xu, B.; Swager, T. M. *Tetrahedron* **1997**, *53*, 15487.

[7] Cameron, C. G.; Pickup, P. G. *J. Chem. Soc., Chem. Commun.* **1997**, 303.

[8] Schiavon, G.; Zotti, G.; Bontempelli, G. *J. Electroanal. Chem.* **1985**, *194*, 327.

[9] Zhu, S. S.; Swager, T. M. *Adv. Mater.* **1996**, *8*, 497.

[10] Jenkins, I. H.; Rees, N. G.; Pickup, P. G. *Chem. Mater.* **1997**, *9*, 1213.

[11] Peng, Z.; Yu, L. *J. Am. Chem. Soc.* **1996**, *118*, 3777.

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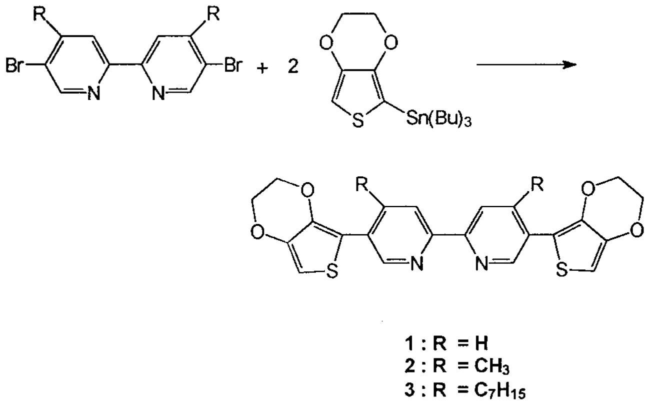
Scheme 1



homologue monomer with bis(ethylenedioxy)bithiophene ends has been recently polymerized,[12] but this compound would not be useful to our scope due to its air sensitivity and bathochromically shifted absorption. This paper reports the synthesis of 5,5′-bis(3,4-(ethylenedioxy)thien-2-yl)-2,2′-bipyridine (**1**) and its 4,4′-dimethyl (**2**) and 4,4′-diheptyl (**3**) homologues (Scheme 1), their oxidative polymerization, the characterization of the resulting polymer films, and the assessment of their ionochromic and electrochemical properties.

Experimental Section

Chemicals and Reagents. All melting points are uncorrected. All reactions of air- and water-sensitive materials were performed under nitrogen. Air- and water-sensitive solutions were transferred with double-ended needles. The solvents used in the reactions were dried by conventional methods and freshly distilled under nitrogen. Acetonitrile was reagent grade (Uvasol, Merck) with a water content of <0.01%. The supporting electrolyte tetrabutylammonium perchlorate (Bu_4NClO_4) was previously dried under vacuum at 70 °C. 3,4-(Ethylenedioxy)thiophene (EDOT) was obtained from Bayer, and all other chemicals were reagent grade and used as received.

The following compounds were prepared according to literature prescriptions: 5,5′-bis[3,4-(ethylenedioxy)thien-2-yl]-2,2′-bipyridine,[12] 2,5-dibromo-4-methylpyridine,[13] and 2-(tributylstannyl)-3,4-(ethylenedioxy)thiophene.[12]

^1H NMR spectra were recorded on a Bruker AC 300 (300 MHz for ^1H); chemical shift values are given in parts per million (ppm) and are referred to tetramethylsilane. Electron-impact mass spectra (EI-MS) were taken on a VG 7070 EQ-HF spectrometer.

5-Bromo-4-methyl-2-methylsulfenylpyridine (4). A mixture of 2,5-dibromo-4-methylpyridine (6.16 g, 24.6 mmol), sodium methanethiolate (2.10 g, 29.6 mmol), tetrabutylammonium bromide (407 mg, 1.30 mmol), and acetonitrile (15 mL) was poured in a closed vessel and heated at 50 °C for 24 h under stirring. Ether and water were added; the organic phase was washed several times with water and dried (Na_2SO_4), and the solvent was evaporated. Flash chromatography (silica gel, petrol ether/ether 98:2) of the residue afforded the title compound as an oil (3.5 g, 65% yield). Anal. Calcd for C_7H_8BrNS: C, 38.56; H, 3.67; N, 6.42. Found: C, 38.51; H, 3.76; N, 6.35. ^1H NMR ($CDCl_3$) δ 2.33 (s, 3 H), 2.55 (s, 3 H), 7.07 (s, 1 H), 8.47 (s, 1 H).

5-Bromo-4-methyl-2-methylsulfinylpyridine (5). To a solution of **4** (3.5 g, 16.10 mmol) in acetic acid (10 mL) was added 35% hydrogen peroxide (602 mg, 17.70 mmol) dropwise. After 24 h of stirring, methylene chloride was added, and the solution, cooled with an ice−water bath, was neutralized with aqueous ammonia. The organic phase was washed with water and dried (Na_2SO_4), and the solvent was evaporated. Flash chromatography (silica gel, CH_2Cl_2/AcOEt 8:2) of the residue afforded compound **5** as a white solid (2.78 g, 74% yield), mp 56 °C. Anal. Calcd for C_7H_8BrNOS: C, 35.92; H, 3.42; N, 5.98. Found: C, 35.79; H, 3.35; N, 5.92. ^1H NMR ($CDCl_3$): δ 2.52 (s, 3 H), 2.82 (s, 3 H), 7.90 (s, 1 H), 8.65 (s, 1 H).

5,5′-Dibromo-4,4′-dimethyl-2,2′-bipyridine (6). CH_3CH_2MgBr (1 M in THF, 7.5 mL, 7.50 mmol) was added dropwise to a solution of **5** (2.72 g, 11.60 mmol) in ether (75 mL), keeping the temperature below 5 °C. After 3 h of stirring at room temperature, water was added, and the reaction mixture neutralized with diluted HCl and extracted with CH_2Cl_2. The organic phase was washed with water and dried (Na_2SO_4), and the solvent was evaporated. The residue was washed, first with ethanol and then with petrol ether, to give the title compound as a solid (810 mg, 41% yield), mp > 200 °C, which was used without any further purification for the next step. ^1H NMR ($CDCl_3$): δ 2.50 (s, 6 H), 8.27 (s, 2 H), 8.69 (s, 2 H).

5,5′-Bis[3,4-(ethylenedioxy)thien-2-yl]-4,4′-dimethyl-2,2′-bipyridine (2). A mixture of **6** (250 mg, 0.73 mmol), 2-(tributylstannyl)-3,4-(ethylenedioxy)thiophene (943 mg, 2.19 mmol), dichlorobis(triphenylphosphine)palladium(II) (42 mg, 0.10 mmol), and DMF (40 mL) were heated at 80−90 °C for 24 h. The solvent was evaporated, and the residue was purified by flash chromatography (silica gel, CH_2Cl_2/CH_3OH 99:1) to give the title compound as a yellow solid (221 mg, 65% yield), mp > 200 °C. Anal. Calcd for $C_{24}H_{20}N_2O_4S_2$: C, 62.07; H, 4.31; N, 6.03. Found: C, 61.92; H, 4.15; N, 5.93. ^1H NMR ($CDCl_3$): δ 2.48 (s, 6 H), 4.28 (s, 8 H), 6.47 (s, 2 H), 8.30 (s, 2 H), 8.70 (s, 2 H). MS: *m/e* 464 ($M^{\bullet+}$).

5-Bromo-4-heptyl-2-methylsulfenylpyridine (7). A solution of **4** (2.63 g, 12.10 mmol) in THF (5 mL) was added dropwise, at −78 °C, to a solution of LDA, prepared from BuLi (1.6 M in hexane, 14.40 mmol, 9 mL) and diisopropylamine (1.46 g, 14.40 mmol) in THF (35 mL). After 10 min of stirring, the temperature was allowed to reach −10 °C and bromohexane (2.00 g, 12.10 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 3 h, and most of the solvent was evaporated. Ether and water were added to the residue, the organic phase was washed with water and dried (Na_2SO_4), and the solvent was evaporated. Flash chromatography of the residue (silica gel, petrol ether/ether 9:1) afforded the title compound as an oil (2.74 g, 75% yield). Anal. Calcd for $C_{13}H_{20}BrNS$: C, 51.68; H, 6.62; N, 4.63. Found: C, 51.57; H, 6.53; N, 4.65. ^1H NMR ($CDCl_3$): δ 0.85 (t, 3 H), 1.20−1.60 (m, 10 H), 2.52 (s, 3 H), 2.60 (t, 2 H), 7.07 (s, 1 H), 8.47 (s, 1 H).

5-Bromo-4-heptyl-2-methylsulfinylpyridine (8). This compound was prepared following the same procedure described above for the synthesis of **5**, starting from **7**. The crude product was purified by flash chromatography (silica gel, petrol ether/AcOEt 7:3) to give the title compound as an oil (72% yield). Anal. Calcd for $C_{13}H_{20}BrNOS$: C, 48.14; H, 6.29; N, 4.40. Found: C, 47.96; H, 6.12; N, 4.27. ^1H MNR ($CDCl_3$): δ 0.85 (t, 3 H), 1.20−1.60 (m, 10 H), 2.75 (t, 2 H), 2.86 (s, 3 H), 7.85 (s, 1 H), 8.65 (s, 1 H).

5,5′-Dibromo-4,4′-diheptyl-2,2′-bipyridine (9). This compound was prepared following the same procedure described above for the synthesis of **6**, starting from **8**. The crude product was purified by flash chromatography (silica gel, petrol ether/AcOEt 9:1) to give the title compound as a solid (57% yield), mp 82−83 °C. Anal. Calcd for $C_{24}H_{34}Br_2N_2$: C, 56.51; H, 6.66; N, 5.49. Found: C, 56.39; H, 6.57; N, 5.36. ^1H NMR ($CDCl_3$): δ 0.85 (t, 6 H), 1.30−1.80 (m, 20 H), 2.85 (t, 4 H), 8.25 (s, 2 H), 8.70 (s, 2 H).

5,5′-Bis[3,4-(ethylenedioxy)thien-2-yl]-4,4′-diheptyl-2,2′-bipyridine (3). This compound was prepared following the same procedure described above for the synthesis of **2**, starting from **9**. The crude product was purified by flash chromatography (silica gel, CH_2Cl_2/AcOEt 9:1) to give the title compound as a solid (63% yield), mp 163−165 °C. Anal. Calcd for $C_{36}H_{44}N_2O_4S_2$: C, 68.36; H, 6.96; N, 4.43. Found: C, 68.27; H, 7.15; N, 4.32. ^1H NMR ($CDCl_3$): δ 0.85 (t, 6 H), 1.30−1.80

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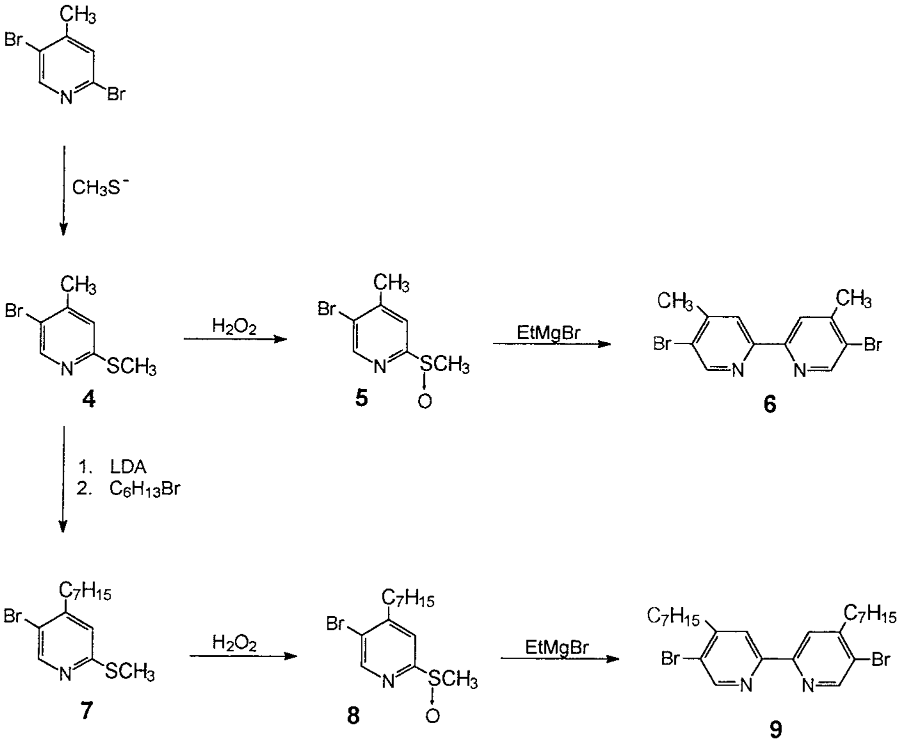
(12) Zhu, S. S.; Swager, T. M. *J. Am. Chem. Soc.* **1997**, *119*, 12568.

(13) Van der Does, L.; den Hertog, H. J. *Recl. Trav. Chim.* **1965**, *84*, 951.

Scheme 2



(m, 20 H), 2.80 (t, 4 H), 4.26 (s, 8 H), 6.48 (s, 2 H), 8.25 (s, 2 H), 8.70 (s, 2 H). MS: *m*/*e* 632 ($M^{\bullet+}$).

Electrochemical Apparatus and Procedure. Experiments were performed at 25 °C under nitrogen in three electrode cells. The counter electrode was platinum; the reference electrode was a silver/0.1 M silver perchlorate in acetonitrile (0.34 V vs SCE). The voltammetric apparatus (AMEL, Italy) included a 551 potentiostat modulated by a 568 programmable function generator and coupled to a 731 digital integrator.

The working electrode for cyclic voltammetry was a platinum minidisk electrode (0.003 cm^2). For electronic spectroscopy, a 0.8 × 2.5 cm indium−tin oxide (ITO) sheet (∼80% transmittance, ∼20 ohm $square^{-1}$ resistance, from Balzers, Liechtenstein) was used. A platinum sheet (15 cm^2) was used in reflection−absorption FTIR spectroscopy.

ESR spectra were taken on a Bruker ER 100D following the procedure previously described;[14] FTIR spectra of the polymer films were taken in reflection−absorption mode on a Perkin-Elmer 2000 FTIR spectrometer; electronic spectra were taken with a Perkin-Elmer Lambda 15 spectrometer.

Electrochemical quartz crystal microbalance (EQCM) analysis was performed with a platinum-coated AT-cut quartz electrode (0.2 cm^2), resonating at 9 MHz, onto which the polymers were deposited. Measurements were performed outside the depositing solution both to measure the mass of polymer films in the dry state and to avoid errors due to polymer roughness. The oscillator circuit was homemade, and the frequency counter was a Hewlett-Packard model 5316B.

The apparatus and procedures used in the in situ conductivity experiments were previously described in detail.[15] The electrode for conductivity measurements was a microband array platinum electrode (5 μm bandwidth) with interband spacing of 5 μm.

Results and Discussion

Synthesis of the Monomers. Compounds **1**−**3** have been prepared by a Stille coupling of 2-(tributylstannyl)-3,4-(ethylenedioxy)thiophene with the proper 5,5′-dibromo-2,2′-bipyridine, following the procedure described in the literature for the synthesis of **1** (Scheme 1).[12]

The synthetic route to 5,5′-dibromo-4,4′-dimethyl-2,2′-bipyridine (**6**) and 5,5′-dibromo-4,4′-diheptyl-2,2′-bipyridine (**9**), depicted in Scheme 2, is based on the reaction of methyl 2-(4-alkyl-5-bromo)pyridyl sulfoxide with Grignard reagent. The formation of 2,2′-bipyridines starting from methyl 2-pyridyl sulfoxides is a convenient process which was described for the first time by Oae et al.[16]

Electrosynthesis of Poly(1). The cyclic voltammogram (CV) of **1** in acetonitrile + 0.1 M Bu_4NClO_4, where it is scarcely soluble ($<5 \times 10^{-4}$ M), displays an oxidation process at $E_p = 0.77$ V (at 0.1 V s^{-1}). Potentiostatic oxidation at the peak leads to the growth of a polymer film on the electrode. The peak height, compared with that of similarly sized ferrocene molecules, corresponds to an apparent number of exchanged electrons $n_{app} = 1$ which is markedly lower than that (2 at least) expected from coupling and doping. Capture by bipy moieties of protons released by coupling is suggested as the most likely cause of this behavior.

We therefore tried to improve the electrodeposition process acting on proton scavenging but our efforts were unsuccessful. Although the oxidation peak of the monomer is ∼3 times increased by addition of excess (10^{-2} M) bipy, the filming process is inhibited. We believe that this is a consequence of deprotonation of the thiophene radical cation which therefore changes its reaction pathway.[3,17] On the other hand the use of acids, which for this reason help polymerizing,[3] is adverse. One

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[14] Zotti, G.; Schiavon, G. *Synth. Met.* **1989**, *31*, 347.

[15] Schiavon, G.; Sitran, S.; Zotti, G. *Synth. Met.* **1989**, *32*, 209.

[16] Oae, S.; Kawai, T.; Furukawa, N. *Phosphorous Sulfur* **1987**, *34*, 123.

[17] Dunand-Sauthier, M. N. C.; Deronzier, A.; Moutet, J. C.; Tingry, S. *J. Chem. Soc., Dalton Trans.* **1996**, 2503.

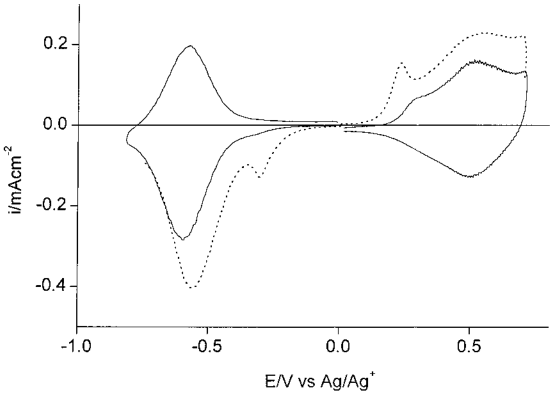


Figure 1. Cyclic voltammetry of as-prepared poly(**1**) in acetonitrile + 0.1 M Bu_4NClO_4; dotted curves indicate charge trapping (see text). Scan rate: 0.1 V s^{-1}. Reversible charge: 0.6 mC cm^{-2}.

equivalent of $HClO_4$ protonates the bipy moiety,[18] shifting the monomer oxidation potential to values (>1 V) that are so highly positive that polarization thereby causes electrode fouling.

The poly(**1**) film is electroactive since it displays an oxidative redox process at $E° = 0.5$ V. In any case the deposition efficiency, measured at this process by the charge yield (ratio of reversible charge over deposition charge at the neutral state) is low (~3%).

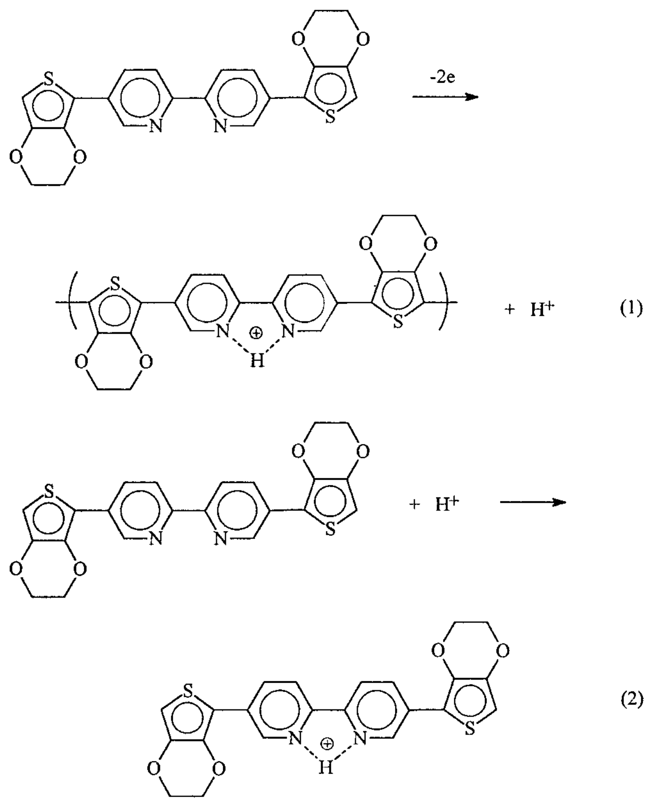
A more efficient electrodeposition is obtained in acetonitrile + 0.1 M $LiClO_4$. In this electrolyte, the monomer is more soluble ($>2 \times 10^{-3}$ M). In fact its color is different (the maximum absorption is shifted from 363 to 375 nm for $LiClO_4$ concentrations ≥ 0.1 M) which points to Li^+ coordination of the bipy moieties. In contrast, no shift is observed at lower Li^+ concentrations ($\leq 10^{-3}$ M) nor is it observed in 0.1 M Na^+ or R_4N^+. In any case the oxidation peak potential in acetonitrile + 0.1 M $LiClO_4$ is the same as in acetonitrile + 0.1 M Bu_4ClO_4, confirming that the electron acceptor properties of the lithium ion are scarce. Oxidation produces the same polymer film obtained in acetonitrile + 0.1 M Bu_4ClO_4, since the film displays the same reversible oxidation process, but the charge yield is in this case considerably higher (10%).

Potentiostatic deposition, monitored by EQCM, produces a linear increase of mass Δm with passed charge Q, with slope $F\Delta m/Q = 160$ gmol^{-1} (as dry mass). Since the monomeric unit (mw = 436 g mol^{-1}) is protonated by one $HClO_4$ molecule (see below) the $F\Delta m/Q$ value for a two-electron coupling would be 268 g mol^{-1} so that the deposition efficiency is estimated to be ~60%.

On the basis of the previous results, we can formulate the following reaction pathway (Scheme 3). Anodic coupling of **1** requires two electrons per monomeric unit with release of two protons. One of them coordinates to the bipy moiety of the polymer (eq 1 in Scheme 3), the other is scavenged by **1** in solution (eq 2 in Scheme 3). The overall balance of one electron per monomer accounts for the n_{app} value of the CV peak.

Poly(**1**) films were routinely produced from 10^{-3} M solution of **1** in acetonitrile + 0.1 M $LiClO_4$ potentiostatically at 0.8 V and with stirring. Deposition charges may be as high as 100 mC cm^{-2}, although beyond 20−30 mC cm^{-2} the electroactivity of the film, particularly in oxidation, may be difficult (a previous reduction helps activating oxidation). This result may be ascribed to the low conductivity of the material (see below).

Scheme 3



Cyclic Voltammetry of Poly(1). The stable CV response of poly(**1**) in acetonitrile + 0.1 M Bu_4NClO_4 is shown in Figure 1. An oxidative redox process is shown at $E° = 0.5$ V. The polymer is also reduced in a reversible process at $E° = -0.6$ V involving the same charge. It must be remarked that in any case the first reduction cycle and the subsequent oxidation cycle (dotted curves) involve some irreversible charge, which phenomenon will be discussed below. EQCM correlation of mass Δm and reversible charge Q_r give for both processes $F\Delta m/Q_r = \sim 1100$ g mol^{-1} (the mass of two $HClO_4$-protonated monomeric units), corresponding to the exchange of one electron per two monomeric units.

The oxidation redox process at $E° = 0.5$ V is easily assigned to the dithiophene moieties in the α-coupled polymer (in the box of Scheme 4). The reversible isoelectronic reduction process at $E° = -0.6$ V is due to protonated bipy moieties since dipping of the filmed electrode in acetonitrile + 0.1 M Bu_4NOH for a few seconds makes the reduction process disappear. Protons were originated by the coupling process and substituted lithium due to their stronger coordination ability. The redox (y-axis symmetrical) shape of the reversible reduction, compared with the capacitive look of the oxidation process typical of conducting polymers, deserves to be noted. The CV peak width at half-height is 200 mV, which is considerably higher than the regular width for noninteracting redox centers (90 mV), thus suggesting a possible mixed-valence interaction between

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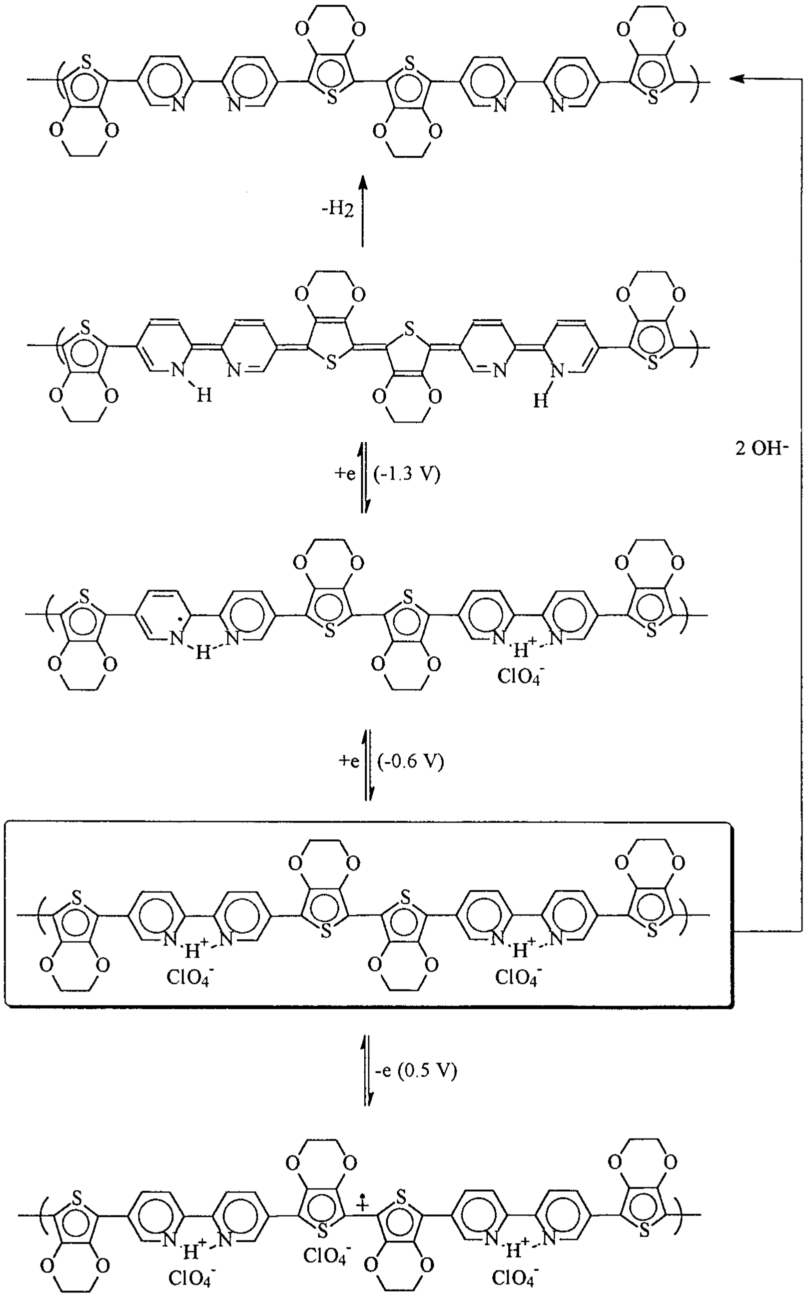
[18] Summers, L. A. In *Advances in Heterocyclic Chemistry*; Academic Press: New York, 1984; Vol. 35, p 281 and references therein.

Scheme 4



redox sites.[19] It must be observed that the reversible reduction occurs at a potential comparable with that of the reduction of methyl viologen[20] and in fact it may be referred to conjugated pyridinium moieties.

In Scheme 4, the bipy moiety is assumed to be monoprotonated since its second protonation step requires extremely strong acidic conditions.[18] This suggestion has been confirmed by EQCM analysis. Deprotonation of the as-prepared polymer occurs with the expected mass decrease, corresponding to one molecule of perchloric acid per monomeric unit.

The reduction peak of the material increases and becomes irreversible if air is allowed into the solution. In particular, under oxygen, the reduction requires a charge 4 times higher than for the reversible reduction. Given the stoichiometry of one electron per two monomeric units for the reversible processes the reduction would correspond to the formation of hydrogen peroxide, as usually encountered with reduced viologens.[20]

The polymer film displays a second irreversible reduction process at −1.3 V which produces the neutral polymer as shown by CV and chromic changes (see below). Only when the polymer film thickness is close to that of the monolayer does the CV show the reversibility of both reduction steps (Figure 2).

After deprotonation, the polymer displays the oxidation redox process shifted to $E° = 0.55$ V and a reversible reduction at $E° = -2.15$ V (Figure 3) involving twice the oxidative charge. In this case the reduction must involve the polyconjugated backbone and be mainly localized at the bipy moieties (Scheme 5). The difference of $E°$ values (2.7 V) is in agreement with the maximum

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[19] Brown, A. P.; Anson, F. C. *Anal. Chem.* **1979**, *49*, 1589.

[20] Bird, C. L. *Chem. Soc. Rev.* **1981**, *10*, 49.

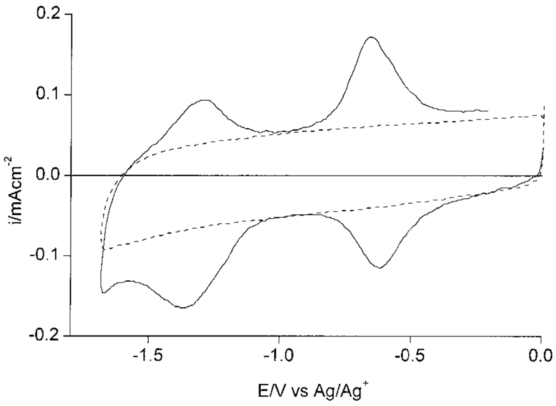

Figure 2. Reductive cyclic voltammetry of thin as-prepared poly(**1**) film in acetonitrile + 0.1 M Bu_4NClO_4. Scan rate: 0.1 V s^{-1}. Reversible charge: 0.175 mC cm^{-2}.

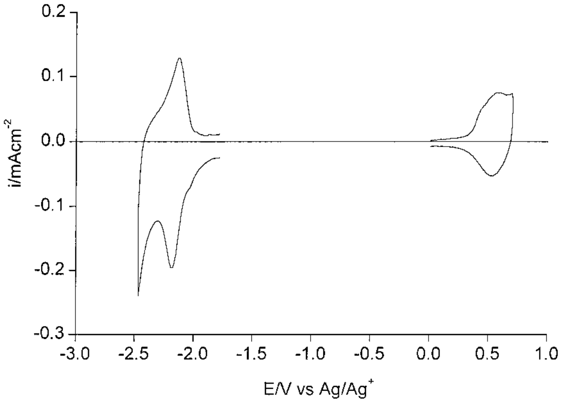

Figure 3. Cyclic voltammetry of neutral poly(**1**) in acetonitrile + 0.1 M Bu_4NClO_4. Scan rate: 0.1 V s^{-1}. Reversible charge: 0.2 mC cm^{-2}.

absorption of the polymer (465 nm, corresponding to an optical gap of 2.67 eV).

Treatment of the neutral polymer with $HClO_4$ restores a reduction process around −0.5 V but introduces into the process a strong irreversibility (in this case proton reduction takes place); moreover, the oxidation process is shifted positively to $E° = 0.7$ V. EQCM experiments have shown that uptake of perchloric acid by the neutral polymer occurs up to the same (1:1) level of the as-prepared material.

It is suggested that the initial geometry of the as-prepared material, bearing cisoid protonated bipy moieties,[18] is removed by deprotonation giving rise to a random distribution of cisoid and transoid conformations of the bipyridine rings.[21] A reversible oxidation at the bithiophene moieties occurs at the same potential of the as-prepared protonated polymer. This may be due to the fact that an increased conjugation of the rings operated by the bridging protons compensates their electron acceptor properties. Upon protonation, the oxidation process is shifted to a higher value, which is explained by an extensive transoid disposition of the bipy moieties with consequent loss of coplanarity and hence of conjugation.

Poly(**1**) is insoluble in any solvent; the protonated form resists even to hot trifluoroacetic acid; in the neutral state it is insoluble even in boiling chlorobenzene. These characteristics point to a relatively high degree of polymerization.

Electrosynthesis and Cyclic Voltammetry of Poly(2) and Poly(3). Compounds **2** and **3** are less soluble in acetonitrile + 0.1 M $LiClO_4$ than **1** (∼3 and 5 × 10^{-4} M, respectively). Their oxidation occurs at $E_p = 1.05$ V, i.e., with a noticeable positive shift with respect to **1**. This result appears to reflect the decoplanarization of the bipy and thiophene rings introduced by the 4-substituent alkyl groups, indicated also by the strong hypsochromic shift of the UV−vis absorption maximum (329 vs 363 nm for **1** in acetonitrile). The result of the anodic shift is that oxidation stops after the passage of a limited amount of charge (∼5 mC cm^{-2}) due to the formation of a thin insulating polymer layer.

The CV of the polymer layers do not show the reversible oxidation of the bithiophene moiety but an irreversible oxidation at high potential. This result is accounted for by a positive shift of the oxidation process produced by the above-mentioned decoplanarization of the rings. In any case the thin polymer films are reversibly reduced with the same CV pattern of poly(**1**), i.e., with the involvement of comparable irreversible and reversible charges. This result is of high relevance for the understanding of the complex reduction process of as-prepared poly(**1**), as it will be shown later.

FTIR Analysis of Poly(1). The FTIR reflection−absorption spectrum of the as-prepared polymer film (Figure 4b) compared with that of the monomer (Figure 4a) evidences (i) the loss of the C_α−H out-of-plane band of the thiophene terminals at 713 cm^{-1} in the monomer,[22] which confirms extensive α-coupling, and (ii) the presence of perchlorate (1110 and 620 cm^{-1}), as expected for protonated bipy moieties. The perchlorate signal is multiple and attributable both to ionic (1110 cm^{-1}) and coordinated ion (satellite bands).[23]

Upon deprotonation, the spectrum (Figure 4c) records the loss of the perchlorate bands. This removal evidences in the 1100 cm^{-1} region a single strong band at 1090 cm^{-1}, assigned to C−O−C stretching of the ethylenedioxy moiety, in place of the two bands at 1180 and 1066 cm^{-1} present in the monomer. A single C−O−C stretching band, shown also by the homopolymer poly(EDOT),[24] is likely due to increased symmetry from the monomer to the polymer chain. Moreover the spectrum shows the loss of a strong band at 1490 cm^{-1}, attributable to a skeletal mode involving the protonated bipy moiety. This suggestion is confirmed by comparison of the spectra of 2,2′-bipyridine and its hydrochloride or hydroperchlorate, which evidences that the acid introduces a strong band at 1485 cm^{-1}. Inspection of the same bipyridinium spectra reveals that the NH stretching band at 3300 cm^{-1} is weak and broad, which accounts for its nondetection in the protonated polymer films.

FTIR analysis of the $HClO_4$ protonation process of the neutral polymer shows that the original bands are restored but with two differences: (i) the perchlorate band at 1110 cm^{-1} (ionic perchlorate) is now without

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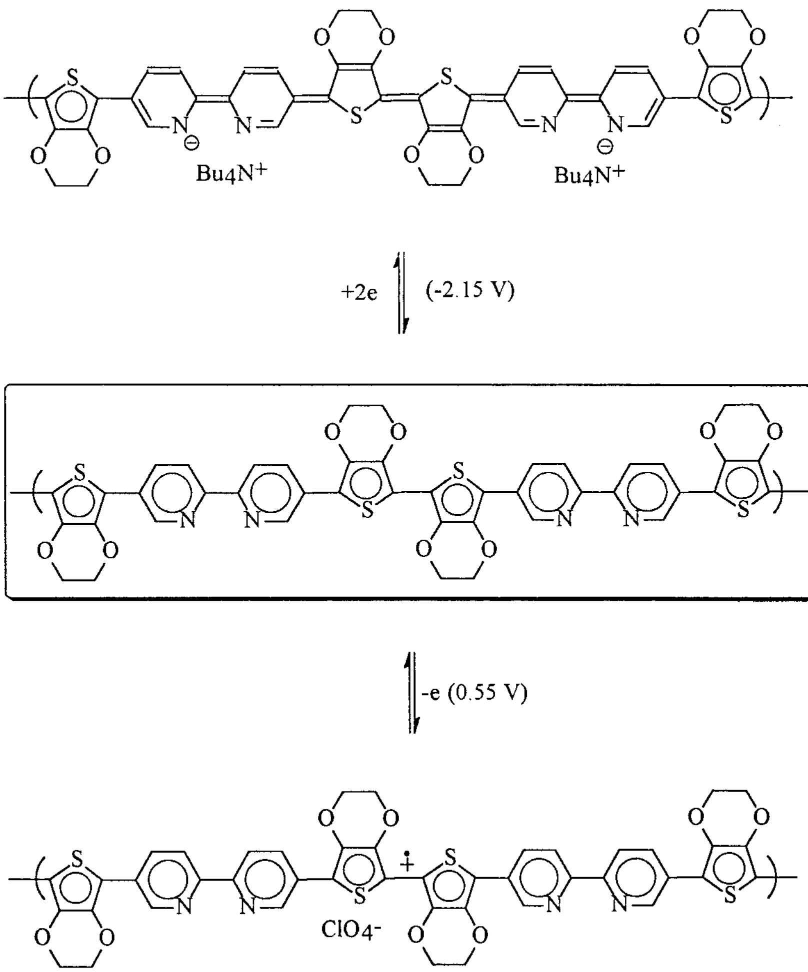
(21) Cumper, C. W. N.; Ginman, R. F. A.; Vogel, A. I. *J. Chem. Soc.* **1962**, 1188.

(22) Rico, M.; Orza, J. M.; Morcillo, J. *Spectrochim. Acta* **1965**, *21*, 589.

(23) Rosenthal, M. R. *J. Chem. Educ.* **1973**, *50*, 331.

(24) Kvarnstrom, C.; Neugebauer, H.; Blomquist, S.; Ahonen, H. J.; Kankare, J.; Ivaska, A. *Electrochim. Acta* **1999**, *44*, 2739.

Scheme 5



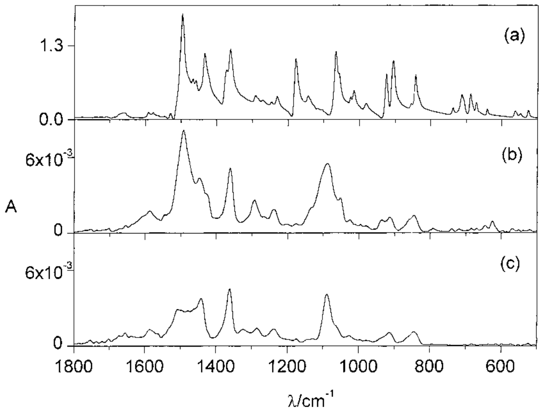


Figure 4. FTIR spectra of (a) **1** (KBr pellet), (b) as-prepared, and (c) neutral poly(**1**) (reflection−absorption).

satellite bands and (ii) the skeletal mode at 1490 cm^{-1} is less intense. Thus it appears that reprotonation does not regenerate the as-prepared material but occurs in a random fashion at structurally different sites. This result, which runs parallel with the previously described sluggish CV behavior and the chromic properties (see below), confirms the previously suggested random cisoid−transoid conformation of the polymer.

In Situ Conductivity and ESR of Poly(1). The in situ conductivity of the polymer was measured. Although bridging of the microband array electrode with a fully electroactive deposit was difficult, we could evaluate roughly the conductivity of the oxidized polymer as 10^{-4} S cm^{-1} at 0.7 V. This conductivity, which is comparable with those of redox-interacting centers,[25] is low probably due to charge localization as recently shown for a series of polyconjugated polymers alternating electron-rich and -poor moieties.[26]

In situ ESR of poly(**1**) during both the oxidation and reduction processes shows the reversible display of a strong signal which reaches its maximum in a plateau at half-wave potential corresponding to $E°$ (Figure 5). The g values are 2.0025 in oxidation and 2.033 in reduction, and the line width is 3 and 5 G, respectively. The maximum spin concentration corresponds, within the experimental uncertainty, to one spin per electron, which indicates the production of stable monomeric radicals.

Charge Trapping in Poly(1). As previously anticipated, the reversible reduction process of the as-prepared polymer is accompanied at the first CV cycle by extra charge which is completely recovered when a single CV scan is applied to the oxidation redox process. The whole process may be repeated indefinitely. The amount of this extra charge, which we will hereafter name “trapped”, is equal to that of the reversible charge. Charge trapping was previously reported for overoxidation defects in polythiophenes[27] and in particular also

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(25) Chidsey, C. E. D.; Murray, R. W. *J. Phys. Chem.* **1986**, *90*, 1479.

(26) Zotti, G.; Zecchin, S.; Schiavon, G.; Berlin, A.; Pagani, G.; Borgonovo, M. Lazzaroni, R. *Chem. Mater.* **1997**, *9*, 2876.

(27) Zotti, G.; Schiavon, G.; Zecchin, S. *Synth. Met.* **1995**, *72*, 275.

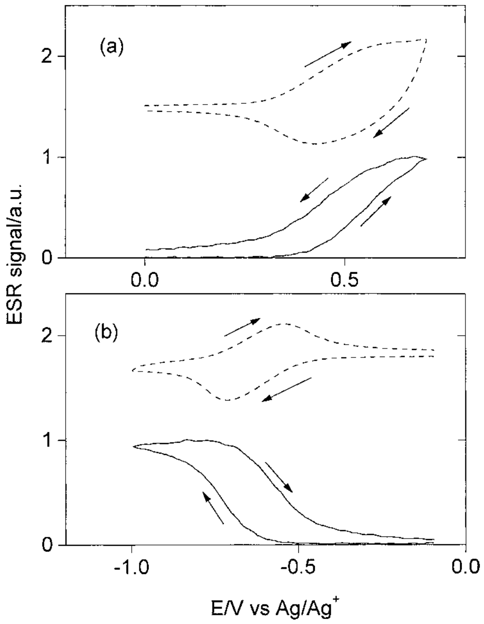

Figure 5. In situ ESR of as-prepared poly(**1**) in acetonitrile + 0.1 M Bu_4NClO_4: (a) oxidation and (b) reduction. Dashed curves show CVs, for comparison.

for the nonsubstituted thiophene analogue of **1**.[9] As a matter of fact this type of defect is commonly shown in the CV as peaks anticipating the main process,[27] whereas in our case there is simply an increase of the intensity of the main process. Moreover the EDOT units are protected by 3,4-capping, unless highly positive potentials (>1.2 V) are used,[28] which is not our case. In contrast to the thiophene, terminal α-positions could be involved in reactions such as formation of quinonic functions[27] but FTIR analysis did not show any major sign of these functional groups in the polymer, which rules out these defects or limits them to a small amount of terminals. FTIR has also shown that the irreversible (trapping) reduction operates a 50% decrease of the $HClO_4$ bands but no other change is shown.

We might tentatively attribute the reduction trapping charge to the formation of dimers, which are so frequently encountered in reduction of viologen[29,30] and pyridinium NAD molecules[31] and involve generally the 4-position of the pyridinium ring. In contrast with this suggestion, the fact that the CV pattern of the 4-substituted polymers is the same of poly(**1**) rules out the occurrence of 4-dimerization processes. Moreover the absence during reduction of relevant IR spectral changes, which in contrast are in line with a simple anion loss, appears to indicate a scarce involvement of the polymer backbone in the dimerization process. It is important to take into account that the charge trapping processes are displayed only by the as-prepared polymer, for which a regular cisoid planar structure is assumed. Thus we suggest that the process is a type of π-dimerization taking place between coplanar chain, analogously with that occurring in, e.g., polythiophenes.[32] The absence of these electrochemically irreversible processes in monolayers, in which chain stacking is reasonably absent, appears to be a strong support to this suggestion. Moreover in situ ESR measurements have provided results in line with this hypothesis: the reversible character of the responses indicates that the irreversible (trapping) charge applied at the first reduction of the as-prepared material does not produce spin-bearing species.

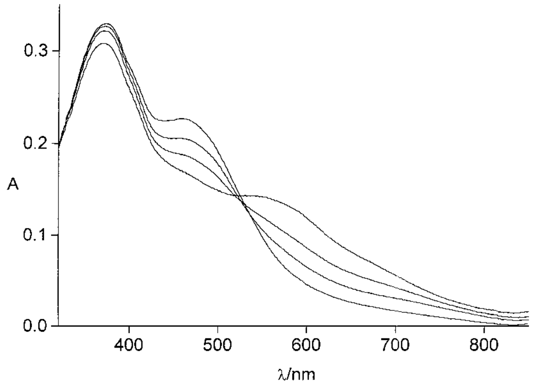

Figure 6. Spectroelectrochemistry of neutral poly(**1**) in acetonitrile + 0.1 M Bu_4NClO_4. Potential range: 0.0/0.7 V. Deposition charge: 5 mC cm^{-2}.

Spectroelectrochemistry of Poly(1). The as-prepared polymer does not show significant chromatic changes upon oxidation, probably because the expected absorption would occur in close correspondence with the dominant band at 525 nm.

In contrast, the neutral polymer, oxidized reversibly from 0 to 0.7 V, shows a chromatic change from yellow to gray-blue. The spectra (Figure 6) show the change from the peak at 465 nm to another at ~600 nm with a clear isosbestic point at 530 nm.

Ionochromic Properties of Poly(1). Ionochromic effects are known with bipy or pyridine moieties in alternation with the dialkoxyphenylene moiety in conjugated sequences[5,6] and attributed to the donor−acceptor nature of the polymer subunits. In these materials the optical transitions involve charge-transfer from the electron-rich dialkoxyphenylene moiety to the electron-poor bipy or pyridine moiety, with enhancement of the effect upon protonation or quaternization of the pyridine.[6] Protonation of **1** itself with $HClO_4$ in acetonitrile (which occurs in a 1:1 ratio) produces a bathochromic shift of the UV−vis maximum from 363 to 431 nm (Figure 7a).

Films of poly(**1**) for ionochromic tests were prepared on ITO electrodes with the passage of 5 mC cm^{-2}. The as-prepared film (violet), which shows a single peak at 525 nm, upon deprotonation with acetonitrile + 0.1 M Bu_4NOH changes to a yellow color with two peaks at 375 and 465 nm (Figure 7b). Back-protonation with acetonitrile + 0.1 M $HClO_4$ makes the film violet again

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(28) Dietrich, M.; Heinze, J.; Heywang, G.; Jonas, F. *J. Electroanal. Chem.* **1994**, *369*, 87.

(29) Tam, K. Y.; Wang, R. L.; Lee, C. W.; Compton, R. G. *Electroanalysis* **1997**, *9*, 219 and references therein.

(30) Lee, C.; Lee, Y. M.; Moon, M. S.; Park, S. H.; ParkK, J. W.; Kim, G.; Jeon, S. J. *J. Electroanal. Chem.* **1996**, *416*, 139 and references therein.

(31) Anne, A.; Hapiot, P.; Moiroux, J.; Saveant, J. M. *J. Electroanal. Chem.* **1992**, *331*, 359.

(32) Hill, M. G.; Mann, K. R.; Miller, L. L.; Penneau, J. F. *J. Am. Chem. Soc.* **1992**, *114*, 2728. Zinger, B.; Mann, K. R.; Hill, M. G.; Miller, L. L. *Chem. Mater.* **1992**, *4*, 1113. Hill, M. G.; Penneau, J. F.; Zinger, B.; Mann, K. R.; Miller, L. L. *Chem. Mater.* **1992**, *4*, 1106. Zotti, G.; Schiavon, G.; Berlin, A.; Pagani, G. *Chem. Mater.* **1993**, *5*, 620. Bauerle, P.; Segelbacker, U.; Gaudl, K. U.; Huttenlocher, D.; Mehring, M. *Ang. Chem. Int. Ed. Engl.* **1993**, *32*, 76. Hapiot, P.; Audebert, P.; Monnier, K.; Pernaut, J. M.; Garcia, P. *Chem. Mater.* **1994**, *6*, 1549. Yu, Y.; Gunic, E.; Zinger, B.; Miller, L. L. *J. Am.Chem. Soc.* **1996**, *118*, 1013.

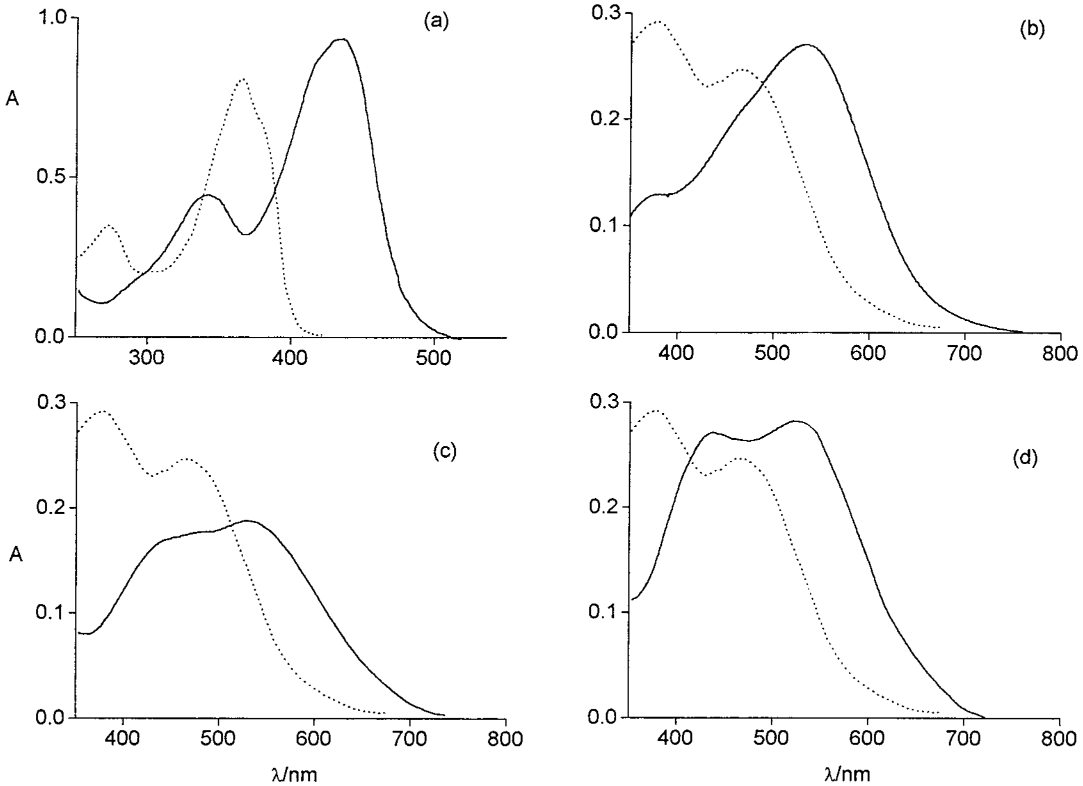

Figure 7. UV−vis spectra of (a) **1** in acetonitrile (- - -) neutral and (—) protonated, (b) poly(**1**) on ITO (—) as-prepared and (- - -) neutral, (c) poly(**1**) on ITO (- - -) neutral and (—) protonated, and (d) poly(**1**) on ITO (- - -) neutral and (—) Fe^{2+}-complexed. Deposition charge for poly(**1**): 5 mC cm^{-2}.

but the spectrum is now made of two peaks at 450 and 530 nm (Figure 7c). Prolonged washing in acetonitrile does not change the spectrum. Subsequent deprotonation and protonation steps are reversible. The absorbance attained by the film in acid is the same down to at least 10^{-3} M acid concentration, which confirms a highly favored protonation.

We attribute the one-peak response of the as-prepared material to the fact that in this material protons are coordinated to cisoid bipy moieties (the lithium electrolyte in the synthesis bath would possibly promote this form via its coordination to monomeric bipy), whereas subsequent deprotonation causes a statistical mixing of cisoid and transoid conformations as pointed out previously. To support this suggestion it must be considered that in the pyridine-based poly(2,5-dialkoxy-phenylene-vinylene)-poly(2,5-pyridyl-vinylene) copolymer[6] the protonated and neutral polymers display a single peak at 537 and 466 nm, respectively. Subsequent protonation occurs at random sites without recreation of the fully coplanar situation. In this way the irreversible reduction of the protonated material and the positive shift of its reversible oxidation are accounted for. This hypothesis agrees with the suggested presence of cisoid−transoid mixtures in analogous materials.[5]

The ionochromic properties of poly(**1**) films were also tested with some divalent transition metal ions (Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+}). The neutral film, dipped in 10^{-2} M solution of the selected perchlorate salt in acetonitrile, becomes immediately brown to violet, according to the ion, causing in any case a bathochromic shift of both bands (Figure 7d). The absorption maxima of the low-energy bands are listed in Table 1. Subsequent prolonged washing in acetonitrile does not change the spectral responses although dipping for 60 s in acetonitrile + 0.1 M ammonia removes the coordinated ion. As in the case of protons, the absorbance attained by the film by treatment with the ion solution is the same down to at least 10^{-3} M ion concentration. Also lithium is able to change the spectrum of the neutral film but the shift is scarce (~5 nm) and is reversed by washing in acetonitrile.

Table 1. UV−Vis Absorption Maxima and $E°$ Values for Poly(1) at Different Ions (10^{-2} M in Acetonitrile)

ion	R_4N^+,Na^+	Li^+	H^+	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
λ_{max}, nm	465	470	525	525	500	485	525
$E°$, V	0.50	0.50	0.70	0.70	0.55	0.55	0.65

Dipping in 10^{-2} M $Fe(ClO_4)_2$ in acetonitrile causes a mass uptake (in the dry state) corresponding to 0.5 $Fe(ClO_4)_2$ moieties per monomeric unit. If the complete saturation of the bipy units in 2:1 complexes $Fe(bipy)_2(ClO_4)_2$ is not believed to be realistic, due to stiffness reasons, a 1:1 coordination of 50% of the sites to $Fe(bipy)(ClO_4)_2$ is suggested. This result appears as a confirmation of the suggested statistical distribution of the dipy moieties in cisoid and transoid conformations, with the former able to yield bidentate coordination.

It is interesting to note that the maximum absorption for Fe^{2+}-complexed polymer films occurs at 525 nm, as for the ter-complex $Fe(bipy)_3{}^{2+}$ in solution. Apparently this result would indicate that the complex is also the same in the solid state. In fact reduction of the film does not occur reversibly at $E° = -1.7$ V, as for the ter-complex,[33] but in ill-defined irreversible peaks. The nonsensitivity of the absorption to the coordination number, which has been recently reported for iron-bipy complexes in DMF,[34] is attributed to the confinement of the electronic transition within a single ligand.

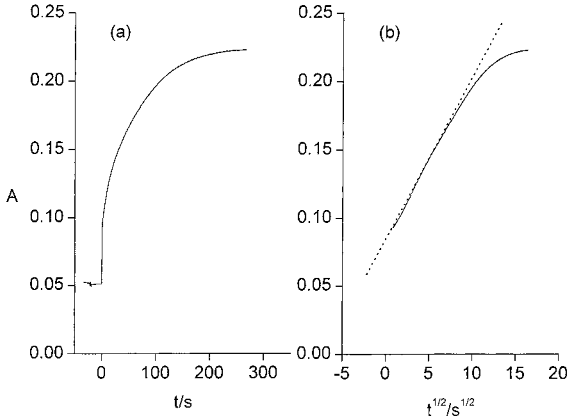

Figure 8. Ionochromic response vs (a) time and (b) square root of time of neutral poly(**1**) in acetonitrile upon addition of 10^{-3} M $HClO_4$. $\lambda = 580$ nm. Deposition charge: 5 mC cm^{-2}.

Kinetic Analysis of the Ionochromic Response. The kinetics of complexation of neutral polymer has been investigated for H^+ and Fe^{2+} in acetonitrile. The absorbance at 580 nm (wavelength of maximum absorption change) attains the maximum change (Figure 8a) in a diffusion-controlled process, as shown by the linear relationship of A and $t^{1/2}$ before approaching the limiting value (Figure 8b). The diffusive control of the rate has been confirmed at different thicknesses: doubling the film thickness doubles the limiting absorbance but does not change the linear relationship of A with $t^{1/2}$. This relationship allows the evaluation of the response times τ of the device. These τ values are inversely proportional to the ion concentration. For the standard film and a 10^{-2} M solution in acetonitrile, τ is 10 s for H^+ and 30 s for Fe^{2+}.

Potentiometric Properties of Poly(1). The oxidative redox potential of the neutral film shifts to more positive potentials upon coordination (see Table 1). The trend follows roughly the electronic transitions, with Fe^{2+} and Cu^{2+} being the most potential shifting ions. In any case, it must be observed that the behavior is rather undifferentiated, both in absorption maxima and redox potentials, which suggests that coplanarization of the bipy rings is more important than the different electronic properties of the ions.

Films for potentiometric tests were prepared on platinum electrodes (1 × 1 cm^2) following the procedure used for the ionochromic tests. The as-prepared films were deprotonated with acetonitrile + 0.1 M Bu_4NOH, subsequently washed in acetonitrile, and tested after conditioning by CV between −1 and 0.7 V. Potentials were measured in aerated acetonitrile solutions vs Ag/Ag^+ reference electrode.

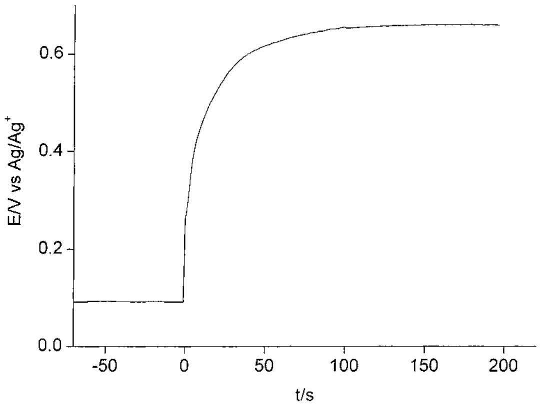

Figure 9. Potentiometric response vs time of neutral poly(**1**) in acetonitrile + 0.1 M Bu_4NClO_4 upon addition of 10^{-2} M $Fe(ClO_4)_2$. Deposition charge: 5 mC cm^{-2}.

In acetonitrile + 0.1 M Bu_4NClO_4, the potential of the filmed electrode attains a stable value (~0.1 V). Adding 10^{-2} M ion causes in a few seconds the shift of the potential to a stable more positive value (e.g., 0.65 V for Fe^{2+}, Figure 9b). With lower concentrations, the same potentials are attained but with times inversely proportional to the concentration (~1000 s from a 10^{-4} M solution, in agreement with the ionochromic kinetic data). The measured potentials are comparable with the redox potentials of the ion-coordinated films.

Conclusions

Anodic oxidation of 5,5′-bis(3,4-(ethylenedioxy)thien-2-yl)-2,2′-bipyridine produces films of an α-coupled polythiophene with regular alternation of protonated bipy units. The polymer films are reversibly oxidized at the bithiophene moieties with one electron every each other moiety and reduced in two complex steps to the neutral material. Deprotonation of the polymer films produces substrates able to coordinate protons and divalent transition metal ions in acetonitrile. The spectral and redox changes accompanying coordination are used to produce ionochromic and potentiometric ion sensor electrodes. Chromatic (from yellow to dark red) and potentiometric (0.5−0.6 V) changes are obtained in a few seconds.

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(33) Prasad, R.; Scaife, D. B. *J. Electroanal. Chem.* **1977**, *84*, 373 and references therein.

(34) Josceanu, A. M.; Moore, P. *J. Chem. Soc., Dalton Trams.* **1998**, 369.