Conductivity In Redox Modified Conducting Polymers. 2. Enhanced Redox Conductivity in Ferrocene-Substituted Polypyrroles and Polythiophenes

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The in situ conductivity of some polypyrroles and polythiophenes redox modified with pendant ferrocene (Fc) groups was investigated in acetonitrile. Redox conductivity at the Fc group is enhanced by electron hopping through the conductive polymer backbone. The hopping rate is increased by a decrease of the Fc–backbone distance and by conjugation of Fc with the backbone itself. The apparent electron-exchange rate constant of the Fc group has been increased from 10^7 to 10^{12} M^{-1} s^{-1}.

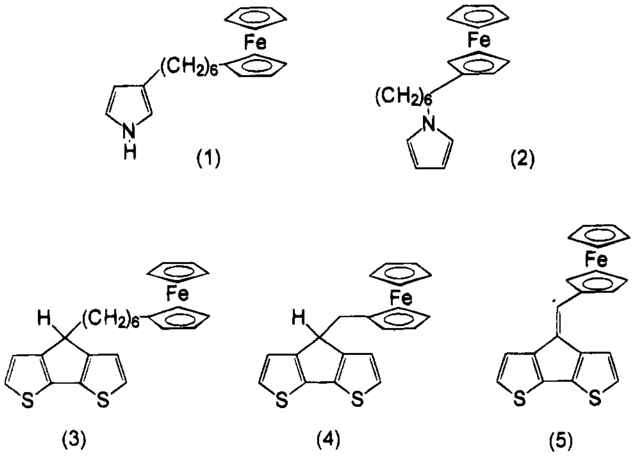
Introduction

In a previous work[1] we investigated the redox conductivity in polythiophenes bearing reducible pendant redox groups. The redox conductivity, though relatively high, was in any case not influenced by the polymer backbone, and this was attributed to the fact that the redox potentials were less negative than the reduction potential of the polyconjugated chain so that there was no overlapping between states belonging to the two systems. The obvious conclusion is that the redox energy level should be located within the band of the polyconjugated polymer in order to observe the electronic states interact.

To this purpose we selected the ferrocene group Fc, the redox process of which is related to an electron state localized within the valence band of polypyrrole and polythiophene chains and therefore interact with the oxidized conducting state of the polymer backbone. With this choice we could also take advantage of a higher air stability of the materials and of an enhanced bipolaron conductivity than in the case of a reduced polyconjugated system.[1]

Several ferrocene-substituted polypyrroles[2] and polythiophenes[3] are reported in the literature. We selected to link the Fc group to pyrrole (in the 1 or 3 positions) and to a dithiophene we previously investigated, namely cyclopentadithiophene. A dithiophene structure was preferred to thiophene since the latter does not allow the obtaining of a good polymer;[3] cyclopentadithiophene in particular allows the polymerization at a coupling site far from the insertion of the substituent therefore producing regular and highly conducting polymers.[4] The Fc group was connected to the heterocyclic moiety via a long *n*-hexyl chain; in the case of cyclopentadithiophene, we have also considered a short linkage such as a one-carbon spacer, both with and without conjugation of Fc with the polymer. The investigated monomers are shown in Scheme 1.

Scheme 1



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. The supporting electrolyte tetraethylammonium perchlorate (TEAP) was previously dried under vacuum at 70 °C. All other chemicals were reagent grade and used as received. The following compounds were prepared according to literature prescriptions: 3-bromo-*N*-(triisopropylsilyl)pyrrole,[5] 4*H*-cyclopenta[2,1-b:3,4-b′]dithiophene

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(CPDT),[6-8] chloromethylferrocene,[9] 4-hexyl-4*H*-cyclopenta[2,1-b:3,4-b′]dithiophene (HCPDT).[4] The monomers **1**−**5** were synthesized as described below.

(6-Bromohexanoyl)ferrocene (6). A solution of 6-bromohexanoyl chloride (4.12 g, 19.3 mmol) in CH_2Cl_2 (25 mL) was added dropwise to a mixture of ferrocene (3.41 g, 18.3 mmol) and $AlCl_3$ (2.57 g, 19.3 mmol) in CH_2Cl_2 (40 mL). After 1 h stirring the reaction mixture was treated with brine (25 mL) and 10% hydrochloric acid (30 mL). The organic phase was separated, washed with water, dried, and evaporated to dryness. Flash chromatography of the residue (silica gel, petrol ether/Et_2O 7:3) afforded the title compound (3.47 g, 52% yield) as a reddish oil. Anal. Calcd for $C_{16}H_{19}BrFeO$: C, 52.92; H, 5.28%. Found: C, 53.01; H, 5.16%. ^1H NMR ($CDCl_3$, 80 MHz) δ 1.40−2.00 (6 H, m, *CH₂*), 2.72 (2 H, t, J = 7.0 Hz, CH_2COFc), 3.42 (2 H, t, J = 6.5 Hz, CH_2Br), 4.15 (5 H, s, unsubstituted Fc protons), 4.48 (2 H, t, J = 2.1 Hz, substituted Fc H^3, H^4), 4.75 (2 H, t, J = 2.1 Hz, substituted Fc H^2, H^5).

(6-Bromohexyl)ferrocene (7). *t*-$BuNH_2 \cdot BH_3$ (6.40 g, 73.6 mmol) was added to a suspension of $AlCl_3$ (4.91 g, 36.8 mmol) in CH_2Cl_2 (100 mL) at 0 °C. The resulting mixture was stirred for 10 min, and a solution of **6** (4.23 g, 11.6 mmol) in CH_2Cl_2 (20 mL) was added dropwise. After stirring for 1 h at 0 °C, the reaction mixture was treated with 0.1 M hydrochloric acid (60 mL) and extracted with AcOEt. The organic phase was washed with brine and dried, and the solvent evaporated under reduced pressure. Flash chromatography of the residue (silica gel, petrol ether/Et_2O 99:1) afforded the title compound (3.52 g, 87% yield) as a reddish oil. Anal. Calcd for $C_{16}H_{21}BrFe$: C, 55.04; H, 6.08%. Found: C, 54.93; H, 5.92%. ^1H NMR ($CDCl_3$, 80 MHz) δ 1.20−1.90 (8 H, m, CH_2), 2.33 (2 H, t, J = 6.5 Hz, CH_2Fc), 3.40 (2 H, t, J = 6.5 Hz, CH_2Br), 4.04 (4 H, s, substituted Fc protons), 4.09 (5 H, s, unsubstituted Fc protons).

3-(6-Ferrocenylhexyl)-*N*-(triisopropylsilyl)pyrrole (8). *n*-BuLi (1.6 M in hexane, 1.25 mL, 2.00 mmol) was added dropwise to a stirred solution of 3-bromo-*N*-(triisopropylsilyl)pyrrole (300 mg, 1.00 mmol) in THF (10 mL) keeping the temperature between 0 and 10 °C. After 5 min of stirring a solution of **7** (520 mg, 1.50 mmol) in THF (5 mL) was added dropwise at the same temperature, and the reaction mixture stirred for 1 h at room temperature. Finally it was poured into water, the organic solvent evaporated under reduced pressure, and the aqueous phase extracted with Et_2O. The dried organic phase was evaporated to dryness, and the residue was purified by flash chromatography (silica gel, petrol ether/CH_2Cl_2 95:5) to give compound **8** (235 mg, 46% yield) as a reddish oil. Anal. Calcd for $C_{29}H_{45}FeNSi$: C, 70.83; H, 9.24; N 2.85%. Found: C, 70.82; H, 9.07; N, 2.71%. ^1H NMR ($CDCl_3$, 300 MHz) δ 1.00−1.20 (21 H, m, $CH(CH_3)_2$), 1.25−1.70 (8 H, m, CH_2), 2.29 (2 H, t, J = 7.6 Hz, CH_2Fc), 2.48 (2 H, t, J = 7.6 Hz, CH_2Py), 4.00−4.04 (4 H, m, substituted Fc protons), 4.07 (5 H, s, unsubstituted Fc protons), 6.12 (1 H, m, pyrrole proton), 6.50 (1 H, m, pyrrole proton), 6.68 (1 H, m, pyrrole proton).

3-(6-Ferrocenylhexyl)pyrrole (1). A mixture of **8** (235 mg, 0.47 mmol) and $(n\text{-}Bu)_4F$ (150 mg, 0.47 mmol) in THF (10 mL) was kept under stirring for 15 min. Water was added, the reaction mixture extracted with Et_2O and the organic phase dried and evaporated to dryness. The residue was purified by reverse phase flash chromatography (RP18 silica gel, acetonitrile/water 9:1) to give **1** as a reddish oil (76 mg, 48% yield). Calcd for $C_{20}H_{25}FeN$: C, 77.64; H, 7.53; N 4.18%. Found: C, 71.33; H, 7.57; N, 4.25%. ^1H NMR ($CDCl_3$, 300 MHz) δ 1.20−1.70 (8 H, m, CH_2), 2.29 (2 H, t, J = 7.6 Hz, CH_2Fc), 2.47 (2 H, t, J = 7.6 Hz, CH_2Py), 4.00−4.04 (4 H, m, substituted Fc protons), 4.07 (5 H, s, unsubstituted Fc protons), 6.07 (1 H, m, pyrrole proton), 6.55 (1 H, m, pyrrole proton), 6.71 (1 H, m, pyrrole proton), 8.00 (1H, broad s, *NH*).

***N*-(6-Ferrocenylhexyl)pyrrole (2).** A solution of pyrrole (110 mg, 1.63 mmol) in DMF (4 mL) was added dropwise to a suspension of NaH (60% in oil, 75 mg, 1.88 mmol) in DMF (10 mL) at 0 °C. The temperature was allowed to reach room temperature, and the reaction mixture was stirred for 30 min. A solution of **7** (570 mg, 1.63 mmol) in DMF (7 mL) was added dropwise at 0 °C and, after 1 h of stirring at room temperature, MeOH was added to destroy the excess of NaH, and the solvent was evaporated. The residue was treated with water and extracted with Et_2O. The organic phase was washed several times with water, dried, and evaporated to dryness. The crude product was purified by flash chromatography (silica gel, petrol ether/CH_2Cl_2 95:5) giving the title compound as an orange solid (481 mg, 88% yield), mp 37 °C. Anal. Calcd for $C_{20}H_{25}FeN$: C, 71.64; H, 7.53; N, 4.18%. Found: C, 71.52; H, 7.41; N,4.12%. ^1H NMR ($CDCl_3$, 300 MHz) δ 1.20−1.90 (8 H, m, CH_2), 2.29 (2 H, t, J = 7.6 Hz, CH_2Fc), 3.85 (2 H, t, J = 7.1 Hz, CH_2N), 4.03 (4 H, s, substituted Fc protons), 4.08 (5 H, s, unsubstituted Fc protons), 6.13 (2 H, t, J = 2.1 Hz, pyrrole H^3, H^4), 6.64 (2 H, t, J = 2.1 Hz, pyrrole H^2, H^5).

4-(6-Ferrocenylhexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (3). *n*-BuLi (1.6 M in hexane, 0.54 mL, 0.89 mmol) was added dropwise to a stirred solution of CPDT (0.15 g, 0.89 mmol) in THF (5 mL), keeping the temperature at 0 °C. After 1.5 h of stirring at room temperature, a solution of **7** (0.30 g, 0.86 mmol) in THF (5 mL) was added at 0 °C and the resulting solution was kept stirring at room temperature for 1.5 h. The reaction mixture was poured into NaCl saturated water and extracted with Et_2O. The organic phase was dried and the solvent evaporated. Flash chromatography (silica gel, petrol ether) of the residue afforded the title compound (0.27 g, 70% yield) as an orange oil. Anal. Calcd for $C_{25}H_{26}FeS_2$: C, 67.26; H, 5.87%. Found: C, 67.57; H, 5.97%. ^1H NMR ($CDCl_3$, 300 MHz) δ 1.15−1.56 (8 H, m, CH_2), 1.78 (2 H, m, CPDTCH_2), 2.29 (2 H, t, J = 7.6 Hz, CH_2Fc), 3.63 (1 H, t, J = 7.1 Hz, H^4), 4.03 (4 H, s, substituted Fc protons), 4.07 (5 H, s, unsubstituted Fc protons), 7.06−7.16 (4 H, AB system, $J^{A,B}$ = 4.8 Hz, thiophene protons).

4-(Ferrocenylmethyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (4). *n*-BuLi (1.6 M in hexane, 1.75 mL, 2.80 mmol) was added dropwise to a stirred solution of CPDT (500 mg, 2.80 mmol) in THF (10 mL), keeping the temperature at 0 °C. After 1.5 h stirring at room temperature, a solution of chloromethylferrocene (prepared from 610 mg of (hydroxymethyl)ferrocene and used immediately without any purification) in THF (10 mL) at 0 °C, and the resulting solution was stirred at room temperature for 2 h. A few drops of MeOH were added and most of the solvent evaporated. The residue was treated with water and extracted with Et_2O. The organic phase was washed with water, dried, and evaporated to dryness. Flash chromatography of the residue (silica gel, petrol ether) afforded the title compound as an orange solid (210 mg, 20% yield), mp 143 °C. Anal. Calcd for $C_{20}H_{16}FeS_2$: C, 63.85; H, 4.25%. Found: C, 63.79; H, 4.25%. ^1H NMR ($CDCl_3$, 300 MHz) δ 2.75 (2 H, d, J = 8.1 Hz, CH_2), 3.62 (1 H, t, J = 8.1 Hz, H^4), 4.09 (5 H, s, unsubstituted Fc protons), 4.11 (4 H, m, substituted Fc protons), 6.85−7.08 (4 H, AB system, $J^{A,B}$ = 5.1 Hz, thiophene protons).

4-(Ferrocenylmethylidene)-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (5). MeONa (108 mg, 2.00 mmol) was added to a stirred solution of CPDT (178 mg, 1.00 mmol) in absolute MeOH (7 mL). After 0.5 h of stirring a solution of ferrocenecarboxaldehyde (224 mg, 1.05 mmol) in absolute MeOH (4 mL) was added dropwise, and the reaction refluxed for 5 h. After cooling, compound **5**, a red solid, was isolated by filtration (212 mg, 57% yield), mp 202 °C. Anal. Calcd for $C_{20}H_{14}FeS_2$: C, 64.17; H, 3.77%. Found: C, 63.95; H, 3.67%. ^1H NMR ($CDCl_3$, 300 MHz) δ 4.29 (5 H, s, unsubstituted Fc protons), 4.48 (2 H, t, J = 1.8 Hz, substituted Fc protons), 4.60 (2 H, t, J = 1.8 Hz, substituted Fc protons), 7.05−7.45 (2 H, AB system, $J^{A,B}$ = 5.1 Hz, thiophene protons), 7.08−7.20 (2 H, AB system, $J^{A,B}$ = 4.8 Hz, thiophene protons), 7.11 (1 H, s, *CH*Fc).

Apparatus and Procedure. Experiments were performed at 25 °C under nitrogen in three electrode cells in acetonitrile AN + 0.1 M TEAP. The counterelectrode was platinum; reference electrode was a silver/0.1 M silver perchlorate in AN

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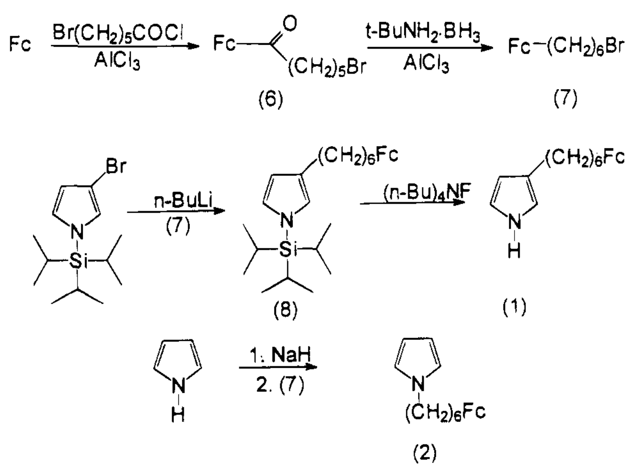
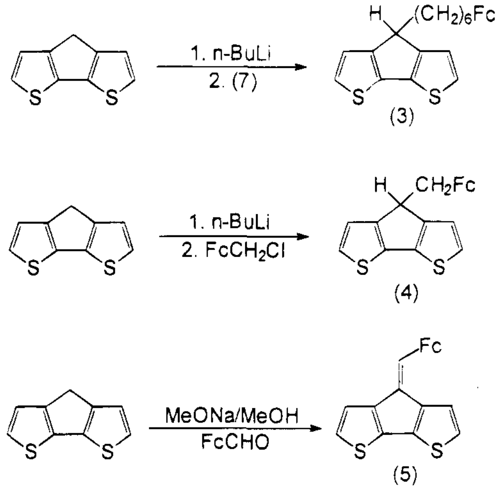
Scheme 2



Scheme 3



(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 minidisc electrode (0.003 cm^2). For electronic spectroscopy a 0.8 × 2.5 cm indium–tin–oxide (ITO) sheet (ca. 20 Ω/square resistance, from Balzers, Liechtenstein) was used. Electronic spectra were taken with a Perkin-Elmer Lambda 15 spectrometer.

The working electrode used in in-situ conductivity experiments and the relevant apparatus and procedures have previously been described in detail.[10] The electrode was a two-band platinum electrode (0.3 cm × 0.01 cm each) with interband spacing of 20 μm, typically polymer-coated with the passage of 20 mC, which assured the attainement of limiting resistance conditions. Measurements were performed bringing the deposit to the desired (gate) potential with the three-electrode potentiostat and applying a small-amplitude (typically 10 mV) dc (drain) voltage between the bands with an additional potentiostat in the two-electrode configuration. After equilibrium was attained (zero gate current), the stable drain current was recorded. Results obtained from different films indicated good reproducibility. Poly(3-methylthiophene) (60 S/cm[11]) was used as conductivity standard.

Results And Discussion

Synthesis of the monomers .The synthetic route we followed for the preparation of the pyrrole-derivative **1** is depicted in Scheme 2.

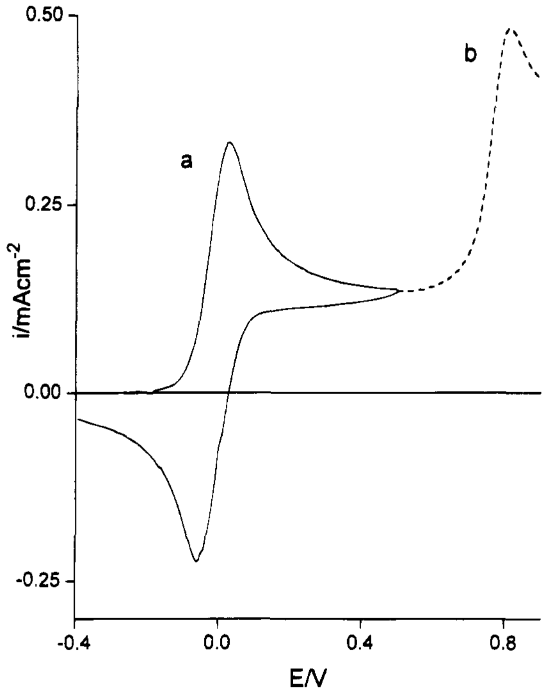


Figure 1. Cyclic voltammogram for 1.0 × 10^{-3} M **1** in AN + 0.1 M TEAP. Scan rate: 0.1 V s^{-1}.

Table 1. Electrochemical Data (Fc Redox potential $E°_m$ and Heterocycle Peak Potential E^p_m of the Monomer; Fc Redox Potential $E°_p$ and Half-Height Width W of the Polymer) for Fc Substituted Pyrroles and Dithiophenes

monomer	$E°_m$/V	E^p_m/V	$E°_p$/V	W/V
1	−0.01	0.80	0.02	0.045
2	−0.01	0.97	0.02	0.045
3	−0.01	0.70	0.02	0.045
4	0.02	0.72	0.11	0.070
5	0.14	0.73	0.25	0.140

3-Bromo-*N*-(triisopropylsilyl)pyrrole was reacted with *n*-BuLi and subsequently alkylated with (6-bromohexyl)-ferrocene (**7**), which in turn was prepared by reduction of the ketone **6** with *t*-BuNH$_2$·BH$_3$ in the presence of AlCl$_3$. The *N*-substituted pyrrole derivative **2** was obtained from pyrrole by reaction with NaH and alkylation with **7** (Scheme 2). The synthetic access to thiophene derivatives **3**–**5** is shown in Scheme 3.

Compounds **3** and **4** were prepared by lithiation of CPDT in the 4 position and reaction with the proper halogen derivative. Condensation of CPDT with ferrocenecarboxyaldehyde in the presence of MeONa furnished compound **5**.

Electrochemical Synthesis and Characterization of the Polymers. Cyclic voltammetry (CV) shows that all the monomers are oxidized reversibly at the Fc group (process a in Figure 1) at potentials given in Table 1. From the table it may be observed that the Fc redox potential is the same for monomers **1**–**3**, which is clearly due to the leveling effect of the long distance (six methylene spacers) of the heterocyclic unit from the Fc group. In contrast the Fc group in **4** and **5** is oxidized with a small (ca. 0.03 V) and with a significant increase (ca. 0.15 V) respectively vs the Fc linked via the *n*-hexyl chain, which is due to a small electronic factor in the first case and to π-interaction with the CPDT moiety in the latter.

At higher potentials the monomers display the oxidation peak of the pyrrole or dithiophene group (CV peak

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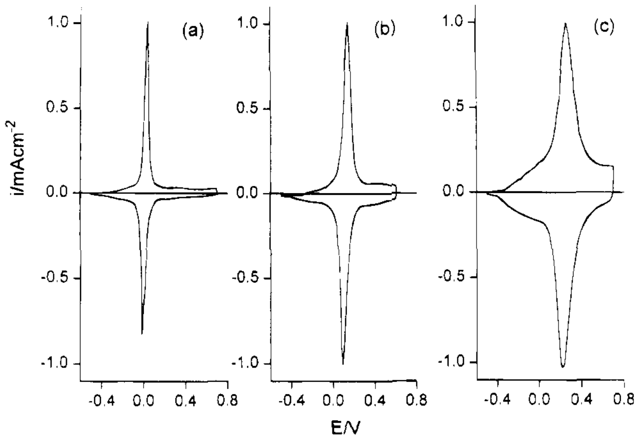

Figure 2. Cyclic voltammograms for (a) poly(**3**), (b) poly(**4**), and (c) poly(**5**) in AN + 0.1 M TEAP. Scan rate: 0.1 V s^{-1}. Reversible charges: (a) 0.8; (b) 1.3; (c) 3.0 mC cm^{-2}.

b in Figure 1), whereby oxidative coupling to polymer occurs. The ratio of the height of the heterocycle CV peak relative to the ferrocene CV peak depends on the monomer, ranging from ca. 1.5 for **2** to ca. 2 for the dithiophenes. In the case of **1** the ratio depends on the monomer concentration, decreasing steeply from 1.1 ($C < 10^{-3}$ M) to 0 ($C > 10^{-2}$ M). This was found to be due to specific adsorption with formation of self-assembled layers.[12] Therefore, high monomer concentrations, which in general favor polymer deposition, are in this case detrimental so that polymer deposition was performed at 5×10^{-3} M. Due to the low solubility of **4** and **5** (ca. 4×10^{-3} and 1.5×10^{-3} M, respectively) the relevant polymerizations were performed at 1×10^{-3} M monomer concentration.

Upon cycling over the peak of the heterocycle oxidation the repetitive CV displays the progressive increase of the Fc redox couple in the polymer which is cyclically deposited. Some CVs of polymer films in monomer free solution are shown in Figure 2.

At low thicknesses (i.e., with a typical reversible charge of 1 mC cm^{-2}) and low scan rates (<10 mV s^{-1}) the CV response appears as a symmetrical cycle (peak potential separation $\Delta E_p = 0$ mV) at redox potentials $E°$ given in Table 1. The process is imposed over a flat capacitive response starting from ca. −0.4 V which is attributable to the oxidation of the polyconjugated backbone. The backbone response is stable to overoxidation up to ca. 0.7 V for polypyrroles and 0.8 V for polydithiophenes and involves a charge which is ca. 25% and 50%, respectively, of that for the Fc couple, indicating the exchange of ca. one electron per four heterocycle rings. The presence of the polypyrrole or polythiophene responses with the expected exchange of charge assures that the polymers are produced without appreciable amounts of defects.

It must be observed that the $E°$ value of the Fc redox couple in poly(**4**) and poly(**5**) is 0.09−0.11 V higher than that in the monomer, at difference with the slight increase (0.03 V) in the other cases in which the Fc is linked via a *n*-hexyl chain. This is a first indication that the polymer backbone influences the Fc oxidation in poly(**4**) and poly(**5**). The interaction with the polymer chain is shown also in the width of the peak. The anomalously high width of poly(**5**) (140 mV, Figure 2) indicates a strong interaction between Fe(II) and Fe(III) centers.[13] From another point of view[14] it indicates a difference of redox potential between two subsequent redox processes and hence a stabilization of a mixed-valence Fe(II)/Fe(III) state. An analogous and higher potential difference has been reported for Fc polymers in which the Fc groups are inserted in the chain and interact via silane[15] or persulfide bridges.[16] For poly(**4**) the width (70 mV) indicates a lower interaction, which probably takes place between Fc centers in adjacent chains made closer by the short methylene spacer.

Table 2. UV−Vis Spectral Data (Monomer and Polymer Absorption Maxima λ_m and λ_p) and Conductivity Data (Polymer Bipolaron Conductivity σ) for Fc-Substituted Dithiophenes

monomer	λ_m/nm	λ_p/nm	σ/S cm^{-1}
3	312	600	40
4	312	560	0.5
5	476	540	2×10^{-3}

Due to the strong adsorption of the monomers onto ITO electrode, which completely inhibits polymerization,[12] the UV−vis properties of poly(**1**) and poly(**2**) could not be determined. The maximum absorptions for poly(**3**) and poly(**4**) (see Table 2) point to long polymers like their ferrocenyl-unsubstituted analogues.[4] For poly(**5**) the spectrum displays a maximum at 540 nm, red-shifted by only 60 nm vs the monomer, whereas in similar polymers[17] the shift is of the range 170−260 nm. This low shift is attributable to a relatively low degree of polymerization, caused by the scarce solubility of the oligomers.

Conduction in Fc-Modified Polypyrroles. Due to the electrode blocking by the pyrrole monomers, the amount of deposited polypyrroles was not sufficient to bridge the conductivity electron that we resorted to electrocopolymerization.

A facile electrocopolymerization of **1** or **2** and pyrrole Py was expected since their oxidation potentials are not too different. On the other hand a successful electrocopolymerization of these monomers is reported.[18] Electrocopolymerization was performed in the presence of 1% water which promotes pyrrole polymerization.[19] CV potential cycling of **1** or **2** in 5×10^{-3} M concentration in the presence of pyrrole Py yields copolymers with the Py/Fc monomer ratio *n* proportional to that of the depositing solution.

This was indicated by the linear plot of the ratio of the polypyrrole oxidation current at −0.3 V i_{Py} over the peak current of the polymerized Fc group i_{Fc} (Figure 3a) as a function of the Py/Fc monomer ratio in the solution (Figure 3b). The copolymer composition was evaluated on the basis of the integrated charges for the oxidation of the ferrocene pendants and the polypyrrole backbone (1 and 0.25 electrons per ferrocene and heterocycle unit, respectively).

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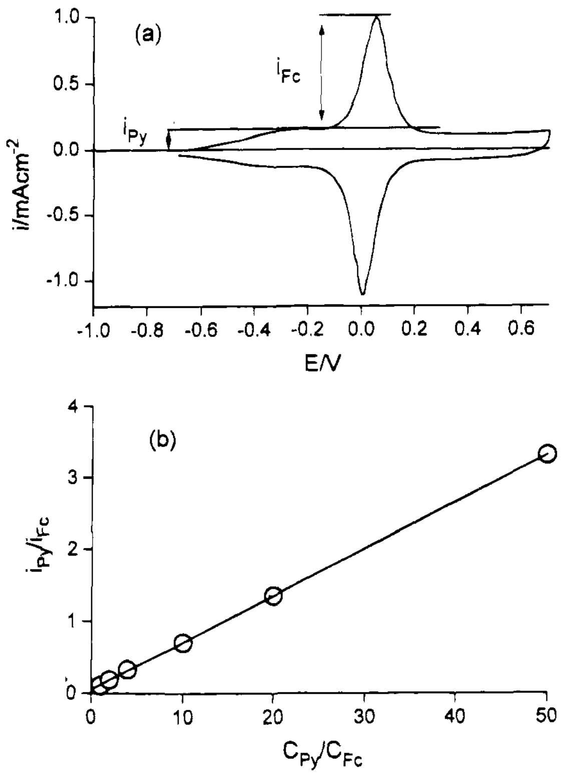

Figure 3. (a) Cyclic voltammogram for poly((**1**)-Py$_3$) in AN + 0.1 M TEAP. Scan rate: 0.1 Vs^{-1}; (b) ratio of polypyrrole and ferrocene peak height in poly((**1**)-Py$_n$) vs ratio of pyrrole and **1** concentrations in filming solution.

The presence of pyrrole in the preparation of the copolymer increases the deposition rate and allows the obtaining of deposits thick enough for in-situ conductivity measurements. Both copolymers poly(**1**-Py$_n$) and poly(**2**-Py$_n$) have been investigated, but only the former will be reported since the latter has given results of lower quality.

Before giving the results of conductivity measurements we must recall that conduction in polyconjugated polymers, which is carried by bipolarons (bipolaron conductivity), has a sigmoidal potential dependence.[20,21] In contrast the potential relationship for redox conductivity is bell-shaped with the maximum at the redox potential.[22] In a regime of mixed bipolaron and redox conductivity, the separation of the two components is best performed by deconvolutive analysis though in most cases simple curve inspection gives the height of the bell-shaped redox conductivity and of the sigmoidal plateau of bipolaron conductivity at the highest potentials.

The bipolaron conductivity of poly(**1**-Py$_n$) increases as the molar fraction of Fc monomeric units X_{Fc} in the polymer is decreased (Figure 4), which may be explained by a progressive increase of coplanarization in the polypyrrole backbone with the reduction of the steric hindrance by 3-substitution and the consequent decrease of the intrachain hopping barrier.

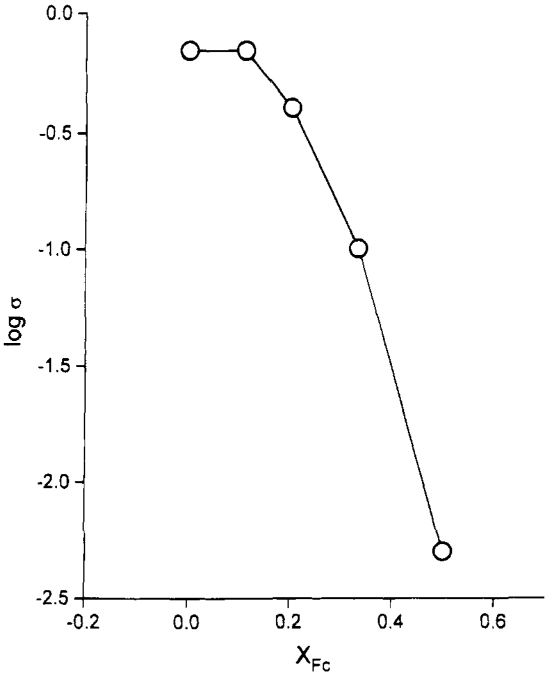

Figure 4. log of bipolaron conductivity σ vs molar fraction of Fc monomeric units X_{Fc} in poly((**1**)-Py$_n$) copolymer.

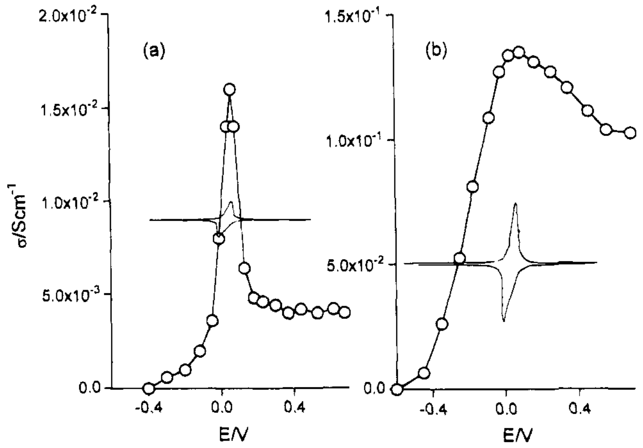

Figure 5. In situ conductivity for (a) poly(**1**-Py) and (b) poly(**1**-Py$_2$). Upper: CVs for comparison.

The in situ conductivity of the 1:1 copolymer poly(**1**-Py) displays clearly the overlapping of the sigmoidal bipolaron conductivity and of a peak in correspondence of the Fc group, due to the redox conductivity (Figure 5a). With increasing *n* the peak decreases and flattens (Figure 5b), becoming hardly discernible in the plateau of the bipolaron conductivity. Up from a pyrrole content *n* higher than 3, the redox conduction virtually disappears. The redox conduction measured in poly(**1**-Py) (ca. 1.5×10^{-2} S cm^{-1}) is even higher than that of the viologen- and nitrophenyl-substituted redox polymers (($3-6) \times 10^{-3}$ S cm^{-1}) we previously investigated,[1] despite the lower electron self-exchange rate constant K_{ex} for Fc (9×10^6 M^{-1} s^{-1} [23] vs 8×10^8 M^{-1} s^{-1} for viologen and nitrophenyl[24]). K_{ex} of Fc groups in the polymers may be evaluated from the conductivity σ and the intersite distance δ (calculated assuming a cubic packing of the sites and a density of 1 g/cm^3) according to the equation: $\sigma\delta^4/K_{ex} = \chi(1 - \chi)(F/N)/6RT$ where χ

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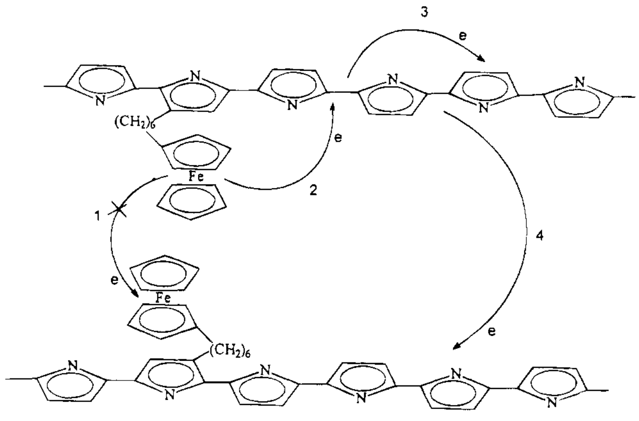

Figure 6. Electron hopping in Fc-substituted polypyrrole.

is the fraction of occupied sites (0.5 for the maximum conductivity).[24] For poly(**1**-Py) we may estimate an apparent electron-exchange rate constant $K_{ex}^* = 2 \times 10^9\ M^{-1}\ s^{-1}$. This enhanced conductivity suggests much more than a favorable reciprocal disposition to hopping of the Fc centers, namely, an enhancement of the electron-exchange rate by mediation of the conducting polymer chain.

In other words, the direct electron-exchange between Fc centres (step 1 in Figure 6) is unfavored in respect with the path constituted by the electron hopping between Fc and the polymer chain (step 2) and along the polymer chain (step 3) or between adjacent chains (step 4). Were the redox conduction supported by hopping through the isoenergetic states of the conductive polymer chain it would be expected to increase with an increase of the chain conduction. On the contrary there is a relative decrease of the redox conduction as the backbone conduction is increased which leads to the conclusion that the Fc–polymer electron exchange (step 2) is (in this case) the rate-determining step of the redox conduction process.

In conclusion the redox conduction does appear to be helped by the polypyrrole chain but does not attain the level of the bipolaron conductivity. The most likely explanation is that the Fc groups are hindered from a strong interaction with the polypyrrole chains by the long spacing *n*-hexyl chain. This aspect of the question was addressed considering Fc polymers from monomers of various length and conjugation of the alkyl chain. To this purpose we selected dithiophene-based monomers since they allow an easy polymer bridging of the electrode for conductivity. For these materials we could obtain the conductivity of the homopolymers, as reported in the following section.

Conduction in Fc-Modified Polydithiophenes. The in situ conductivity of poly(**3**) (Figure 7a) at the plateau is high (40 S cm^{-1}) and comparable with that of analogous ferrocenyl-unsubstituted polymers.[4] No peak of conductivity is displayed as a sign of redox conduction, which was expected on the basis of the much lower electron transfer rate between the Fc pendant and the polymer backbone encountered in the poly(**1**-Py) copolymer.

Reducing the spacing between Fc and the polymer backbone from six methylene groups in poly(**3**) to one methylene group in poly(**4**) evidences the Fc–backbone hopping. The conduction of poly(**4**) (Figure 7b) is sigmoidal as for poly(**3**) but for a lower plateau of conductivity (0.5 S cm^{-1}) which is in line with the higher energy of the electronic optical transition (maximum absorption at 560 vs 600 nm). In this case a slope in correspondence of the $E°$ value of Fc with a conductivity of ca. 0.1 S cm^{-1} indicates that the redox conduction is operative with an intensity ($K_{ex}^* = 1.2 \times 10^{10}\ M^{-1}\ s^{-1}$) strongly enhanced in respect with the case of the hexyl chain.

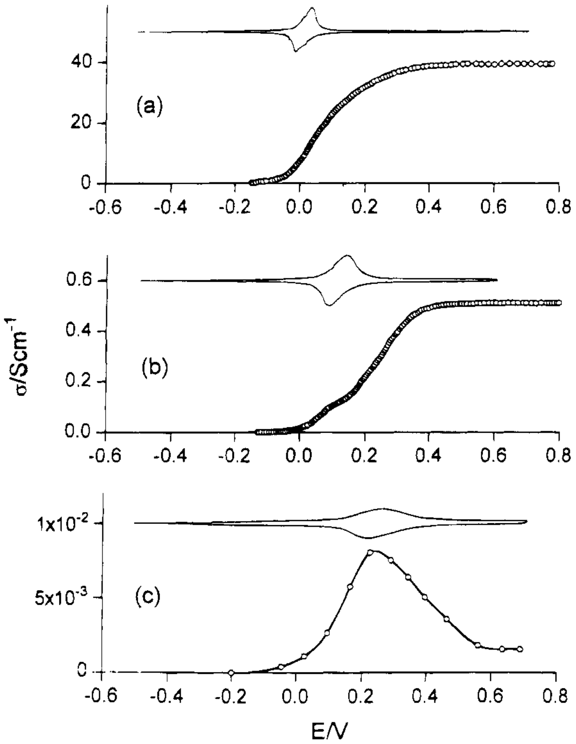

Figure 7. In situ conductivity for (a) poly(**3**), (b) poly(**4**), and (c) poly(**5**). Upper: CVs for comparison.

An even higher redox conduction is obtained via the conjugation of Fc with the CPDT moiety. The Fc redox conduction of poly(**5**) (Figure 7c) appears as a peak relatively high (8 × 10^{-3} S cm^{-1}) compared to the plateau bipolaron conductivity (2 × 10^{-3} S cm^{-1}). Thus the redox conductivity does overcome that due to the backbone carriers, but the latter is low and appears to limit the charge transfer. Since intrachain hopping does not find obstacles in chain twisting given that the substituent is far from the coupling site, the fact is mainly attributable to the high interbackbone spacing introduced by the bulky Fc substituent. Enhancement of redox conductivity could be therefore displayed by an increase of the polymer conductivity via copolymerization of **5** with 4-*n*-hexylcyclopentadithiophene HCPDT, i.e., a monomer which produces a homopolymer highly conducting thanks to a reduced interchain distance.[4,25] Polymerization from 1 × 10^{-3} M solution of **5** containing HCPDT in HCPDT/**5** ratio *n* varying from 1 to 50 has given copolymers with the corresponding ratio of monomeric units, as evaluated by the method used for the poly(**1**/Py$_n$) copolymer. Control of bipolaron conductivity by interchain hopping was evidenced by analysis of the plateau conductivity as a function of the interchain distance, which may be roughly considered proportional to the cubic root of the molar fraction of Fc monomeric units X_{Fc} in the polymer.

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(25) Bradamante, S.; Berlin, A.; Canavesi, A.; Gobetto, R.; Zotti, G. in preparation.

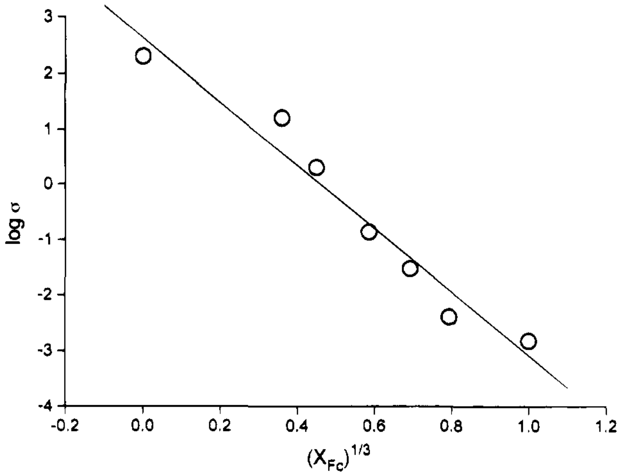

Figure 8. log of bipolaron conductivity σ vs $(X_{Fc})^{1/3}$ (X_{Fc} = molar fraction of Fc monomeric units) in poly((**5**)-HCPDT$_n$) copolymer.

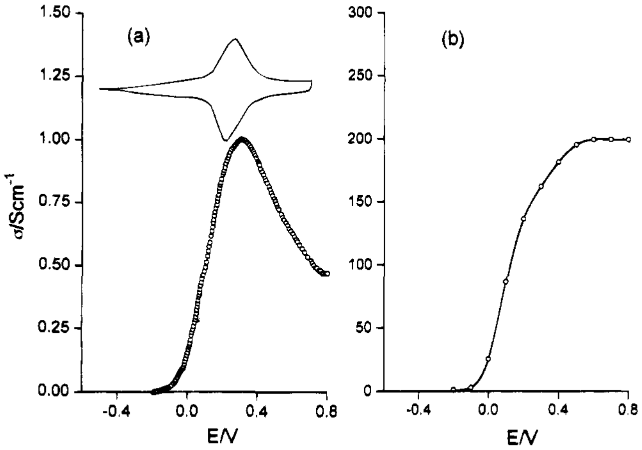

Figure 9. (a) In situ conductivity for poly((**5**)-HCPDT$_{10}$) copolymer. Upper: CV of poly(**5**) for comparison; (b) in situ conductivity of poly(HCPDT).

The relationship of the logarithm of conductivity σ vs $(X_{Fc})^{1/3}$ is fairly linear (Figure 8) as theoretically expected and experimentally found in such cases.[26] The peak of the redox conductivity is kept as the bipolaron conductivity is increased (Figure 9a) and attains a maximum conductivity of ca. 1 S cm^{-1} at poly(**5**-HCPDT$_{10}$). This value corresponds to $K_{ex}^* = 2 \times 10^{12}$ M^{-1} s^{-1}, a value which overcomes the limits of diffusion control (ca. 10^{11} M^{-1} s^{-1}) since in fact the electron exchange is not direct but mediated by the polyconjugated chain. Only for *n* values higher than 10 the redox contribution to conductivity decreases, due to a substantial decrease of the carrier contribution by Fc, and the shape of the curve vs potential tends to become sigmoidal approaching that of pure poly(HCPDT) (Figure 9b). The fact that the redox conductivity follows the increase of the bipolaron conductivity is proof that in this case the electron-exchange between the redox pendant and the polymer chain is highly efficient.

Conclusions

From the results obtained previously[1] and in the course of the present investigation, it results that a redox pendant in a conducting polyconjugated system exchanges electrons with the surrounding polymer sites only on condition that its energy is comparable with that of the polymer sites. The route of the redox charge transport may be controlled by either the electron transport within the conducting chain or the electron hopping between redox center and polymer chain. In the latter case it was found that the redox exchange is more efficient at a shorter distance from the chain and that conjugation provides a further efficient route to conduction. Applying all there steps we could obtain a progressive increase of the apparent electron-exchange rate constant for ferrocene from 10^7 to 10^{12} M^{-1} s^{-1}.

From a practical point of view, we recall that a redox group may act as a switching molecular system for charge transport so that interesting applications of redox polymers to electronic devices are open.[27] We have shown that under certain conditions the limited conduction of simple redox polymers may enjoy enhancement by insertion of the redox centres into a polyconjugated chain.

We expect that more interesting results may be obtained moving the redox group from the side position into the polymer backbone. This is an intriguing aspect which we are exploring at present.

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