Electrosynthesis of a Tetrathiafulvalene-Derivatized Poly(thiophene)

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ABSTRACT: A new thiophene derivative containing a tetrathiafulvalene (TTF) moiety covalently attached to the thiophene ring via a linear oxadecyl spacer has been synthesized. Although in acetonitrile the voltammogram of this compound exhibits the cyclic voltammetric features of TTF and 3-alkylthiophenes, all attempts of electropolymerization remained unsuccessful, presumably because of the scavenging of the thiophene cation radicals by TTF. In contrast, electropolymerization can be achieved by application of repetitive potential scans in nitrobenzene solutions. This result suggests, in agreement with UV-visible absorption spectra, that the formation of a donor-acceptor complex between nitrobenzene and the TTF moiety decreases its reactivity toward thiophene cation radicals. The analysis of the electrochemical behavior of the resulting polymer shows that, although the polymer exhibits the characteristic voltammetric signatures of TTF and poly(3-alkylthiophenes), the redox processes are complicated by the superimposition of the discrete oxidation steps of TTF on the much wider oxidation process of the supporting conjugated poly(thiophene) backbone.

Introduction

The electropolymerization of precursors of polyaromatic conjugated polymers such as pyrrole or thiophene constitutes a very efficient method for the modification of electrode surface properties.[1] However, the realization of modified electrodes capable of specific activity such as electrocatalysis or molecular recognition requires that the precursor monomer contain covalently attached prosthetic groups. Whereas this approach has been extensively developed in the case of N-substituted poly(pyrroles),[1a,b] a more limited number of functional poly(thiophenes) (PTs) have been synthesized. This situation results from the fact that, although 3-substituted PTs retain high levels of electronic conductivity when the electronic and steric substituent effects are properly taken into account and controlled,[1c] they require in general more tedious syntheses than their N-substituted pyrrole analogues. Over the past few years, PTs 3-substituted by various functional groups such as water-solubilizing alkanesulfonate or carboxylic groups,[2] complexing polyether chains,[3] or chiral groups[4] have been reported, whereas only a few examples of PTs derivatized by redox mediators such as viologens,[5] quinones,[6] or ferrocene[7] have been synthesized. In this context, the derivatization of PT by tetrathiafulvalene (TTF) can be of particular interest for several reasons.

On the one hand, TTF derivatives have been shown to act as efficient redox mediators in enzymatic carbon-paste electrodes.[8] From this viewpoint, the covalent grafting of TTF on a thiophene monomer could lead simultaneously to the formation of a conducting electrode material, through the electropolymerization of the thiophene ring, and to the immobilization of the redox mediator. On the other hand, cation radical salts of TTF derivatives and poly(thiophenes) are representative examples of the main two classes of organic metals, namely, molecular conductors and conjugated polymers. Although these two classes of materials differ in many respects, the association of some of their structural characteristics and properties may contribute to mutual fertilization by the development of new materials of both fundamental and technological interest.

In this context, we recently reported the synthesis of the first examples of hybrid oligomers involving a linear combination of TTF and oligothiophenes.[9] As an alternative approach, we wish to report here the electropolymerization of a thiophene monomer with covalently attached TTF.

A first attempt in this direction was reported in a recent communication describing the synthesis of three thienyl monosubstituted TTF derivatives.[10] However, only in one case did anodic oxidation of the monomer give rise to polymerization. Furthermore, since doped PTs are usually dark blue, the orange color of the obtained thin polymer film indicates a rather short conjugation length. This limited conjugation may result from a distortion of the PT backbone caused by steric interactions between TTF groups linked to the thiophene ring by too short spacers (3-4 carbons). As a matter of fact, it has been shown that the neutralization of the steric effects of simple isopropyl or phenyl groups already requires the insertion of a spacer containing at least three or four carbons.[11] These conclusions have been confirmed by a recent analysis of the structural conditions of substitution of PT by viologen which has shown that a spacer of at least eight carbons was necessary to preserve the conjugation length of the PT backbone.[5b] We report here the synthesis and electrochemical properties of a new TTF-derivatized poly(thiophene), poly(1).

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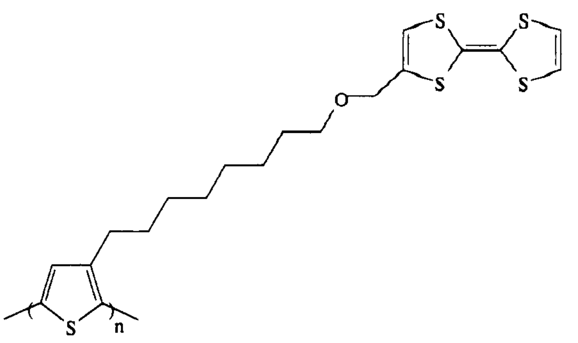


Poly (1)

On the basis of the above conclusions, an oxadecyl spacer was inserted between the thiophene ring and the TTF moiety to minimize steric hindrance and hence preserve the conjugation of the PT backbone. It is shown that this compound undergoes electropolymerization in nitrobenzene and that the resulting electroactive polymer retains the characteristic electrochemical features of PT and TTF.

Experimental Section

The synthesis of the monomer 3-(10-tetrathiafulvalenyl-9-oxadec-1-yl)thiophene (1) is depicted in Scheme I. 3-(8-Bromooctyl)thiophene (2) was prepared using the method described in the literature.[12] Condensation of 1,8-dibromooctane (10) and 4-methoxyphenol (9) in the presence of KOH[13] afforded 8-(4-methoxyphenoxy)octyl bromide (8) in 70% yield. Cross-coupling of the corresponding Grignard reagent with 3-bromothiophene (7) in the presence of Ni(DPPP)Cl$_2$ (DPPP = Ph$_2$P(CH$_2$)$_3$PPh$_2$)[14] gave compound 6 (yield 70%), which was subsequently converted into 3-(8-bromooctyl)thiophene (2) by refluxing with HBr in Ac$_2$O (yield 75%). ^{1}H NMR (CDCl$_3$) (ppm): 1.35 (8H, m); 1.64 (2H, m); 2.19 (2H, m); 2.64 (2H, t, J = 7.5 Hz); 3.42 (2H, t, J = 7.0 Hz); 6.95 (2H, d, J = 4.9 Hz); 7.25 (1H, m).

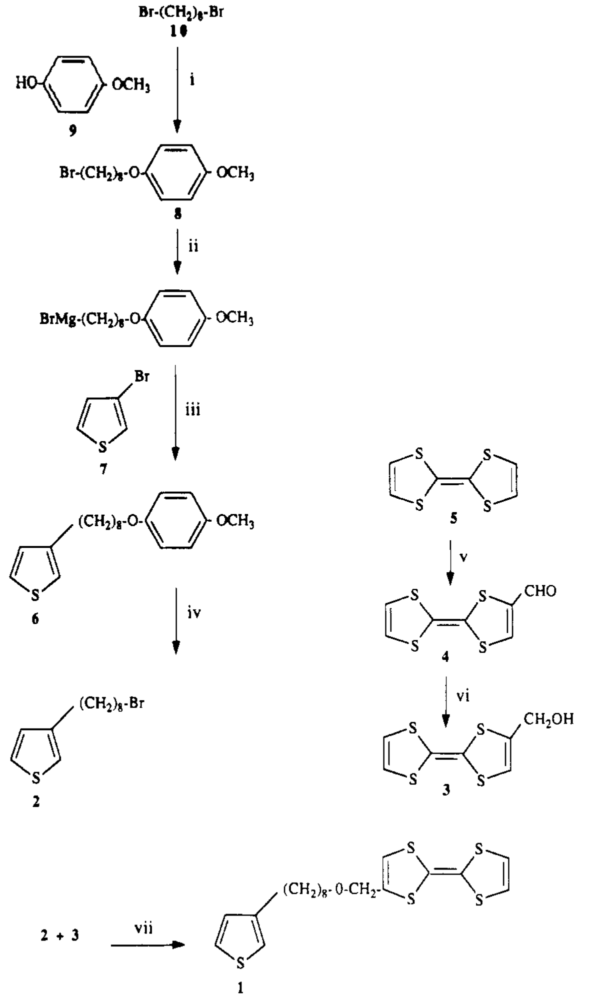
Formylation of TTF (5) by *N*-methylformanilide[15] afforded formyl-TTF (4) (yield 61%). Hydroxymethyl-TTF[16] (3) was obtained in 93% yield by reduction of 4 using NaBH$_4$ in methanol. The coupling of 2 and 3 in the presence of NaH in dry THF afforded the target compound 1 as a viscous yellow oil (yield 35%). ^{1}H NMR (CDCl$_3$) (ppm): 1.32 (8H, m); 1.57 (4H, m); 2.62 (2H, t, J = 7.5 Hz); 3.43 (2H, t, J = 6.5 Hz); 4.21 (2H, s); 6.17 (1H, s); 6.30 (2H, s); 6.92 (2H, d, J = 4.7 Hz); 7.23 (1H, m). ^{13}C NMR (ppm): 26.04; 29.25; 29.37 (two carbon atoms); 29.55; 30.27; 30.54; 67.94; 70.43; 109.60; 110.10; 115.66; 118.97; 119.13; 119.77; 125.04; 128.29; 135.09; 143.22.

Electropolymerizations were carried out in a three-electrode single-compartment cell from a reaction medium involving 0.1 M monomer and 0.1 M tetrabutylammonium hexafluorophosphate (Fluka, puriss) in nitrobenzene (Aldrich, ACS reagent) using the already described procedure.[11a] The solutions were degassed by nitrogen bubbling prior to electropolymerization, which was performed under a nitrogen atmosphere. The polymer was grown on platinum microelectrodes of 7 × 10^{-3} cm^2 area, a platinum wire was used as counter electrode, and a saturated calomel electrode (SCE) was used as reference. After electrodeposition the polymer films were rinsed with hexane and placed in another cell containing 0.1 M Bu$_4$NPF$_6$ in acetonitrile (HPLC grade). Electrodeposition and cyclic voltammetry were performed with a PAR 273 potentiostat–galvanostat, and UV–visible absorption spectra were obtained on a Perkin-Elmer Lambda 2 spectrometer.

Results and Discussion

Figure 1 shows the cyclic voltammogram (CV) of an acetonitrile solution containing 10^{-3} M 1 and 0.1 M Bu$_4$NPF$_6$. This CV exhibits two successive well-defined redox systems with anodic peak potentials E_{pa1} and E_{pa2} at 0.37 and 0.74 V and cathodic peaks E_{pc1} and E_{pc2} at 0.31 and 0.68 V. For each redox system, the 60-mV value of ΔE_p ($E_{pa} - E_{pc}$) is consistent with a single electron transfer.

Scheme I[a]



[a] Reagents and conditions: (i) KOH/MeOH, reflux, 1 h; (ii) Mg/Et$_2$O; (iii) Ni(DPPP)Cl$_2$/Et$_2$O, 15 h, room temperature; (iv) HBr/Ac$_2$O/Bu$_4$NBr, 100 °C, 20 h; (v) LDA, -78 °C, *N*-methyl-*N*-phenylformamide, room temperature, 20 h; (vi) NaBH$_4$/MeOH, 20 min, room temperature; (vii) NaH/THF, 18C6, reflux, 22 h.

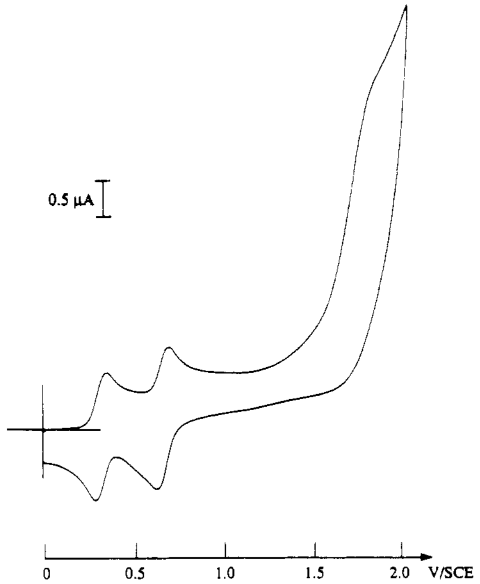


Figure 1. Cyclic voltammogram of 1 (10^{-3} M in 0.1 M Bu$_4$NPF$_6$/CH$_3$CN, scan rate 100 mV/s).

The close agreement of these potential values with literature data on TTF[17] confirms the covalent anchoring of the TTF moiety on the thiophene monomer. These two reversible redox systems are followed by an intense

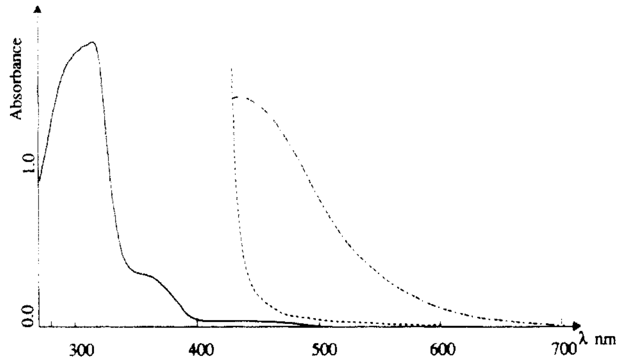


Figure 2. UV–visible absorption spectra of 1: solid line, 1 in acetonitrile; dotted line, nitrobenzene alone; dotted–dashed line, 1 in nitrobenzene.

anodic wave at ca. 1.90 V corresponding to the irreversible oxidation of the 3-alkylthiophene moiety.[11a]

All attempts to electropolymerize 1 from acetonitrile solutions remained unsuccessful. Although the exact causes of this are not known, it is evident that inhibition of polymerization results from the presence of the TTF moiety on the monomer. Since the electropolymerization of thiophene proceeds through the chemical coupling of the cation radicals resulting from the anodic oxidation of the thiophene ring,[1c] a possible cause for the inhibition of polymerization could involve the scavenging of the thiophene cation radicals by the highly oxidizable TTF moiety. Such effects have been already observed in attempts to electropolymerize thiophene monomers containing sulfide groups.[18] In a second set of experiments, electropolymerization was undertaken in nitrobenzene, in which the most conductive poly(thiophene) films have been obtained.[19] Dissolution of 1 at a concentration of 0.1 M in nitrobenzene leads instantaneously to a dark red coloration. The UV–visible absorption spectra of 1 (Figure 2) show that, whereas the spectrum obtained in acetonitrile is similar to that of TTF, in nitrobenzene, the broad band emerging on the low-energy side of the solvent absorption suggests the formation of a donor–acceptor complex between 1 and nitrobenzene. This hypothesis appears consistent with previous reports on TTF–*m*-dinitrobenzene complexes.[20]

Figure 3 shows the CVs resulting from recurrent potential scans in an electrosynthesis medium containing 0.1 M 1 and 0.1 M Bu_4NPF_6 in nitrobenzene. The first CV shows broad anodic waves at ca. 0.70 and 1.15 V, whereas reduction waves occur at 0.50 and −0.10 V during the reverse scan. Contrary to the case of acetonitrile, repetitive cycling leads to an intensification of the CV waves, indicative of material deposition. However, whereas the intensity of the second anodic wave and of the two cathodic ones significantly increases, the height of the first anodic wave remains almost constant. As will be discussed, these different behaviors may reflect the potential dependence of the conductivity of the conjugated PT backbone. The increase of the wave intensity is accompanied with a positive shift of the oxidation waves and a negative shift of the reduction waves. These potential shifts result in a large increase of ΔE_p for the two redox systems, which suggests that the rate of electron transfer decreases as the thickness of the deposit increases.

Owing to the poor wave resolution, their assignment is not straightforward. Besides complications arising from the multiple electrochemical and chemical reactions involved in the overall deposition process, the very large ΔE_p values are partly due to the high viscosity of the solvent, which has been shown to affect the diffusion rate and hence the heterogeneous rate of charge transfer.[21] Similar effects have been observed during the electropolymerization of 3-alkylthiophenes in viscous media.[22] Electropolymerization of thiophene derivatives by means of multisweep voltammetry results in the progressive development of a new redox system in a potential region less anodic than the potential required to oxidize the monomer to its cation radical.[3b,22] In the case of 3-alkylthiophenes, this new redox system is generally observed around 1.0 V/SCE.[22] A closer examination of the CVs of Figure 3a shows that after the first anodic scan a third anodic wave emerges around 1.30 V. Although this peak becomes difficult to distinguish during subsequent scans due to the broadening of the waves, the increase of the anodic potential limit to 2.20 V produces an intensification of this third wave (Figure 3b), which implies that it corresponds to the oxidation of the deposited PT backbone. These results suggest that the first anodic wave at 0.70 V can be ascribed to the formation of the TTF cation radical, whereas the broad second wave includes both the formation of the TTF dication and the oxidation of the as-grown poly(thiophene).

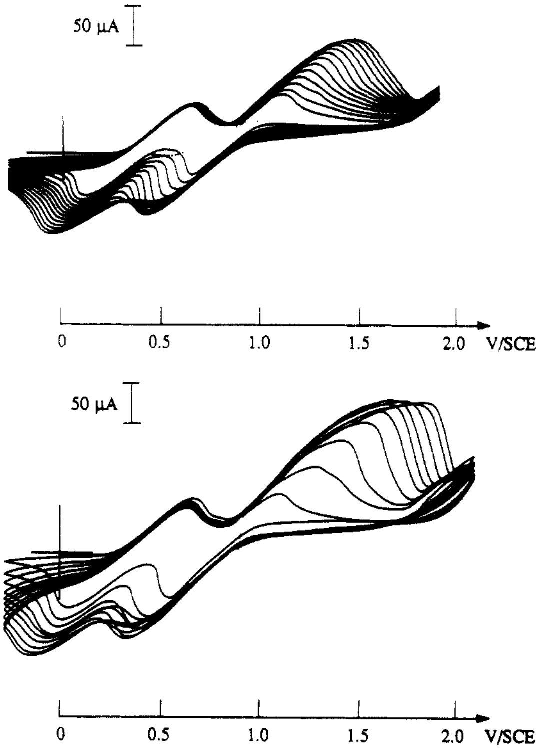


Figure 3. Cyclic voltammograms obtained by successive potential scans in 0.1 M 1 + 0.1 M Bu_4NPF_6/nitrobenzene (scan rate 100 mV/s): (a, top) between −0.30 and +2.00 V/SCE; (b, bottom) between −0.30 and +2.20 V/SCE.

To summarize, although electropolymerization is inhibited in acetonitrile, it takes place in nitrobenzene. These strongly different behaviors suggest that the formation of a donor–acceptor complex between the TTF moiety and nitrobenzene decreases the ability of TTF to scavenge the thiophene cation radicals, thus allowing the electrodeposition of an electroactive polymer. More detailed information on the electrochemical properties of this polymer have been obtained by analyzing its voltammetric behavior in a monomer-free electrolytic medium.

Figure 4a shows the CV of poly(1) deposited in the conditions of Figure 3b on a Pt microelectrode. This stabilized CV is obtained after a break-in period of ca. ten voltammetric cycles during which the wave intensity increases steadily. Such a behavior has been already

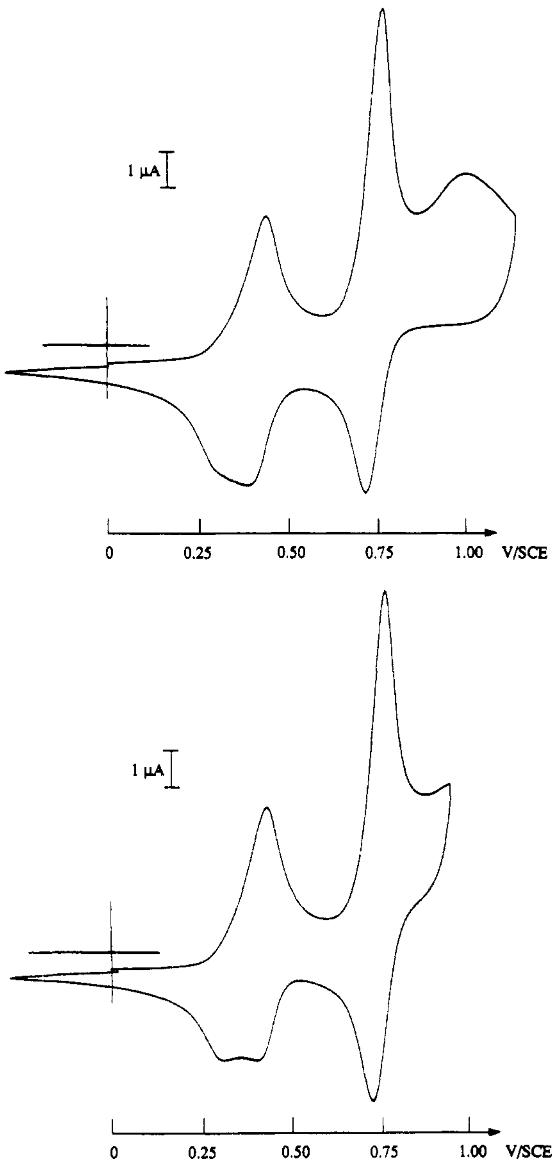


Figure 4. Cyclic voltammograms of poly(1) in 0.1 M Bu_4NPF_6/CH_3CN (scan rate 10 mV/s): (a, top) between −0.30 and +1.20 V/SCE; (b, bottom) between −0.30 and +1.00 V/SCE.

observed for TTF covalently attached to a polystyrene backbone.[23] The CV in Figure 4a shows well-defined anodic peaks at 0.47 and 0.82 V corresponding to the successive generation of the TTF cation radical and dication. These two peaks are followed by a third broader wave at 1.06 V assigned to the oxidation of the PT backbone. Due to the vicinity of the reduction wave of TTF^{2+} and to the uncertainty in the position of the current baseline, the reduction wave of the PT system is difficult to assess. However, using the half sum of the anodic and cathodic current peaks of the second TTF redox system as the current baseline allows the definition of the symmetrical CV generally observed for poly(3-alkylthiophenes) with long alkyl chains.[11] The reverse scan shows the cathodic waves corresponding to the successive reduction of TTF^{2+} and $TTF^{\bullet +}$ at 0.76 and 0.41 V, respectively. However, the shape of the second wave is more complex and involves subcomponents at 0.41 and 0.32 V that become better resolved when the scan is reversed before the oxidation of PT (Figure 4b). Similar CV shapes have been observed for TTF covalently bound to a metal oxide surface[24] or to an insulating polystyrene backbone.[23] In this latter case, spectroelectrochemical experiments have led to the assignment of the 0.41-V peak as the reduction of the TTF cation radical and of its dimer

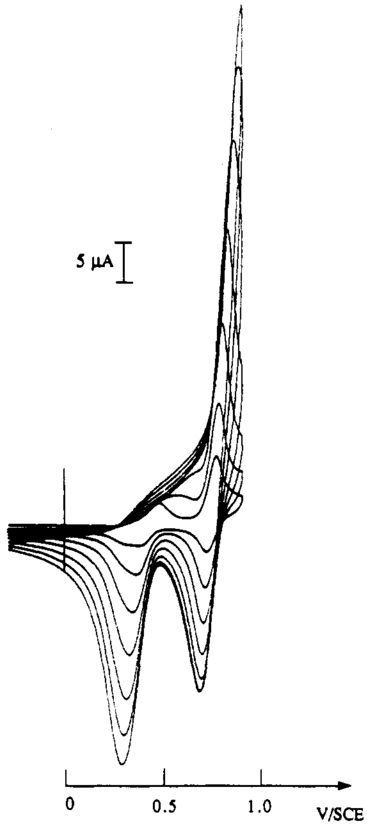


Figure 5. Cyclic voltammograms of poly(1) in 0.1 M Bu_4NPF_6/CH_3CN: scan rate 10, 30, 60, 100, 150, 200, and 250 mV/s.

dication (eqs 1 and 2) and to the assignment of the 0.32-V peak as the reduction of the mixed-valence dimer (eq 3).

$$TTF^{\bullet +} + e^- \rightarrow TTF^0 \qquad (1)$$

$$(TTF)_2^{2+} + e^- \rightarrow (TTF)_2^{+} \qquad (2)$$

$$(TTF)_2^{+} + e^- \rightarrow 2TTF^0 \qquad (3)$$

For both TTF redox steps ΔE_p fits exactly the 60 mV expected for a single electron transfer. However, for the first system, this value is obtained only with the 0.41-V peak. The two successive monoelectronic transfers of TTF have been confirmed by coulometric measurements which gave relative values of 1:1:0.5 for the two TTF systems and the PT system, respectively. Taking into account the poor resolution of the CV, the 0.5 value obtained for PT appears to be in satisfactory agreement with the 0.25 oxidation level generally observed.[1c] These coulometric data lead to a surface coverage of 2×10^{-7} mol·cm^{-2}. This value and the thickness/deposition charge ratio determined for poly(3-decylthiophene) and poly(3-tetradecylthiophene) (12–15 μm/C[11]) led to a rough estimation of the minimal film thickness of 0.5–0.6 μm.

Figure 5 shows the cyclic voltammograms recorded at various scan rates on a poly(1) film. The peak currents scale linearly with scan rate as expected for surface-attached species. However, for scan rates higher than 150 mV/s, a departure from linearity occurs, indicating that the process progressively evolves toward a diffusion-controlled regime. As already observed during polymer deposition (Figure 3), the intensity of the first anodic wave exhibits only a very small increase with scan rate. This phenomenon must be discussed in relation with the specificity of the charge transport process in poly(1), which involves several imbricated mechanisms.

The oxidative doping of the PT proceeds via the successive generation of cation radicals (polarons) and

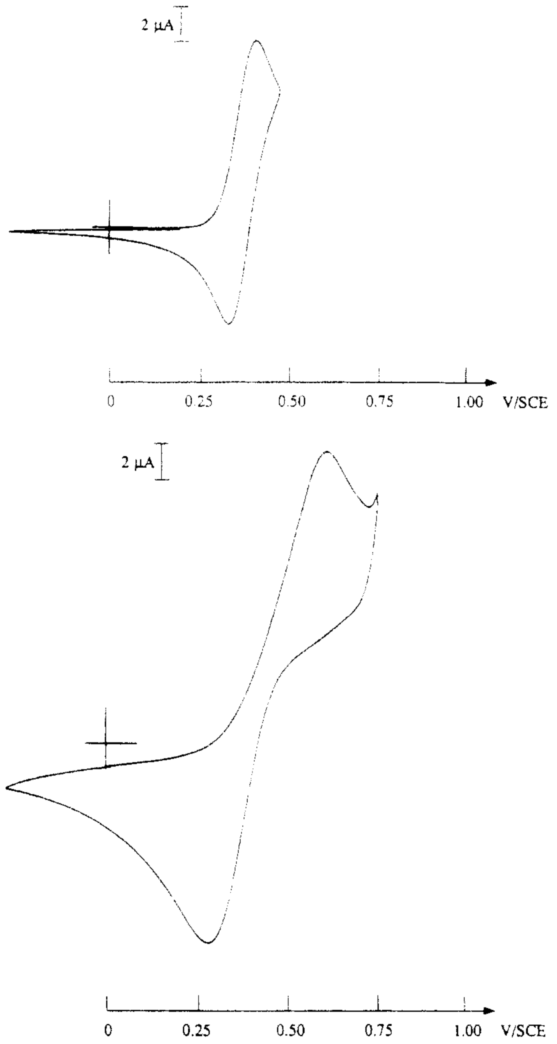


Figure 6. Cyclic voltammograms of ferrocene in 0.1 M Bu$_4$NPF$_6$/CH$_3$CN (scan rate 50 mV/s): (a, top) on a Pt electrode; (b, bottom) on a poly(1) electrode.

dications (bipolarons) delocalized over the π-conjugated chain. Due to various factors such as the presence of different conjugation lengths and interactions among charged sites, the electrochemical doping of PTs departs from an ideal Nernstian process[25] and results generally in broad oxidation waves extending from ca. 0.30–0.40 to 1.0–1.20 V.[26] This specific behavior has important consequences for the electrochemical response of poly(1).

At the beginning of a positive potential scan, the PT backbone is in its neutral insulating form; consequently, electrons removed from the TTF moiety during oxidation to TTF$^{\bullet+}$ are transported to the electrode surface by means of a classical hopping mechanism.[27] When the potential of formation of TTF^{2+}, i.e., 0.70 V, is reached, the conductivity of the doped PT chain is high enough to ensure electrical communication between the TTF moiety and the electrode, thus suppressing the kinetic limitation observed for the first oxidation step. Similarly, upon scan inversion, the reduction of TTF^{2+} is not limited by the film resistance, and a linear dependence of the current peak vs scan rate is observed. When the potential corresponding to the beginning of the reduction of TTF$^{\bullet+}$ is reached, the conductivity of the PT backbone has already significantly decreased; however, the conductivity of TTF$^{\bullet+}$ contributes to maintain a high overall electronic conductivity in the film which can explain the linear dependence of the TTF$^{\bullet+}$ reduction current with scan rate.

To support this interpretation of the kinetic limitation of the first TTF oxidation step, the electrochemical response of a fast redox couple electroactive in the same potential region has been analyzed on a poly(1) electrode. Figure 6 shows the CVs of ferrocene recorded on a naked Pt electrode and on poly(1). The comparison of these responses shows that in the latter case ferrocene oxidation occurs at ca. 0.65 V. This 250-mV overpotential appears to be consistent with a slower rate of electron transfer related to the limited conductivity of poly(1) in this potential region. On the other hand, the strong intensification of the ferrocene CV waves on poly(1) suggests a larger number of active sites than on naked Pt. This result clearly shows that the electroactivity of the poly(1) electrode is not limited to the film–solution interface but also involves the bulk of the polymer.

Conclusion

A new PT derivative containing a TTF moiety covalently attached to the thiophene ring via a long oxyalkyl spacer has been synthesized. This compound undergoes electrochemical polymerization in nitrobenzene thanks to the formation of a donor–acceptor complex with the attached TTF moiety. Although the resulting polymer exhibits the characteristic cyclic voltammetric signatures of TTF and PT, interference of the TTF and PT redox processes results in an electrochemical behavior more complex than the simple superimposition of those of the constitutive building blocks. Owing to the imbrication of the multiple elementary redox steps, a detailed and quantitative description of the electrochemical behavior of poly(1) will require a model of a considerable complexity. Although the definition of such a model is far beyond the scope of the present work, these preliminary results demonstrate the validity of our approach for the realization of TTF-modified electrodes.

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