

ARTICLES

Conjugated Polymetallorotaxanes: In-Situ ESR and Conductivity Investigations of Metal–Backbone Interactions

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Electrochemical studies of polymetallorotaxane films of a general formula **poly[1,3,Mⁿ⁺]** where Mⁿ⁺ is copper(I), cobalt(II), zinc(II), or lithium(I) are reported for both metalated and demetalated (**poly[1,3,-]**) forms. Cyclic voltammograms (CV) recorded for polymetallorotaxanes containing redox-active metals, with an exception of the Li one, in addition to the electroactivity of the complexing metal exhibit two redox couples associated with the consecutive oxidation/reduction of the oligothiénylene units in the wiring polymer. For **poly[1,3,Cu⁺]**, the CV studies are completed by ESR spectroelectrochemical investigations combined with in-situ conductivity measurements as a function of the electrode potentials. In the ESR response, two signals of different origin can be distinguished: a broad signal originating from Cu(II) paramagnetic ions (ΔH_{pp} of ca. 265 G) and that due to unpaired spins of the polymer backbone (ΔH_{pp} of ca. 21 G). Potential dependencies of these two signals as well as potential-induced conductivity variations are consistent with the postulate of two independent conductivity processes occurring via mixed-valence Cu(II)/Cu(I) moieties and through bipolaron-type charge carriers. For comparison, ESR and conductivity responses to the working electrode potential change were measured for **poly[1]** and **poly[2]**, i.e., thienylene unit-based polymers constituting wiring backbones in the polymetallorotaxanes studied. The comparison of these results clearly indicates that metal-complexed rings constitute barriers which lower charge-carrier mobility. As a result, **poly[1]** and **poly[2]** exhibit significantly higher electronic conductivity (σ of ca. 5×10^{-3} S/cm) as compared to the conductivity of the corresponding polymetallorotaxanes (σ of ca. 2×10^{-5} S/cm).

Introduction

In the past few years, significant research efforts have been undertaken to prepare conjugated polymers–transition metal complexes hybrid systems.¹ In these materials the transition metal complex is either linked to the conjugated backbone via an alkali spacer or coordinated directly to the conjugated polymer. The latter are frequently termed “conjugated metallopolymers”. An obvious result of this direct coordination is an enhancement of the electronic interactions between the electroactive metal centers and the electroactive polymer backbone.^{1b} There are several consequences of these interactions, for example, electrical transport enhancement,² electrocatalytic activity,³ photorefringence properties,⁴ photoconductivity,⁵ several new electronic, photophysical and electrochemical properties,⁶ and electrocatalytic properties.⁷

Among the macromolecular systems described above, polymetallorotaxanes represent a subclass of metallopolymers in which metal is incorporated into a pseudorotaxane environment. Initial research in this area involved the preparation of a system containing bisphenanthroline-based metallorotaxane as the pending group in conjugated polypyrrole.⁸ Then new architectures have been proposed in which bisphenanthroline-based metallorotaxane units were mutually connected by oligothiophene molecular wires.⁹ These new assemblies can be considered as promising materials for molecular electronics¹⁰ and sensors.¹¹

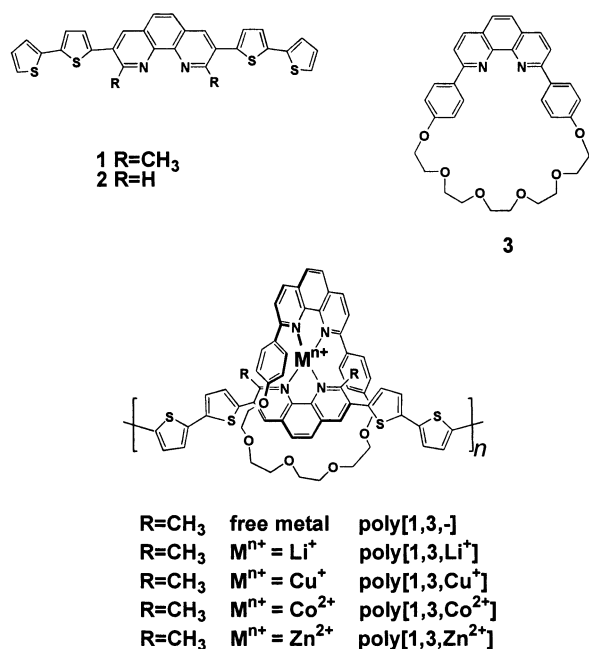
Among systems studied, copper(I) conjugated polymetallorotaxanes have drawn special attention. They have been synthesized using a copper(I)-templated strategy and electropolymerization.⁹ A very similar procedure has previously been used with success by Swager et al.,¹² who connected electropolymerizable oligothiényl derivatives to linear 2,2'-bipyridine. In our recent works, we have developed a specific strategy to connect oligothiényls of various lengths with derivatized U-shaped or linear 1,10-phenanthroline-based ligands,¹³ with the aim of controlling the structure and, by consequence, ensuring better tuning of the electronic coupling between the rotaxane coordinating site and the conjugated wiring backbone. Subtle changes in the coordinating unit dramatically improve the metalation–

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CHART 1: General Formulas of Linear Ligands 1 and 2, Macrocycle 3 and Various Polyrotaxanes.

demetalation properties of these materials. Wiring a 1,10-phenanthroline-type ligand in a linear fashion facilitates metal exchange in the polymetallorotaxanes obtained. Moreover, sterically hindered phenanthroline units improve the stability of complexes formed in a low oxidation state,¹⁴ leading in this manner to the possibility of tuning the electronic properties of a given metallopolymer by simple metal exchange.¹⁵

This paper can be considered, to some extent, as a continuation of our previous work.^{13b} In particular we discuss the electrochemical behavior of linearly wired ligand-based copper(I), cobalt(II), zinc(II), and lithium(I) polymetallorotaxanes, **poly[1,3,Mⁿ⁺]**, obtained by electropolymerization of copper(I) complex (**1,3,Cu**)⁺ i.e., complex with ligands **1** and **3** as schematically depicted in Chart 1. General formulas of all polymetallorotaxanes investigated, together with the list of their abbreviations used in the subsequent text, are also presented in Chart 1. The preparation of polymetallorotaxanes containing metals other than copper can be relatively easily achieved by copper removal from **poly[1,3,Cu⁺]**, followed by recomplexation. This classical procedure was used, for the first time, in nonconjugated organic polymers containing entwined redox-active metal centers.¹⁵

To better elucidate the nature of the redox processes occurring in the present polymetallorotaxanes, we have carried out a comparative investigation of the electrochemical behavior of various **poly[1,3,Mⁿ⁺]**, their metal-free (**poly[1,3,-]**) analogues, and linear metal-free conjugated polymers obtained by electropolymerization of **1** or **2** (Chart 1) and subsequently abbreviated as **poly[1]** and **poly[2]**. Additionally, for **poly[1,3,Cu⁺]**, its demetalated forms **poly[1,3,-]**, **poly[1]**, and **poly[2]**, we have performed joint in-situ cyclic voltammetry–ESR spectroscopy (CV-ESR) and cyclic voltammetry–conductivity experiments. The goal of these investigations is to correlate the redox states and the conducting properties and to establish the nature of charge storage configurations. Both techniques are well suited for this purpose. In particular, the ESR-CV joint experiments enabled us to establish the spin–charge relationship in the electrochemically oxidized polymetallorotaxane and to identify signals originating from both paramagnetic centers, i.e., metal cations and unpaired spins in the polymer backbone.

Experimental Section

Reagents, Chemicals, and Electrochemical Procedures.

Air- and moisture-sensitive reactions were carried out in oven-dried glassware in an argon atmosphere. The ligands 2,9-dimethyl-3,8-bis(2,2'-bithienyl-5-yl)-1,10-phenanthroline (**1**) and 3,8-bis(2,2'-bithienyl-5-yl)-1,10-phenanthroline (**2**) were prepared as described previously,^{13b} and the macrocycle ligand (**3**) was prepared according to a classical procedure.¹⁶ CH₂Cl₂ (Carlo Erba, 99.5%) and CH₃CN (Carlo Erba, 99.8%) were distilled from P₂O₅ or calcium hydride, respectively, and stored in a drybox in an argon atmosphere. The supporting electrolyte *n*-Bu₄NPF₆ was purchased from Fluka (puriss. p.a.) and dried at 100 °C under vacuum. Cu(CH₃CN)₄BF₄ was prepared as previously described.¹⁷ AgNO₃ (Fluka, 99%), LiClO₄ (Fluka, purum > 98%), *n*-Bu₄NCN (Aldrich, 96%), Co(ClO₄)₂(H₂O)₆ (Aldrich, 99%), and Zn(BF₄)₂(H₂O)_x (Aldrich) were used as received. Solutions and polymers were always freshly prepared before experiments. The electrochemical syntheses of films used for in-situ ESR spectroelectrochemical experiments were carried out in a drybox in an argon atmosphere. The electrochemical equipment consisted of a PAR Model 273A with a classical three-electrode arrangement. The electrolyte solutions used for CV and CV-ESR studies were 0.3 mol L⁻¹ *n*-Bu₄NPF₆ in CH₂-Cl₂. A 0.07 cm² platinum electrode was used as the working electrode. The working electrode was carefully polished before use with 1 μm diamond paste and cleaned in an ultrasonic bath with absolute ethanol. Potentials were relative to a 0.01 mol L⁻¹ Ag⁺/Ag reference electrode (*E*_{1/2} (ferrocene) = 0.17 V and *E*_{1/2} (Cu(dap)₂BF₄) = 0.49 V vs this reference for 10⁻³ mol L⁻¹ solutions in the same supporting electrolyte). Electrosynthesis of **poly[1]**, **poly[2]**, and **poly[1,3,Cu⁺]** films were performed from 2 × 10⁻³ mol L⁻¹ monomer solutions by continuous cycling between -0.2 and 1.1 V at *v* = 50 mV/s. The films obtained were then copiously washed with fresh CH₂-Cl₂ before cycling. For demetalation experiments, cyanide solution was prepared from *n*-Bu₄NCN dissolved in CH₃CN and lithium/cyanide solution using stoichiometric amounts of *n*-Bu₄NCN and LiClO₄ dissolved in CH₃CN. The films were dipped for 20 min in one of these solutions and washed with CH₃CN and then with CH₂Cl₂ before cycling. Remetalations were performed by dipping films for 1 h either in a copper(I) solution made of Cu(CH₃CN)₄BF₄ dissolved in CH₃CN or in Co(ClO₄)₂(H₂O)₆ (0.1 mol L⁻¹), or in Zn(BF₄)₂(H₂O)_x (0.1 mol L⁻¹) acetonitrile solutions, followed by copious rinsing with fresh CH₃CN and then CH₂Cl₂.

ESR Spectroelectrochemistry. ESR spectroelectrochemical experiments were carried out with an EMX-X band Bruker spectrometer in a small electrochemical quartz cell with two platinum wires (working and counter electrodes) and an Ag wire used as a pseudo-reference. The Ag electrode was checked against the ferrocene/ferricinium couple (*E*^o = 0.2 V/Ag) after each experiment. Polymer films were grown as described previously by electropolymerization using a charge of 12.8 mC in a conventional three-electrode cell. After rinsing, the film adhering to the electrode was transferred in the ESR spectroelectrochemical cell. Potential cycling was performed in monomer-free electrolyte (CH₂Cl₂/0.3 mol L⁻¹ *n*-Bu₄NPF₆). The redox state of the polymer was monitored by a DC voltage applied to the working electrode over a potential window ranging from -0.2 to +1.6 V vs Ag in increments of 0.1 V. For each experimental point the ESR susceptibility was determined by double integration of the ESR signal and by comparison with the signal of a calibrated reference placed in the same dual cavity.

TABLE 1: Electrochemical Properties of the Various Polymers: $E_{1/2}$ Values (V) Determined by Cyclic Voltammetry^a

Poly[1,3,M ⁿ⁺]	charge of matrix		charge of metal complex		
	$E_{1/2\text{I}}$ (V)	$E_{1/2\text{II}}$ (V)	$E_{1/2}\text{M}^{2+}/\text{M}^+$	$E_{1/2}\text{M}^+/\text{M}^0$	$Q_{\text{matrix}}^c/Q_{\text{M}^{2+}/\text{M}^+}^d$
Cu ²⁺	0.80	1.04	0.52		1.25
Co ²⁺	0.81	1.02	−0.71	−1.37	1.30
Zn ²⁺	0.65	0.88	−1.35	−1.52	2.2
Li ⁺	0.78	0.93			
free metal polyrotaxane	0.6–1.0 ^b	0.6–1.0 ^b			
Poly[1]	0.80	1.10			
Poly[2]	0.69	0.96			

^a $E_{1/2} = (E_{\text{p}}^{\text{ox}} + E_{\text{p}}^{\text{red}})$ in CH₂Cl₂, 0.3 M *n*-Bu₄NPF₆; working electrode: Pt; reference electrode: 0.01 M Ag⁺/Ag ($E_{1/2}$ (ferrocene) = 0.17 V).

^b After demetalation, the two peaks corresponding to the wiring polymer become less defined and give a broad redox wave over the indicated potential region. ^c Q_{matrix} : overall matrix charge. ^d $Q_{\text{M}^{2+}/\text{M}^+}$: charge of M²⁺/M⁺ complexing centers.

In-Situ Four-Probe Resistance Measurements. An array of gold microelectrodes was deposited on a glass substrate using the evaporation technique.¹⁸ Inter-electrode spacing was of 2 μm , and the surface of each microelectrode was 0.66 mm². The deposition of a homogeneous layer of **poly[1,3,Cu]⁺** capable of bridging three adjacent electrodes required 8 mC cm^{−2}. A homemade stabilized power supply was used to connect the two outer electrodes. The electrical resistance was recorded with a BD91 Kipp & Zonen X-Y-Y' recorder, calibrated with a RS components ohmmeter, and the sample thickness of the polymer film in the reduced state was measured using a Tencor profilometer.

Results and Discussion

Electrochemical Properties of Synthesized Polymers. The results of the electrochemical investigations of all polymetallo-rotaxanes **poly[1,3,Mⁿ⁺]** as well as **poly[1]** and **poly[2]**, which can be considered as metal-free conjugated polymers, are summarized in Table 1. For clarity, it is better to start the discussion by the description of the CVs of **poly[1]** and **poly[2]**, which constitute molecular wire elements in the polymetallo-rotaxanes of the **poly[1,3,Mⁿ⁺]** type. Both polymers display, in the anodic potential range, two well-resolved waves, assigned to the two one-electron consecutive doping processes of the molecular wire chain segments consisting of tetrathienyl units. The CV profiles of **poly[1]** and **poly[2]** differ from those recorded for polymers containing 2,2'-bipyridine^{6b,6f,12a} or U-shaped phenanthroline¹⁹ building blocks which, in the same experimental conditions, show two unresolved waves. This marked difference in the electrochemical doping behavior may originate from the differences in the conjugation between the π systems of the chain building blocks. This problem was studied in detail in the case of poly(alkylthiophenes).²⁰ Regio-regular poly(3-alkylthiophenes) whose better conjugation is clearly manifested by a large bathochromic shift of their π – π^* transition bands, as compared to the corresponding bands of their regiorandom analogues, give two clear redox waves. Regiorandom poly(3-alkylthiophenes) give, in turn, one broad redox wave consisting of several unresolved contributions. Using this analogy, one may postulate that the quarterthienyl unit in the linear **poly[1]** and **poly[2]** polymers is better conjugated than in previously reported systems. It should be noted here that this statement, based on the analogy with poly(thiophene) derivatives, is purely hypothetical and several other effects can contribute to this splitting of the redox waves, such as intra- and interchain electronic interactions and others as well as the sequence of the tetrathienophene units' oxidation. One should also note an anodic shift of about 100 mV of the redox waves of **poly[1]** as compared to the corresponding waves in **poly[2]**. The inductive effect of the methyl substituent should result in

the opposite shift. We therefore postulate that the observed behavior originates from substituent-induced chain conformational changes such as, for example, torsions which are not favorable for the conjugation and make the oxidation of the π -system more difficult.²¹

The CVs of polymetallo-rotaxanes **poly[1,3,Mⁿ⁺]** exhibit electrochemical responses characteristic of both the conjugated polymer backbone and the complexed metals, except in the case of Li(I). This is not unexpected since lithium reduction requires highly reducing potentials which are not compatible with the limited cathodic window of CH₂Cl₂²² (see Table 1). In particular, the presence of cobalt or zinc metal centers is evidenced by the potential values of two successive metal or ligand localized one-electron transfers, in agreement with the redox potential values reported previously for the corresponding entwined homoleptic¹⁵ or heteroleptic⁸ complexes covalently linked to polypyrrole. In addition, a significant anodic shift (0.1 V) of the half-potential value of the formal redox states M(II)/M(I) in the case of the copper and cobalt polymetallo-rotaxanes has been observed as compared to the polypyrrole-based systems.^{13b}

The electrochemical responses corresponding to the conjugated backbone of the polymetallo-rotaxanes consist of two waves, in agreement with the electrochemical behavior of end-capped tetrathienylenes.²³ It should be noted here that two well-resolved waves are obtained only if the coordinated metal is present. Demetalation of all the polymetallo-rotaxanes studied results in a broad and poorly defined CV response. The origin of this different behavior of the demetalated polymer is not clear at the present time. It may be postulated that the removal of the complexing metal induces some conformational disorder in the wiring polymer, which in turn leads to a distribution of the oxidation potentials and, by consequence, to a merge of two distinct oxidation waves into one poorly defined peak. Thus, the presence of two distinct waves in Li polymetallo-rotaxane may indicate lithium coordination to the bis(phenanthroline) unit.^{13a} Interestingly, the corresponding redox waves of **poly[1,3,Zn²⁺]** are lesser resolved than those recorded for Cu(I) and Co(II) polymetallo-rotaxanes and significantly shifted toward cathodic potentials. In fact, they resemble more the electrochemical behavior of demetalated polymetallo-rotaxanes, i.e., **poly[1,3,-]**, indicating a rather small influence of the coordinating metal center on the conjugated molecular wire. This behavior is somehow similar to that reported for various metalloporphyrins, where a clear correlation between the $E_{1/2}$ values corresponding to the oxidation of the ligand and the coordinating metal electronegativity has been established for the M(II) series.²⁴

For polymetallo-rotaxanes with a metal redox active, i.e., all the present systems but the lithium one, the electrochemical response of metal centers can be used as a probe for the

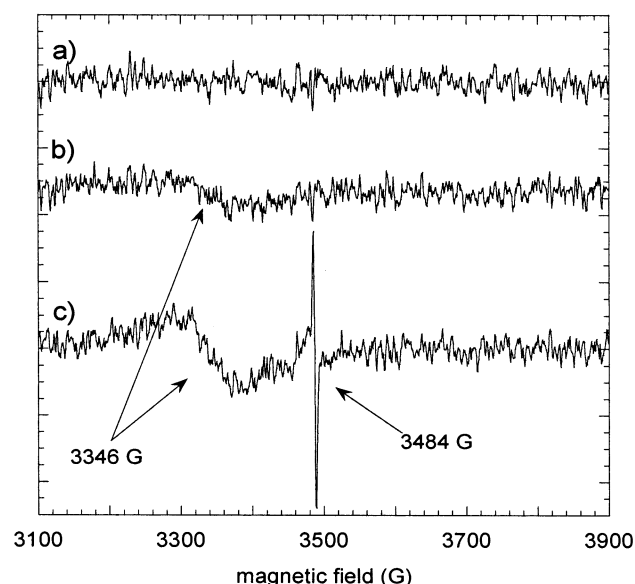


Figure 1. ESR spectra for different values of the applied potential (Ag^+/Ag reference): (a) 0.2 V, (b) 0.45 V, (c) 1.1 V.

estimation of the redox activity of the wiring conjugated backbone. The ratio of Coulombic charge $Q_{\text{matrix}}/Q_{\text{M}^{2+}/\text{M}^+}$ (Table 1) (where Q_{matrix} corresponds to the charge associated with the oxidation of the polymer molecular wire, whereas $Q_{\text{M}^{2+}/\text{M}^+}$ is the charge needed to oxidize the complexed metal) is, in this case, a convenient parameter to characterize this activity. If we assume that two-step oxidation of the 2,5-thienylene tetramer unit requires the abstraction of two electrons and the oxidation of the metal involves the removal of one electron, the $Q_{\text{matrix}}/Q_{\text{M}^{2+}/\text{M}^+}$ ratio should be equal to 2. In reality for strongly coordinated metals such as copper or cobalt, this ratio is significantly lower than 2 (Table 1). This observation seems to indicate that not all 2,5-thienylene segments are fully oxidized. Alternatively one may suggest that the number of metal cations in the coordination complex is higher than the number of bis-phenanthroline cavities. This is of course impossible. For zinc polymetallorotaxane, the $Q_{\text{matrix}}/Q_{\text{M}^{2+}/\text{M}^+}$ ratio is significantly higher than 2. Since in all three cases of complexes studied (zinc, cobalt, copper), the value of Q_{matrix} was essentially the same, a higher value of $Q_{\text{matrix}}/Q_{\text{M}^{2+}/\text{M}^+}$ found for zinc polymetallorotaxane reflects lower zinc complex stability as compared to cobalt and copper ones.²⁵

It should be added at the end of this section that, in Table 1, formal oxidation states are attributed to zinc atoms. In reality, the redox process involves the phenanthroline ligand whose ability to undergo the reduction process is enhanced by the presence of a coordinating metal.

In-Situ ESR-CV Spectroelectrochemical Studies. The in-situ ESR experiments were carried out only for **poly[1,3,Cu⁺]**. Representative ESR spectra, recorded at different potential values during the anodic scan, are presented in Figure 1. Two signals at different g are expected for the oxidized state of polyrotaxane studied: a signal at lower field associated with the oxidation of copper to the paramagnetic Cu(II) cation and a signal at higher field originating from the presence of a radical cation in the backbone of the doped (oxidized) polymer. At $E = 0.2$ V, no ESR signal is detected. At this potential, the complexed metal is in its reduced diamagnetic state similarly to the polymer backbone. Thus the absence of any ESR signal at this potential is consistent with the expected reduced (undoped) state.

An increase of the potential to $E = 0.45$ V results in the appearance of a broad (ΔH_{pp} of about 265 G) and weak ESR signal attributable to the presence of a Cu(II) paramagnetic center (Figure 1b). The measured ESR parameters are similar to those reported previously for a Cu(II) catenate.²⁶ At $E = 1.1$ V, the oxidation of the conjugated polymer backbone takes place, which is manifested by the appearance of a relatively sharp ($\Delta H_{\text{pp}} = 21$ G) Lorentzian signal in addition to the broad signal originating from Cu(II) (Figure 1c). The ESR parameters of this signal are consistent with the formation of thienylene radical cations (polarons) created upon the electrochemical oxidation. It should be, however, pointed out that the halfwidth of this signal is much higher than typically registered for doped conducting polymers such as polyaniline, polyacetylene, and others which typically show lines of ΔH_{pp} inferior to 2 G.²⁷ Since the narrowing of ΔH_{pp} in conducting polymers is associated with spin-carrying charge mobility, the increase in the value of this parameter in **poly[1,3,Cu⁺]** reflects lower charge mobility and, consequently, lower conductivity in polymetallorotaxanes as compared to classical conducting polymers. This was confirmed by in-situ conductivity measurements (vide infra).

Figure 2a shows the potential dependence of the two ESR signal intensity registered in the potential range from +0.2 to +1.2 V. In this experiment, the oxidation scan was run first and then followed by the reduction scan in the reverse direction. Above $E = 0.4$ V, the Cu(II) spin density reaches an average plateau value indicating that no spin coupling occurs between the neighboring copper centers. However, in addition to this plateau, obtained in the oxidation scan, three local maxima in spin density are clearly observed at 0.48, 0.78, and 1.1 V, which very well correlate with the redox waves observed in the CV of **poly[1,3,Cu⁺]** (Figure 2b). Interestingly, in the reduction scan, the polymer film gives rise to only two spin density maxima at potential values close to those of the redox waves corresponding to the reduction of copper and to the first redox wave of the polymer reduction. Surprisingly, the matrix spin density is very low and reaches only ca. 5% of the copper(II) spin density, whereas both oxidizable components of **poly[1,3,-Cu⁺]** show comparable electroactivity (see Table 1). In the simplest interpretation, such behavior can be regarded as a clear manifestation of the recombination of initially formed radical cations (polarons) to spinless dications (bipolarons). This is not unexpected, since bipolarons are the dominant charge-storage configurations in essentially all thienylene-based conducting polymers.²⁸ The onset of the spin appearance can be correlated with the onset of the first oxidation wave of the polymer oxidation (Figure 2). However, contrary to the case of copper spin response, the spin response of the polymer is smooth and monotonic and does not follow the current peaks recorded in the CV experiment. This underlines the efficiency of the polaron recombination process.

In an attempt to verify whether the electrochemical spin response of the polymer depends on the presence of the metal center, we have performed a joint ESR-CV experiment of copper polymetallorotaxane after its demetalation. The removal of Cu(I) centers has been carried out using cyanide as the complexing agent for the metal and Li^+ ions as a scaffolding agent for preventing irreversible collapse of the structure.⁹ As expected, the ESR signal of Cu(II) disappears after the demetalation, whereas the ESR signal from the oxidation of the polymer does not undergo significant modification (not shown). Thus, the preferential bipolaron formation in the polymer matrix occurs independently of the presence (or absence) of the metal.

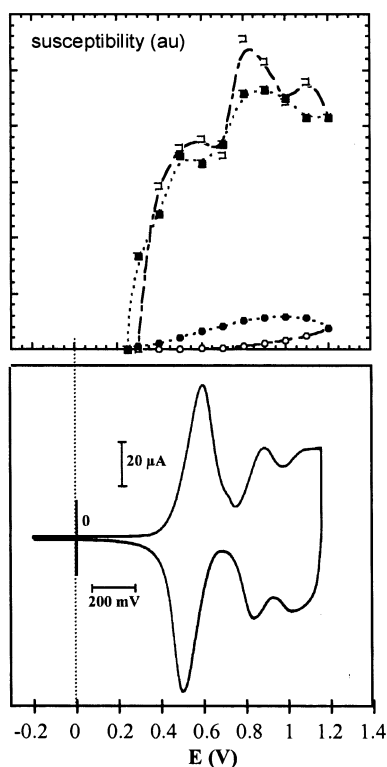


Figure 2. Top: ESR susceptibility versus electrochemical potential on **poly[1,3,Cu⁺]** film (arbitrary units): Integrated surface area of (a) signal centered at 3346 G: (\square) during the oxidation scan, (\blacksquare) during the reduction scan, (b) signal centered at 3484 G: (\circ) during the oxidation scan, (\bullet) during the reduction scan. Bottom: Cyclic voltammetry ($\nu = 100$ mV s⁻¹) in CH₂Cl₂/*n*-Bu₄NPF₆ (0.3 mol L⁻¹), Pt electrode, Ag⁺/Ag reference, of a freshly prepared **poly[1,3,Cu⁺]** film.

To summarize, the above-discussed results are consistent with a model of the coordination polymer in which spins of the paramagnetic metal cations do not couple, whereas the spins created upon the oxidation of wiring conjugated units quickly recombine to give bipolarons. Moreover, the interaction between the spins of Cu(II) and those of the wiring polymer is extremely weak since demetalation of the polymer does not influence significantly the spin response of the thienylene building unit.

Finally, it should be stated that the coulometric data, combined with ESR spectroelectrochemical data provide important information concerning the sequence of the electrochemical oxidation of tetrathienylene units. The fact that one-half of the charge is consumed in the first polymer oxidation wave with no concomitant creation of spins implies that one-half of tetrathienylene units are being oxidized to spinless dications (bipolarons), whereas the other half remain intact. Thus, the oxidized and non-oxidized segments alternate. The second oxidation wave results in the oxidation of the remaining neutral tetrathienylene units. An alternative picture would imply the oxidation of all tetrathienylene units to radical cations (polarons) during the first oxidation process, followed by their oxidation to spinless dications (bipolarons) at the potentials of the second oxidation wave. In view of the ESR spectroelectrochemical data, the latter picture must be excluded. This behavior is reminiscent of the alternating charge segment recently reported for an entirely conjugated polyTTF.²⁹

In-Situ Conductivity Studies. For **poly[1,3,Cu⁺]**, in addition to the electrochemical spin response studies, we have carried out simultaneous cyclic voltammetry–conductivity studies in which electrical resistance of the polymer was measured in situ as a function of the working electrode potential. These measure-

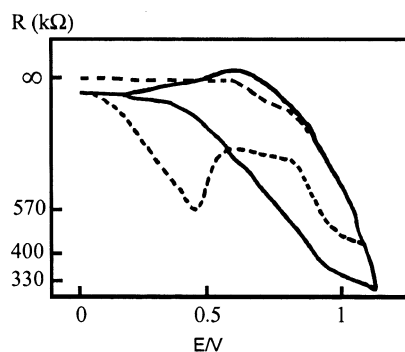


Figure 3. In-situ resistance measurements in CH₂Cl₂/*n*-Bu₄NPF₆ (0.3 mol L⁻¹) ($\nu = 5$ mV s⁻¹) using six-band platinum microelectrodes (2 μ m spacing) on (a) a freshly prepared **poly[1,3,Cu⁺]** film (overall electrosynthesis 8 mC) (dashed line), (b) after dipping for 20 min in CH₃CN/(*n*-Bu₄NCN + LiClO₄) (0.1 mol L⁻¹) (solid line).

ments have been performed with the goal of identifying the redox states responsible for the electronic conductivity enhancement. The results are shown in Figure 3. **Poly[1,3,Cu⁺]** shows two bell-shaped potential windows of enhanced conductivity, which is typical of the redox doping-induced conduction.³⁰ This bimodal conductivity profile is consistent with the segmented nature of the polymer backbone and has been observed previously in bipyridine- and salicylene-based metallopolymer.³¹ The resistance reaches two minima (Figure 3). The first minimum is centered at the Cu(II)/Cu(I) formal potential, and the corresponding conductivity is 2.3×10^{-5} Ω^{-1} cm⁻¹. Upon further increase of the potential, the resistance of the polymer increases and reaches a well-defined plateau at $E = 0.7$ V, i.e., at the potential which corresponds to the complete oxidation of Cu(I) to Cu(II). Evidently, mixed-valence of copper is necessary to promote charge-carriers hopping in the polymer studied, since the maximum of conductivity is observed at the potential of the first redox peak where the Cu(I)/Cu(II) ratio is roughly 1, as determined from coulometric measurements. At this potential range, the polymer backbone remains still undoped. It is rather surprising that this conductivity increase is observed only in the oxidation cycle and in the reduction cycle no such phenomenon is registered. One of the possible explanations is partial oxidative degradation of the system at the potentials close to the reverse potential (> 1 V). Further studies are required to properly address this problem.

The second potential window for enhanced conductivity is observed at potentials corresponding to the second redox wave of the polymer oxidation. At the potential of minimum resistance the conductivity reaches the value of 2.9×10^{-5} Ω^{-1} cm⁻¹. Upon further potential increase, the resistance of the polymer rises while conductivity drops. This is an obvious effect of the over-oxidation of the polymer (not shown). The correlation of the spin response with the conductivity changes clearly indicates that the dominant charge carriers are spinless bipolarons. The high value of ΔH_{pp} measured for spins created upon electrochemical doping of the polymer, reflecting low mobility of charge carriers, is consistent with a relatively low value of the maximum conductivity measured for **Poly[1,3,Cu⁺]**, significantly lower than reported for classical conjugated polymers.³²

After removal of the Cu(I) centers, carried out in exactly the same manner as in the case of ESR studies (vide supra), the potential window of enhanced conductivity corresponding to the potential values of copper redox activity disappears (Figure 3). Thus the redox processes responsible for the conductivity enhancement are, in this case, entirely associated with the oxidative doping of the polymer. Contrary to the case of **poly-**

[1,3,Cu⁺], in **poly**[1,3,-] both redox processes characteristic of the polymer contribute to the enhancement of conductivity, since the drop in the sample resistance starts at ca. 0.6 V, i.e., at the potential of the onset of the first redox peak corresponding to the oxidation of the polymer chain. This resistance drop is essentially monotonic in the potential window of the two-polymer chain redox couple until the overoxidation potential is reached (not shown here). The resulting conductivity of fully doped **poly**[1,3,-] is only slightly higher than that measured for its metalated form, i.e., **poly**[1,3,Cu⁺].

A rather low conductivity measured for fully doped **poly**[1,3,Cu⁺] and **poly**[1,3,-] is consistent with the ESR studies. A high value of ΔH_{pp} (21 G) is observed in both cases for radical cations (polarons) created upon the oxidation of the wiring polymer. One must, however, be aware of the fact that the ESR line broadening may originate not only from low mobility of the charge carriers but also from interactions of polarons with paramagnetic impurities (in this case, Cu(II)).³³ It seems that in, our case, Cu(II) cations do not contribute to the broadening of the polaron ESR line since, after demetalation, its width remains essentially the same.

The results presented above indicate that the coordinating metal influences the conductivity only in the intermediate oxidation state of **poly**[1,3,Cu⁺], whereas, for the fully doped polymer, its influence is much smaller, as evidenced by similar conductivities of **poly**[1,3,Cu⁺] and **poly**[1,3,-]. We were also tempted to verify the influence of the presence of the complexing rotaxane ring on the conductivity of the doped polymer. For this reason, we have carried out in-situ conductivity—CV joint studies—for **poly**[2], which in fact is an analogue of the wiring polymer in polymetallorotaxanes studied.

Poly[2] exhibits a resistance vs potential profile similar to that registered for **poly**[1,3,-] and to the conductivity profile previously reported for U-shaped 2,9-bis(oligo-thienyl)-1,10-phenanthroline polymers.^{19b} Thus, as in the previous case, the sample resistance starts to drop at the potential of the beginning of the first redox process and continues to decrease monotonically through the second oxidation process. However, linear **poly**[2] is much more conductive in the fully doped state, i.e., at the potential of 1.1 V, giving a conductivity value of $5 \times 10^{-3} \text{ S cm}^{-1}$ at 1.1 V in *n*-Bu₄NPF₆/CH₂Cl₂ and $1.5 \times 10^{-2} \text{ S cm}^{-1}$ in *n*-Bu₄NPF₆/CH₃CN. Similar results were obtained for **poly**[1]. Evidently, both coordinated metals and threaded rings in polymetallorotaxanes constitute barriers, decreasing charge carriers mobility. Presumably, this is due to the presence of insulating threaded macrocycles which make the interchain transfer of carriers more difficult.³⁴

Conclusion

To summarize, we have carried out electrochemical studies of polymetallorotaxanes **poly**[1,3,Mⁿ⁺], their demetalated form **poly**[1,3,-], and polymers constituting the wiring backbone **poly**[1] and **poly**[2]. These investigations were completed by ESR spectroelectrochemical measurements and in situ conductivity vs electrode potential studies. The results obtained enable us to formulate the following conclusions. The electrochemical responses of the components of the polymetallorotaxanes studied are well separated, which indicates significant charge localization on both the rotaxane-coordinating macrocycle and the connecting tetrathienylene units. As seen from the in-situ conductivity measurements, the coordinated metal contributes to the overall conductivity of the system via mixed valence state, whereas the connecting conjugated polymer contributes via a classical polaron/bipolaron mechanism. This opens up the

possibility of tuning the electrical properties by metal exchange. The comparison of the conductivity and ESR response of **poly**[1,3,Cu⁺], **poly**[1,3,-], **poly**[1], and **poly**[2] indicates that coordinating macrocyclic sites constitute barriers decreasing charge-carrier mobility.

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