Conducting-Polymer Electrochemical Switching as an Easy Means for Control of the Molecular Properties of Grafted Transition Metal Complexes

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Dedicated to Professor Olivier Kahn

Abstract: Copper(II) 3′,4′-bis(*N*,*N*′-oxamato)terthiophene has been synthesized and electropolymerized. The copper(II)-complex centers are not affected by the polymerization process, which involves coupling between C_α carbon atoms of the terthiophene units and leads to a new conjugated polymer consisting of polythiophene chains bearing bis(oxamato) – Cu^{II} groups regioregularly grafted onto the polymer backbone. The polymer is stable with respect to polythiophene electroactivity, and no demetallation or modification of the Cu oxidation state occurs over a large potential range. In this material, the two moieties exhibit direct electronic interaction, which makes it possible to use the conductive polymer backbone as a molecular wire or a nanocontact capable of inputting to the bis(oxamato) – Cu^{II} groups through the polythiophene-switching reaction. FTIR, XPS, and XAS spectroscopies have been used to study the effect of the state of the conducting polymer upon the properties of the copper(II) center (electron density, ligand field strength, size of cavity, force constants of some bonds). These properties can be controlled to some extent by the potential applied to this device. From the point of view of the copper(II) center, this effect is similar to the grafting of substituents with various electronic properties.

Keywords: conducting materials · electrochemical switching · EXAFS spectroscopy · molecular electronics · polythiophene

Introduction

In the field of materials science, conducting polymers have attracted great interest for both fundamental and potential applications. The grafting of a transition metal complex onto a conductive polymer backbone has been widely used in order to add a specific function to the material.[1] When the metal complex is separated from the backbone by a saturated spacer there is no direct electronic interaction between the two parts and any interaction is mainly steric. In contrast, when the polymer is functionalized through a conjugated spacer the complex is in direct electronic communication with the π-conjugated backbone, and the interaction between the two subunits of the material modifies their properties.[2–10]

Several studies devoted to such materials have focused on the influence of conjugated grafted groups upon the conductive backbone. Ruthenium has been used to enhance the photosensitivity of the parent organic polymer.[2] Poly(phenylenevinylene) that incorporates 2,2′-bipyridine units has been studied, and conformational changes of the backbone upon coordination of metal ions demonstrated.[3] Applications of this material in capting devices were proposed. Electrochromic materials, with colors unique to each metal, have been reported.[4]

Other studies have focused upon the use of the conjugated polymer backbone to promote electron transfer between metal centers. Yamamoto et al. reported the synthesis of poly(bipyridine) (poly(bpy)) and post-metallation with Ru^{II}, Ni^{II}, and Cu^{I}.[5] They showed that even though post-metallation is somewhat inefficient, the conductivity of poly(bpy)Ru is several orders of magnitude higher than that of poly(bpy). Furthermore, they interpreted electrochemical broadening of the Ru^{III}/Ru^{II} redox peak as evidence for electronic interactions between ruthenium through the poly(bpy) backbone. However, no such effect was seen in later

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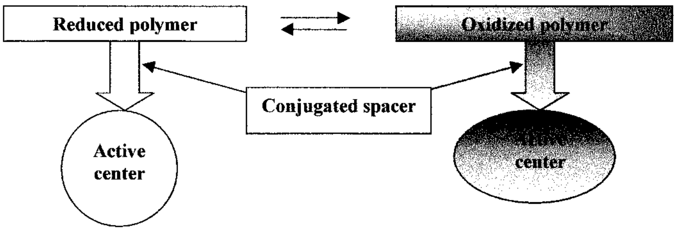
studies dealing with the same type of structure.[6, 7] Zotti et al. compared ferrocene-substituted polythiophenes in which the ferrocene units are separated from the conductive backbone by a saturated or a conjugated spacer.[8] They found that the hopping rate between ferrocenes is increased by conjugation. Pickup et al. demonstrated that electron transfer between the metal center in $Ru(bpy)_2$poly(benzimidazole) is assisted by the conjugated polymer backbone.[9] Swager et al. studied polymetallorotaxanes and demonstrated that the matching of the polymer and Cu^{II}/Cu^{I} redox potentials in one of their structures resulted in a Cu^{II}/Cu^{I} contribution to conductivity.[10] Vidal et al. connected several conducting chains around a metal center in an intertwined structure through self-assembling properties by using oligothiophene-substituted phenanthroline and copper(I).[11] Even though they ran into severe demetallation problems in some of their structures, they showed that copper(I) enhances the macroscopic conductivity by one order of magnitude in one of their materials in which the redox process of the metal and that of the oligothiophene are close in potential.

The influence of the conductive backbone upon the properties of conjugated grafted groups has received little attention[12–17] and it is only recently that Wrighton et al.[12] demonstrated for poly[5,5′-(2-thienyl)-2,2′-bithiazole] a frequency dependence of a polymer-coordinated functional group (a metal carbonyl) upon the potential applied to the material. More recently, we have shown that the electron density of a phenyl group can be modulated in poly(*N*-phenylpyrrole), whereas no such effect is seen with poly(*N*-benzylpyrrole),[13] and we demonstrated that the π-electron density and the size of the complexing active center in poly[3′,4′-bis(*N*,*N*′-ethyloxamyl)terthiophene] depend on the applied potential.[14] Li et al.[15] showed that the pK_a of poly(3-thiophene acetic acid) can vary by pH ± 3. Finally, Higgins et al. have discussed the use of conductive polymers in order to generate redox-switchable hemilabile ligands.[16] In all these studies, the nature of the grafted groups (redox state, chemical composition, etc.) is unchanged, but their properties are modified by the switching reaction of the polymer backbone. This reaction allows macroscopic control (through the applied potential) of the π-electron density of the backbone, and these modifications are transmitted to the grafted active center through conjugation, as depicted in Scheme 1.[17] From the active center point of view, the effects are similar to grafting substituents with various electronic effects.[13]

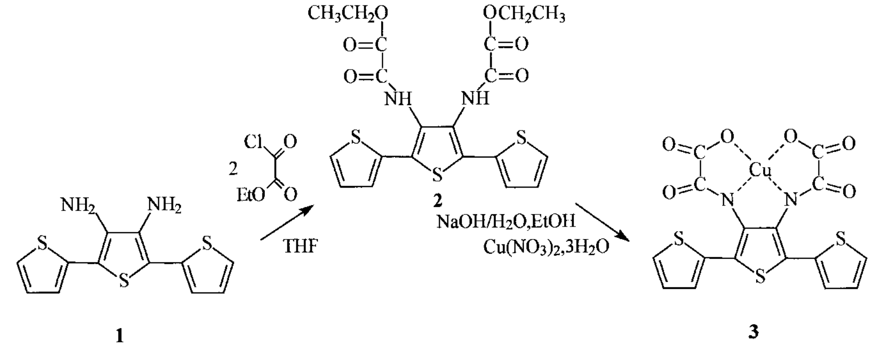
This strategy fits in the growing field of electrochemical switching,[18] which is widely applied in supramolecular chemistry as an easy means of controlling the molecular architecture of redox-active supramolecular systems. It is applied in this paper to the field of transition metal complexes. The properties of such a molecular structure are mainly controlled by the ligand field, the strength of which varies with the σ-donating, π-donating, and π-withdrawing characters of the ligands. Herein, we show that using conductive polymers as nanowires to connect transition metal complexes makes it possible to control the ligand π-electron character and to tune some properties of the complex by a physical macroscopic command (i.e., the potential applied to the material) instead of chemical substitution.



Scheme 1. Schematic representation of a conducting polymer operating as a "switchable electrochemical connector" for the control of the molecular properties of grafted transition metal complexes (active site).

Results and Discussion

The monomers used in this study are 3′,4′-bis(*N*,*N*′-ethyloxamyl)terthiophene (EOAT) and the corresponding copper(II) 3′,4′-bis(*N*,*N*′-oxamato)terthiophene complex (OAT-Cu). This consists of an electropolymerizable terthiophene group and a complexing cavity or a complex functional group directly grafted onto the central thiophene unit. Electronic interaction between the chelating unit and the polymeric chain is thus assured, whereas steric effects induced by the chelating cavity are minimized. These molecules are obtained by a multistep synthesis (Scheme 2), the various intermediates of which are substituted thiophene derivatives. Among transition metals, copper(II) was chosen in order to separate the polymer backbone redox properties from that of the coordinated metal center; this which makes it possible to switch the polythiophene moieties of the material without changing the redox state of the copper. Furthermore, polymerization of the copper(II) complexes has been preferred to post-complexation of the parent organic polymer in order to avoid partial metallation.[5]



Scheme 2. Synthetic route to the OAT-Cu complex.

Electrochemical behavior of the monomer and polymer characterization

An irreversible oxidation peak at 1.1 V is observed during the anodic sweep of a solution of OAT-Cu (10^{-3} M in H_2O with 0.1 M $LiClO_4$, 50 mV s^{-1}). Organic monomer EOAT presents a similar oxidation peak that was attributed to terthiophene oxidation yielding a very reactive radical cation.[14] The presence of a copper ion within the chelating cavity does not significantly affect the oxidation potential of the terthiophene units, in agreement with reference [19].

During successive cycles between 0 and 1.0 V of a 10^{-2} M solution of OAT-Cu (in H_2O with 0.1 M $LiClO_4$), growth of an electrochemical response in the 0–0.8 V range is observed. This indicates that an electroactive material is deposited on the electrode. This film is only slightly electroactive in water; nevertheless, film growth remains regular, and the thickness of the layers deposited can be controlled by the number of cycles used during electrosynthesis.

Electroactivity: The electrochemical behavior of the film was studied in acetonitrile that contained 0.1 M $LiClO_4$. During the first cycles, the electroactivity is very weak but grows quickly until stabilization occurs and well-defined reversible peaks centered at 0.55 V are observed. The low electroactivity in an aqueous medium can be explained by the hydrophobic character of the polythiophene chains, and its increase in acetonitrile by the progressive incorporation of this solvent in the polymer. The current peak intensity varies linearly with the scan rate, indicating that the electrochemical response is not diffusion-limited.

UV-visible spectroscopy: The λ_{max} (363 nm) for OAT-Cu is 12 nm higher than that of EOAT (351 nm); this shows that Cu^{II} complexation induces an increase in the monomer conjugation length. In contrast, poly(OAT-Cu), synthesized in the potentiodynamic mode on a semitransparent ITO electrode and reduced at 0 V for 20 minutes, has an intense absorption band at 443 nm, that is, 44 nm below that of reduced poly(EOAT).[14] The poly(OAT-Cu) conjugation length is, therefore, lower than that of poly(EOAT), suggesting that the polymer chains are shorter in the former. Nevertheless, the poly(OAT-Cu) λ_{max} remains significantly greater than that of polyterthiophene or sexithiophene, which indicates that the electropolymerization process does not stop after radical-cation dimerization. Cu^{II} $d \rightarrow d$ transitions are not observed because of the huge differences in the molar extinction coefficients associated with this band ($\varepsilon \approx 100\,M^{-1}L\,cm^{-1}$) and that of the $\pi \rightarrow \pi^*$ polythiophene backbone ($\varepsilon \approx 10^5\,M^{-1}L\,cm^{-1}$). This prevents the use of this technique to measure the strength of the ligand field.

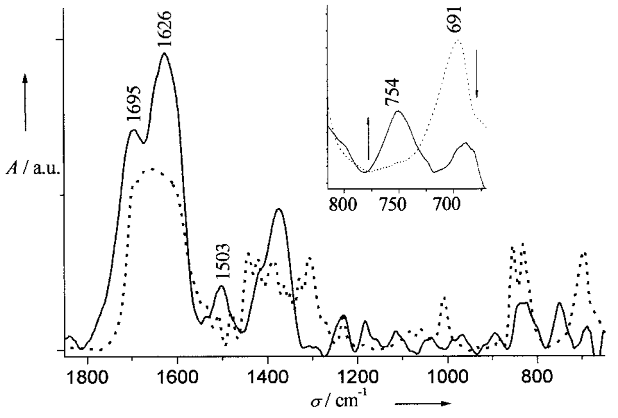


Figure 1. FTIR spectra of the OAT-Cu complex (in KBr) in the transmission mode (dashed line) and poly(OAT-Cu) films deposited on a Pt electrode from aqueous 10^{-1} M $LiClO_4$ and 10^{-2} M OAT-Cu, polarized at 0 V (reduced form), in the reflection mode (solid line). Inset: close-up of the 825–670 cm^{-1} region.

IR spectroscopy: Infrared spectra of poly(OAT-Cu), synthesized in the potentiodynamic mode, have the poly(thiophene) vibration bands[20] and those characteristic of the complexed oxamato-grafted groups.[21, 22] The ratio of the intensities of the 691 and 754 cm^{-1} vibration bands decreases upon polymerization (Figure 1); this indicates that polymerization involves the C_α carbon atoms of the terthiophene units.[20] The complexed oxamato groups are characterized by two intense bands at 1626 and 1695 cm^{-1}, which are associated with the complexed amide and carboxylate C=O stretching, respectively. These two bands are at around 1700 and 1760 cm^{-1} for poly(EOAT)[14]—quite different from those of poly(OAT-Cu). According to several studies,[22] this frequency shift can be associated with Cu^{II} complexation. These two vibration bands are located at similar frequencies in the OAT-Cu monomer (in the form of a single broad band), which suggests that the complexing groups are not affected by polymerization. Moreover, no IR bands at 1700 and 1760 cm^{-1} are observed in poly(OAT-Cu); this indicates that demetallation does not occur during electropolymerization.

X-ray photoelectron spectroscopy (XPS): XPS enabled us to obtain precise information on the film stoichiometry. In particular, the copper/monomer ratio can be measured, and analysis of each signal provides indications about the polymer-doping level and the oxidation state of the copper.

The elemental stoichiometry of poly(OAT-Cu) surface layers is reported in Table 1, and compares well with that of the monomer and with the theoretical ratios calculated for an assumed elemental stoichiometry of $C_{16}CuN_2Na_2O_6S_3$. The good agreement between theoretical and experimental results shows that the oxamatoterthiophene–copper structure is unchanged by electropolymerization. The only difference between the OAT-Cu monomer and poly(OAT-Cu) lies in the Na^+ signal. Indeed, the Na^+/Cu ratio is almost zero in the polymer and reveals counter-ion exchange during polymerization; Na^+ is probably replaced by H^+.

Table 1. Experimental XPS ratios for poly(OAT-Cu) films in the reduced form (polarized at 0 V) compared to theoretical ratios for an empirical formula of $C_{16}CuN_2Na_2O_6S_3$.

	C : N	C : S	C : O	C : Cu	Na : Cu
experimental ratios	7.7	5.4	2.8	16.1	ε
theoretical ratios	8.0	5.3	2.7	16.0	2.0

Moreover, no decomplexation during successive cycles in the electrolytic medium is observed. The film can be polarized at various potentials with no copper(II) loss, indicating that poly(OAT-Cu) is stable with respect to the polymer backbone electroactivity.

The C_{1s} carbon signal has three principal components. The band at 285 eV (C_a, 70% of the total signal) is due to aromatic carbon atoms and the two other bands located at 287.2 (C_b) and 288.8 eV (C_c) are associated with amide (N–C=O) and carboxylate (O–C=O) carbon atoms,[23] respectively (15% each of the total signal). Components C_b and C_c have similar binding energies and percentages of the total signal in the OAT-Cu monomer; this confirms that the chelating cavity is not changed by polymerization. The sulfur signal in reduced poly(OAT-Cu) consists of a single S_{2p}(I) doublet at 163.9 and 165.0 eV. A weaker S_{2p}(II) doublet at 165.4 and 166.4 eV appears in the oxidized polymer. The latter is associated with oxidized sulfur atoms, and makes it possible to determine the doping level by calculating the $I_{S_{2p}(II)}/I_{S_{2p}(total)}$ ratio. A value of 14% for poly(OAT-Cu) is obtained. The XPS Cl_{2p} signal (perchlorate) is seen in the oxidized polymer, but not in the reduced polymer; this indicates that perchlorate is inserted in the film upon oxidation. Furthermore, $I_{Cl_{2p}}/I_{S_{2p}}$ for an oxidized film gives 16%, which is in good agreement with the doping level determined by the sulfur signal, but is significantly lower than that obtained for poly(EOAT).[14]

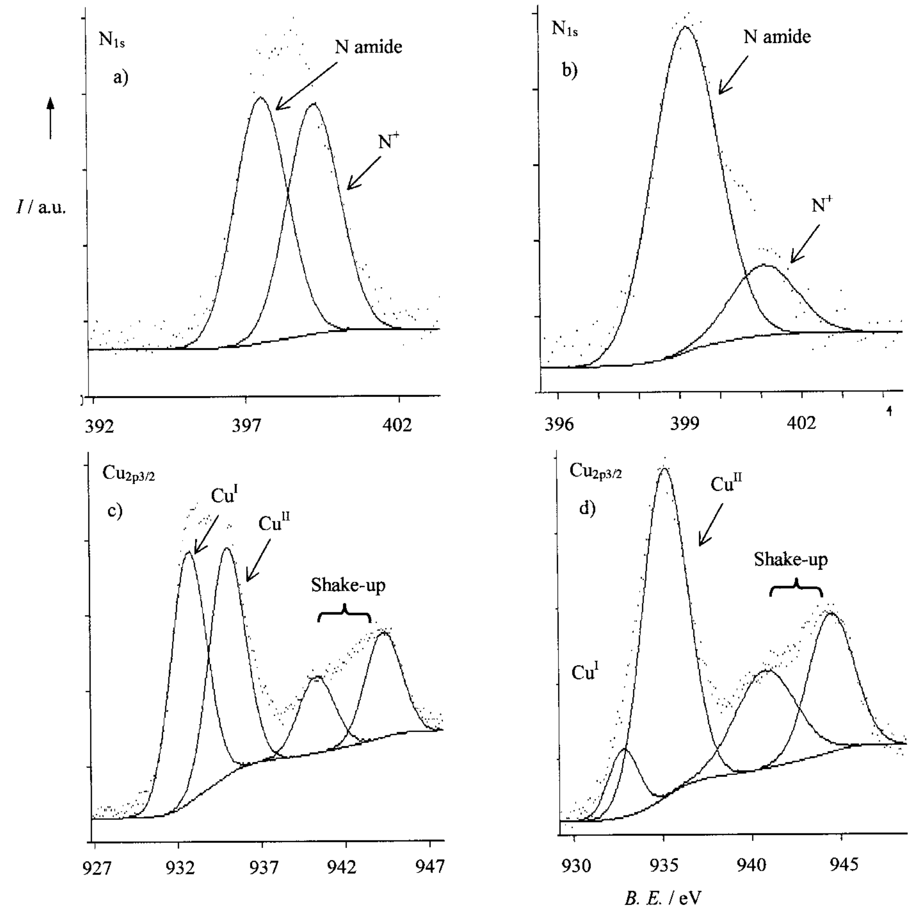


Figure 2. Evolution of the XPS signals for poly(OAT-Cu) in the reduced form as a function of the time of exposure of the sample to the X-ray radiation: a) N_{1s}-core line spectrum recorded after 90 min, b) N_{1s}-core line spectrum recorded immediately, c) $Cu_{2p_{3/2}}$-core line spectrum recorded after 90 min, and d) $Cu_{2p_{3/2}}$-core line spectrum recorded immediately.

Copper and nitrogen XPS signals are not stable over time (Figure 2) because of the photoreduction of copper(II) to copper(I); this occurs in the XPS chamber and has already been widely studied.[24] Indeed, the nitrogen signal exhibits two bands at 399.1 and 400.7 eV associated with neutral and oxidized nitrogen, respectively (Figure 2). The first band is stronger when the nitrogen signal is taken at the beginning of the experiment, whereas the second increases relatively when the nitrogen signal is taken after the other element analysed. A similar evolution is seen in the copper signal, which consists of two bands at 935 (Figure 2) and 955 eV (not shown) accompanied by satellites corresponding to Cu^{II} when this element is analysed before the others. However, bands at 932.7 (Figure 2) and 952.5 eV (not shown) associated with Cu^{I} appear during the accumulation and can become predominant when the copper signal is recorded at the end of the experiment. These variations can be minimized by using a low temperature or choosing the order of accumulation. Under the latter conditions, XPS signals reveal that most of the copper atoms are in the +2 oxidation state and that nitrogen atoms in the reduced polymer (399.1 eV) do not bear positive charges. A further confirmation of the oxidation state of copper is provided by XANES spectroscopy.

X-ray absorption near-edge structure (XANES) spectroscopy: The lack of a single crystal of OAT-Cu and the poor crystallinity of the corresponding polymer means that it is not possible to obtain structural information by X-ray diffraction techniques. Therefore, we studied the XANES and EXAFS (extended X-ray absorption fine structure analysis) spectra of monomer and polymer samples in order to probe the copper oxidation state and, to some extent, the geometry of the copper atom in both structures. Figure 3 displays normalized XANES spectra at the copper *K* edge for the monomer, OAT-Cu (a), and the reduced polymer, poly(OAT-Cu) (b).

Two facts emerge from this figure:

- The two spectra are almost identical with respect to their shape and transition energies.
- Both edges are typical of Cu^{II} complexes with a very weak $1_s \rightarrow 3_d$ pre-edge feature and an absorption edge centered

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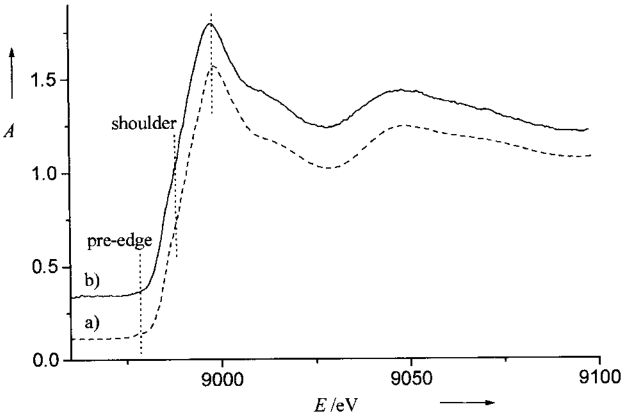


Figure 3. Normalized XANES spectra at copper K edge for: a) OAT-Cu complex in transmission mode (room temperature), and b) poly(OAT-Cu) films in the reduced form (polarized at 0 V) in the total-electron-yield mode (80 K).

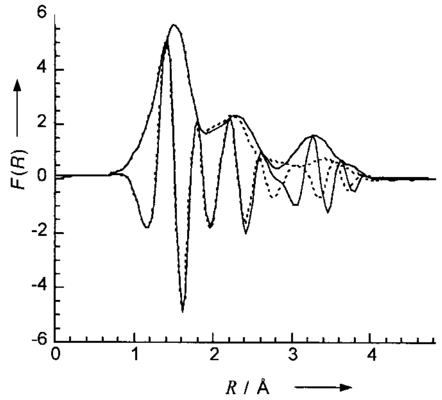


Figure 4. Modulus and imaginary part of the calculated Fourier transforms at copper K edge of [MnCu(opba)(dmso)$_3$].[28] EXAFS signal from single (dashed line) and multiple (solid line) scattering paths.

at ≈8990 eV.[25] Peaks characteristic of Cu^I below 8985 eV are not detected.[25b]

The similarity of the two spectra is the most important feature and clearly shows that copper(II) atoms are in a similar environment in both structures. Furthermore, both spectra exhibit the characteristic shoulder of copper(II) in an elongated tetragonal surrounding on the low-energy side of the edge.[25, 26] The energy gap between this shoulder and the pre-edge is equal to 8.6 eV, a value that gives an estimate for the destabilization of the 4p$_z$ metal orbital, z being the elongation axis.[25c, 26] This value is similar to that found in [MnCu(obbz)]·H_2O (obbz = oxamidobis(benzoato)), that is, 8.6 eV.[27] It has been suggested that, in elongated tetragonal copper(II) complexes, the further the apical site is from the metal ion, the more displaced toward the low energies is this shoulder.[25c] In the present case, the copper(II) ion appears to be in an essentially square-planar D_{4h} environment. The axial ligands, if any, are far from the metal.

Extended X-ray absorption fine structure analysis (EXAFS): Using the crystal structure[28] of [MnCu(opba)(dmso)$_3$] (opba = *o*-phenylenebis(oxamato)) in which the copper(II) complexing cavity is similar to that of OAT, we have calculated the FEFF EXAFS signal of OAT-Cu with either single scattering paths only or the inclusion of multiple scattering contributions. Figure 4 shows the modulus and imaginary part of these calculated Fourier transform spectra. It appears that up to 2.7 Å, multiple scattering may be neglected. Hence, the simulations for all samples have been carried out using the single-scattering model.

Monomer: For the monomer, the signal/noise ratio makes it possible to use an EXAFS domain up to 13 Å^{-1} and to generate the corresponding Fourier transform in k^3 between 2 and 13 Å^{-1}, thanks to the transmission mode. The k space experimental EXAFS signal $k\chi(k)$ versus k at the copper K edge for the monomer, and the corresponding Fourier transforms, are given in Figure 5a and Figure 6a, respectively.

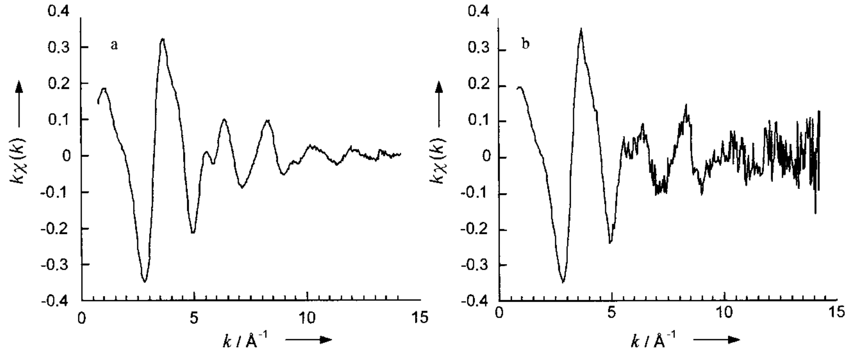


Figure 5. Experimental EXAFS k space spectra: a) OAT-Cu complex in the transmission mode (room temperature), and b) poly(OAT-Cu) films in the reduced form (polarized at 0 V) in the total-electron-yield mode (80 K).

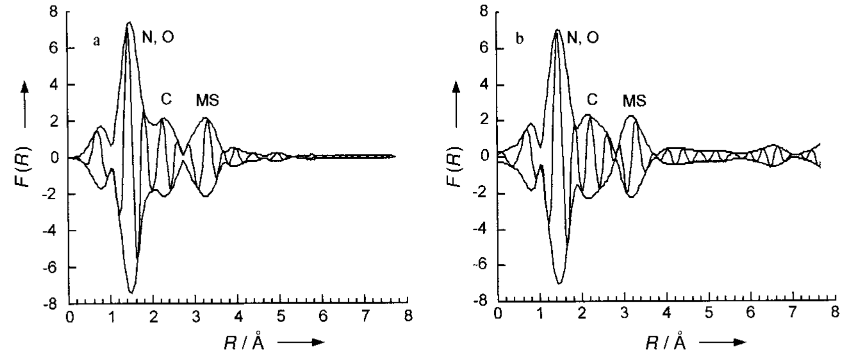


Figure 6. Fourier transforms of the EXAFS signal ($k^3\chi(k)$) at copper K edge: a) OAT-Cu complex in the transmission mode (room temperature), and b) poly(OAT-Cu) films in the reduced form (polarized at 0 V) in the total-electron-yield mode (80 K).

The Fourier transform spectra are composed of three main peaks. According to the structure expected for these materials, it can be proposed that the first peak corresponds to the two nitrogen and the two oxygen atoms from the oxamato ligands, and the second to the six carbon atoms belonging to the oxamato ligands and to the thiophene unit to which the complexing cavity is attached. The third peak, above 2.7 Å, corresponds to multiple scattering contributions, as evidenced by the calculated FEFF EXAFS signal (Figure 4).

The number and postulated nature of neighbors, the neighbor distances, the Debye – Waller factors, and the other parameters resulting from the quantitative analysis (from ab initio amplitude and phase functions $|f_t(k,R_i)|$ and $|\phi_t(k,R_i)|$ calculated by the FEFF7 code[29]) of EXAFS data for the three first coordination spheres of the monomer at the copper K edge are given in Table 2, and the non-phase-shift-corrected Fourier transform modulus of the experimental data (solid line) is compared with that of the refined theoretical signal (dashed line) in Figure 7a.

Table 2. EXAFS results at the Cu K edge for the OAT-Cu complex and poly(OAT-Cu) films polarized at 0 V (reduced form) and 0.9 V (oxidized form).

		N	R [Å]	σ [Å]	Γ [Å^{-2}]	ρ(%)
OAT-Cu complex	Cu–N	2	1.93	0.03	0.9	4
	Cu–O	2	1.98	0.04	0.9	
	Cu–C	6	2.75	0.08	0.9	
reduced poly(OAT-Cu)	Cu–N	2	1.95	0.02	0.8	7
	Cu–O	2	1.99	0.04	0.8	
	Cu–C	6	2.76	0.09	0.8	
oxidized poly(OAT-Cu)	Cu–N	2	1.95	0.03	0.8	4
	Cu–O	2	1.99	0.03	0.8	
	Cu–C	6	2.72	0.09	0.8	

Within the framework of the single-scattering approach, the EXAFS signal is reasonably fitted if one assumes that Cu^{II} ions are surrounded by two nitrogen, two oxygen, and six carbon atoms with average Cu–N, Cu–O, and Cu–C bond lengths of 1.93, 1.98, and 2.75 Å, respectively, with a least-squares fitting parameter of 4 % for OAT-Cu. For comparison, in $[MnCu(pba)(H_2O)_3]\cdot 2H_2O$ (pba = 1,3-propylenebis(oxamato)) the Cu–O and Cu–N bond lengths were found to be 1.990 and 1.933 Å from X-ray diffraction,[30] whereas EXAFS experiments on [MnCu(obbz)] give a mean Cu–(O,N) bond length of between 1.93 and 1.95 Å, depending on the number of aquo ligands in the coordination sphere of the Cu^{II}.[27] Our values for the Cu–(O,N) bond lengths in OAT-Cu and reduced poly(OATCu) are in agreement with these studies,[27, 28, 30] and the use of the calculated FEFF EXAFS phase and amplitude makes it possible to separate Cu–O and Cu–N bond lengths in the fitting procedure, even though the contributions of these atoms are not resolved in the EXAFS Fourier transform.

Reduced polymer: Attempts to grow thick films that can be peeled off the electrode for EXAFS study in the transmission mode failed. Therefore, the polymer samples were studied as thin films in the total-electron-yield mode. As a consequence, the signal-to-noise ratios are much smaller than that of the monomer and the Fourier transforms in k^3 are taken between 2 and 11 Å^{-1}. Figure 5b displays the k space experimental EXAFS spectra $k\chi(k)$ versus k at the copper K edge for the reduced polymer and the corresponding Fourier transforms are given in Figure 6b. The similarity of the experimental $k\chi(k)$ values and the Fourier transform modulus, when compared to that of the monomer, calculated in the same conditions, demonstrates that the local structure of the Cu^{II} ion is almost the same for both compounds. Therefore, there is the same number of nearest neighbors in both compounds. Within the framework of the single-scattering approach, the reduced polymer EXAFS signal is reasonably fitted (see Table 2 and Figure 7b) if one assumes that Cu^{II} ions are surrounded by two nitrogen, two oxygen, and six carbon atoms with average Cu–N, Cu–O, and Cu–C bond lengths of 1.95, 1.99, and 2.76 Å, respectively, with a least-squares fitting parameter of 7 % for OAT-Cu when the ab initio amplitude and phase are used.[29] Distance variations between the monomer and reduced polymer are thus below the intrinsic imprecision of EXAFS.

From the complete analyses of the XANES and EXAFS data, it is now possible to describe the structure of the monomer and the corresponding polymer and to state that the topography of the metal coordination sites is not perturbed by polymerization. Poly(OAT-Cu) consists of polythiophene chains bearing bis(oxamato)–Cu^{II} groups regioregularly grafted onto the polymer backbone, as depicted in Scheme 3. Copper atoms are in a local D_{4h} geometry and in a +2 oxidation state. They are surrounded by two oxygen and two nitrogen atoms as first neighbors, and by

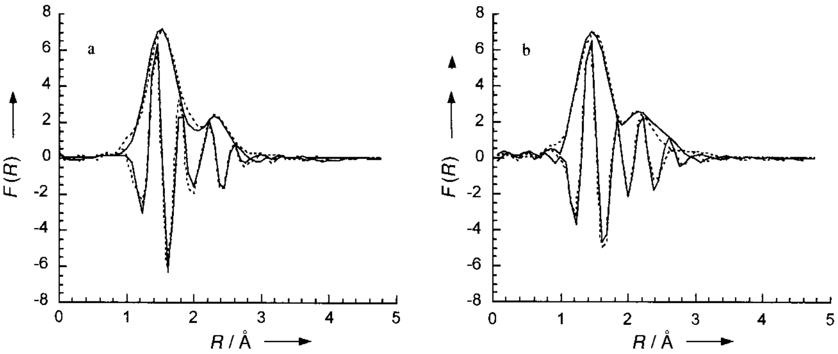
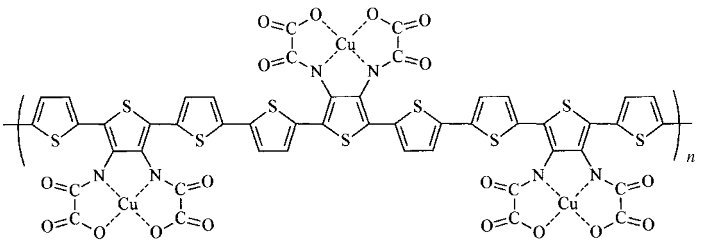


Figure 7. Comparison of non-phase-shift-corrected Fourier transforms of the experimental data (solid line) with that of the refined theoretical signal (dashed line): a) OAT-Cu complex in the transmission mode (room temperature), and b) poly(OAT-Cu) films in the reduced form (polarized at 0 V) in the total-electron-yield mode (80 K). (Note that the differences in amplitudes and widths of the various peaks observed when comparing the spectra of the two samples (monomer and polymer) are the result of differences in temperature used for the experiments: at room temperature, the Debye – Waller factor, which accounts for thermal vibration and static disorder, is greater than at low temperature; this induces a broadening of the whole peak.)



Scheme 3. Representation of poly(OAT-Cu) based on spectroscopic analyses.

six carbon atoms as second neighbors. In this material, it is possible to switch the polythiophene backbone from its reduced (insulating) state to its oxidized (conducting) state. The polymer is stable with respect to polythiophene electroactivity, and no demetallation or modification of the Cu oxidation state occurs over a large potential window.

Controlling the molecular properties of the grafted copper(II) complexes by means of the polythiophene switching reaction

In poly(OAT-Cu), the two moieties of the material have a direct electronic interaction, which makes it possible to use the conductive polymer backbone as a molecular wire or a nanocontact capable of inputting to the bis(oxamato) – Cu^{II} groups through its switching reaction. The following part of this work will be devoted to the study of the influence of the redox state of the polymer backbone upon the electronic properties of the copper(II) and the bis(oxamato)-complexing cavity. In order to do so, the films have been polarized at various potentials and the physicochemical responses of the complex have been studied by means of IR, XPS, XANES, and EXAFS spectroscopies. A similar study on poly(EOAT) showed that the π-electron density and the size of the complexing cavity can be tuned by means of the applied potential.[14]

IR spectroscopy: External reflectance IR spectroscopy was performed on films polarized at various potentials between their conducting and insulating states. Figure 8 presents the IR spectra (2000 – 1400 cm^{-1}) of poly(OAT-Cu) polarized at 0 V and +1.0 V.

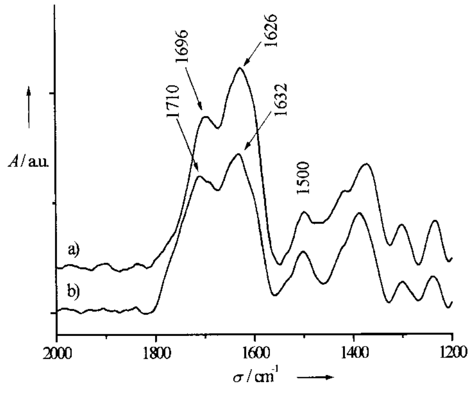


Figure 8. FTIR spectra in the 2000 – 1200 cm^{-1} region of poly(OAT-Cu) films deposited on a Pt electrode from aqueous 10^{-1}M $LiClO_4$ and 10^{-2}M OAT-Cu and polarized in acetonitrile with 10^{-1}M $LiClO_4$ at: a) 0 V (reduced form); b) 0.9 V (oxidized form).

The two bands at 1626 and 1695 cm^{-1}, associated with the complexed amide C=O and carboxylate C=O stretching, respectively, undergo frequency shifts. The former is shifted by 6 cm^{-1} and the latter by as much as 14 cm^{-1}. Both bands shift to higher frequencies when the polymer backbone goes from its reduced to oxidized states, which is expected since positive charges increase its π-electron-withdrawing character. These results are similar to those obtained in the IR analysis of poly(EOAT) in which the amide stretch goes from 1708 to 1723 cm^{-1} when the film is polarized at −0.2 and +1.0 V.[14] However, in poly(EOAT) no frequency shift of the ester C=O stretch with the applied potential occurs. In poly(OAT-Cu), the carboxylate C=O stretch appears to be sensitive to the applied potential, which probably indicates that the copper center makes it possible to propagate the electronic effect upon the carboxylate groups.

These variations suggest that the oxidation state of the polymer backbone is felt by the complexing cavity and the copper(II) atoms, and controls, to some extent, the strength of the force constants associated with the amide C=O and the carboxylate C=O groups.

X-ray photoelectron spectroscopy (XPS): XPS analysis makes it possible to probe the energy levels of core electrons of nitrogen and copper(II) atoms of the complex center. Several poly(OAT-Cu) films polarized at 0 and +1 V were analyzed. The study was performed so as to minimize the copper(II) photoreduction effect, which is responsible for the time dependence of the XPS spectra, as already mentioned. Results were compared with poly(EOAT) in order to distinguish as precisely as possible between evolution of the XPS spectra due to the modification of the polythiophene backbone polarization state and to copper(II) photoreduction.

Nitrogen signal: Figure 9 shows the XPS nitrogen signal of poly(EOAT) polarized at 0 (Figure 9a) and +1 V (Figure 9b). A strong modification of the N_{1s} signal is observed upon oxidation of the polythiophene backbone. The single band in the reduced poly(EOAT), characteristic of amide N–H, splits into two peaks, with one appearing at the high-energy side of the main peak, indicating the presence of positively charged nitrogen (at 401 eV). A similar evolution is seen in poly(OAT-Cu), as depicted in Figure 9c and 9d, even though reduced poly(OAT-Cu) does not show a single band because of competing copper(II) photoreduction. Indeed, upon oxidation of the polymer, the ratio between low- and high-energy nitrogens goes from 3 to 1. Oxidation of both poly(EOAT) and poly(OAT-Cu) therefore increases the proportion of high-energy nitrogens and indicates that positive charges in the oxidized polymers are partially delocalized upon the complexing cavity. This electronic effect makes it possible to change to some extent the electron density of some of the nitrogen atoms grafted onto the polymer backbone.

Copper signal: Table 3 compares the copper XPS signal for reduced and oxidized poly(OAT-Cu), and for various copper complexes,[31–32] as a function of the copper oxidation state or of the ligand. Oxidation of the $[Cu^{II}(o\text{-phen(bi)}_2)]^{2-}$ to $[Cu^{III}(o\text{-phen(bi)}_2)]^{-}$ complexes (phen = phenanthroline,

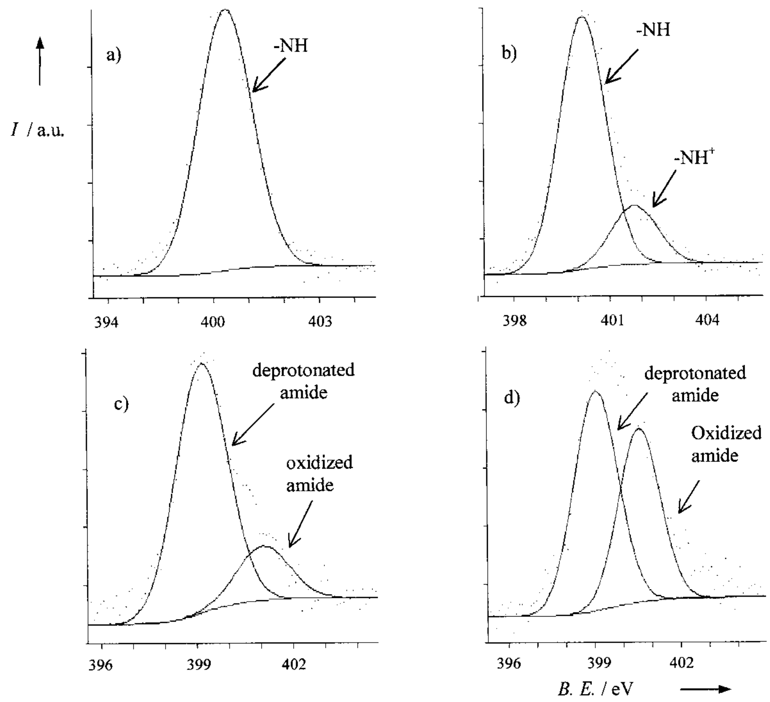


Figure 9. Curve-fitting analysis of the N_{1s}-core line spectra obtained from XPS measurements. Top: poly(EOAT) films generated in acetonitrile with 10^{-1}M $LiClO_4$ and 10^{-2}M EOAT, and polarized at: a) – 0.2 V (reduced form); b) 1.0 V (oxidized form). Bottom: poly(OAT-Cu) films generated in aqueous 10^{-1}M $LiClO_4$ and 10^{-2}M OAT-Cu, and polarized in acetonitrile with 10^{-1}M $LiClO_4$ at: c) 0 V (reduced form); d) 0.9 V (oxidized form).

Table 3. Cu_{2p} binding energies for poly(OAT-Cu) films polarized in reduced and oxidized states as compared to Cu^{II} and Cu^{III} complexes.

	Cu_{2p}3/2 binding energies [eV]		Cu_{2p}1/2 binding energies [eV]	
	main	satellite[a]	main	satellite[a]
reduced poly(OAT-Cu)	935.0	944.7	954.7	963.8
oxidized poly(OAT-Cu)	935.2	944.5	955.0	963.4
$[Cu^{II}(o\text{-phen(bi)}_2)]^{2-}$[b]	934.7	943.8	954.8	963.0
$[Cu^{III}(o\text{-phen(bi)}_2)]^{-}$[b]	935.5	944.6	955.8	964.1
$[CuSO_4(dip)_3] \cdot 7\,H_2O$[c]	934.7	944.5	954.5	963.7
$[Cu(AcO)_2(en)_2] \cdot H_2O$[c]	935.7	944.5	955.5	964.2
$[CuCl_2(en)] \cdot H_2O$	936.0	944.4	955.9	964.0

[a] Binding energies of the satellite peak of higher intensity. [b] Ref. [31]. [c] Ref. [24].

bi = biureto) leads to a shift of the whole Cu_{2p}-core line spectrum (main peaks and satellites) towards higher binding energies.[31] In contrast, modification of the Cu_{2p} signal for poly(OAT-Cu) samples switched from their reduced to their oxidized states results in a displacement of the principal peaks towards higher energies (0.2 and 0.3 eV for $Cu_{2p_{3/2}}$ and $Cu_{2p_{1/2}}$, respectively, cf. Table 3) accompanied by a shift in the opposite direction of the satellites (displacement of 0.2 and 0.4 eV towards lower energies). Although each one of these modifications is relatively small, the evolution of the gap between the principal peak and the satellite binding energy (splitting of the satellites) is significant, with a decrease in the satellite splitting of 0.4 eV for the $Cu_{2p_{3/2}}$ signal and of 0.7 eV for the $Cu_{2p_{1/2}}$ signal upon oxidation of the polymer backbone.

The evolution of the main peak is comparable to that of Cu^{II} complexes with ligands of decreasing electron-donating character[24, 32] and suggests a decrease in the electron-donating character of the ligands on oxidizing poly(OAT-Cu). Furthermore, it has been proposed that the satellite splitting decreases with decreasing ligand-orbital energy[24] and, therefore, the observed evolution is likely to indicate that the switching of the polythiophene backbone modulates the energy level of the ligand-orbital energy. Oxidation decreases the energy level of the π orbitals,[13b] which decreases the energy level of the bis(oxamato) orbital and gives smaller satellite splitting. Finally, copper(II) compounds exhibit a negative correlation between the splitting of the satellites and the main-peak binding energies.[24] It has been proposed that this correlation reflects the modification of the chemical environment, that is, the electronic properties of the ligands and the amount of overlap between copper and ligand orbitals. Figure 10 shows the variation in the binding energy of the $Cu_{2p_{1/2}}$ as a function of the satellite splitting for poly(OAT-Cu) in the reduced and oxidized state, and for some copper(II) complexes with various ligands. Poly(OAT-Cu) samples fit well in the general evolution of this curve.

Overall, XPS results (nitrogen and copper signals) show that the polythiophene redox reaction is felt by copper(II) atoms as if the ligands surrounding the metal were either chemically changed or substituted by a group that modifies the strength of the ligand field.

X-ray absorption near-edge structure (XANES) spectroscopy: The XANES spectra of oxidized and reduced poly(OAT-Cu) at the copper *K* edge are depicted in Figure 11. The two spectra are very similar, with the low-energy side of the edge exhibiting the characteristic shoulder of Cu^{II} in an elongated tetragonal surrounding. This clearly indicates that the oxido-reduction process does not affect the oxidation state of the copper nor its structural environment (D_{4h}). Although at first sight comparable, there are significant differences in the slope of the edge, which shifts by 1.7 eV in the high-energy direction when the polymer is oxidized.

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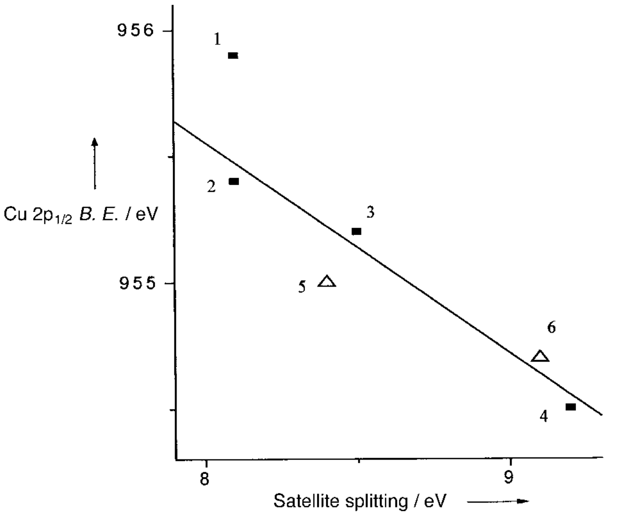


Figure 10. Variations of the binding energy of the Cu$_{2p_{1/2}}$ as a function of the satellite splitting for poly(OAT-Cu) in the reduced and oxidized state, and for some copper(II) complexes with various ligands:[24] 1) [CuCl$_2$(en)]; 2) [CuCl$_2$(en)$_2$]; 3) [CuBr$_2$(en)$_2$]; 4) [CuSO$_4$(dip)$_3$]; 5) oxidized poly(OAT-Cu); 6) reduced poly(OAT-Cu).

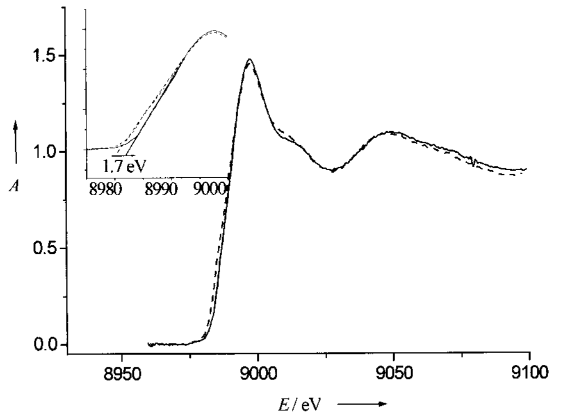


Figure 11. Comparison of XANES spectra recorded at the copper K edge for poly(OAT-Cu) films generated in aqueous 10^{-1}M LiClO$_4$ and 10^{-2}M OAT-Cu, and polarized in acetonitrile with 10^{-1}M LiClO$_4$ at: 0 V (reduced form, dashed line) and 0.9 V (oxidized form, solid line).

This represents a notable modification of the electron density of the Cu^{II}, but remains smaller than the shift observed when the metal center changes its oxidation state.[25] Indeed, the shift of the whole XANES spectrum is 3.5 eV when $[Cr^{II}(H_2O)_6]^{2+}$ is oxidized to $[Cr^{III}(H_2O)_6]^{3+}$.[33] The change in the XANES spectra indicates that the electron density of copper(II) decreases when the polythiophene backbone in poly(OAT-Cu) is switched from the reduced to the oxidized state. This agrees well with the results from IR spectroscopy and the XPS analysis and clearly shows that this reaction induces a variation of the ligand π-donating character that could be associated with a modification of the metal–ligand distances and/or of the symmetry of the ligands around the metal.

Extended X-ray absorption fine structure analysis (EXAFS): In order to investigate this last point, EXAFS spectra of oxidized and reduced poly(OAT-Cu) were compared. Our previous study on poly(EOAT) indicated that the switching reaction in the polythiophene backbone modifies the size of the bis(oxamato)-complexing cavity.[14] The N–N distance was predicted to be smaller for oxidized poly(EOAT) by as much as 0.06 Å as a consequence of quinonic deformation of the polythiophene backbone. EXAFS spectroscopy makes it possible to investigate the metal–ligand distance and can thus give experimental indications of the geometric variation of the complexing cavity.

Figure 12 compares the modulus and the imaginary part Im[*F(R)*] of the Fourier transform EXAFS signals in k^3 taken between 2 and 11 Å^{-1} for oxidized and reduced poly(OAT-Cu). The two spectra are almost identical, indicating that there is the same number of nearest neighbors in both compounds, with contributions of several layers of approximately identical intensity and position; this clearly shows no or very little variation of copper–ligand distances upon oxido-reduction of the material.

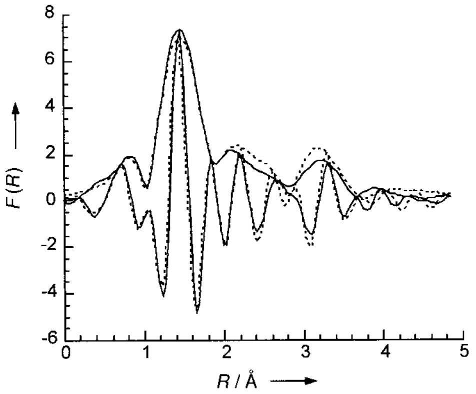
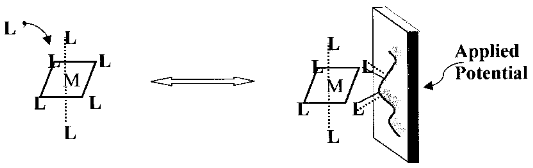


Figure 12. Comparison of non-phase-shift-corrected Fourier transform modulus and imaginary part for poly(OAT-Cu) films polarized at: 0 V (reduced form, dashed line) and 0.9 V (oxidized form, solid line).

Within the framework of the single-scattering approach, the oxidized polymer EXAFS signal fits well (see Table 2), if one assumes that Cu^{II} ions are surrounded by two nitrogen, two oxygen, and six carbon atoms with average Cu–N, Cu–O, and Cu–C bond lengths of 1.95, 1.99, and 2.72 Å, respectively, with a least-squares fitting parameter of 4%. Distance variations between the oxidized and reduced polymer are thus below the intrinsic imprecision of EXAFS for the first coordination sphere (Cu–N, Cu–O), whereas the variation of the average Cu–C bond length from 2.76 Å (reduced polymer) to 2.72 Å (oxidized polymer) could be significant and goes in the expected direction considering the fact that quinonic deformation of the polythiophene backbone is the driving force for the structural modification of the complexing cavity.

The results obtained using FTIR, X-ray photoelectron, and X-ray absorption spectroscopy are consistent and clearly show that the polythiophene redox reaction is felt by the copper(II) atoms. Oxidation increases the π-withdrawing character of the conjugated ligands and the effects are similar to those observed when the ligands surrounding the metal are either chemically changed or substituted. Changing the potential applied to the material and chemically modifying the coordination sphere of the metal, as depicted in Scheme 4,



Scheme 4. Formal equivalence of changing the potential applied to the material and modifying the coordination sphere of the metal by chemistry and synthesis.

are formally equivalent. This strongly suggests that physical and chemical properties of inorganic complexes can be tuned and addressed using the switching reaction of a conducting polymer as an easy means of control.

As already mentioned, the strategy developed in this study fits in with the growing field of electrochemical switching,[18] widely applied in supramolecular chemistry as an easy means of controlling the molecular architecture of redox-active supramolecular systems. However, the usually used reversible redox systems (ferrocenes, nitrobenzenes, quinones, etc.) are here replaced by the conductive polymer backbone and its reversible switching reaction. This has several advantages:

1) The system is directly attached to the electrode surface—consequently, a molecular device with realistic electronic-platform configuration is generated and can be addressed at will.
2) The conductive properties of the polymer backbone makes it possible to transmit the electrochemical input over a longer distance than that of an adsorbed or chemically bonded monolayer.
3) The number of active centers in the device and the size of the device can be controlled by the thickness of the film, by the dilution of the active centers along the polymer backbone, and by the dimension of the electrode.
4) The molecular device is intrinsically massively parallel and therefore the failure of one of its components (a single polymer chain or a single active center) does not induce failure of the device.
5) The switching reaction of a conductive polymer is amongst the fastest electrochemical reactions, and so far its intrinsic limit has not been reached, even using ultramicroelectrodes.
6) The interaction between the redox-switchable system (polymer backbone) and the active center is not only steric or electrostatic, but also electronic because of conjugation between the two.
7) The device can be used in a binary mode in which the polymer is switched between its insulating and conductive states, as shown in this study, but could also be run in a pseudoanalogic mode in which it is switched between two potential values in the so-called capacitive region in which the polymer remains conducting thanks to closely spaced multiple redox states. In this latter mode, one needs fully delocalized systems in which progressive modification of the π-electron density of the backbone generates a progressive variation of the transition metal electron density.

Conclusion

In this study we have built a new conjugated polymer consisting of polythiophene chains bearing bis(oxamato)–Cu^{II} groups regioregularly grafted onto the backbone, in which the two moieties of the material are in direct electronic contact. The copper atoms are in a local D_{4h} geometry and are in the +2 oxidation state, as shown by XANES and XPS analyses. They are surrounded by two oxygen and two nitrogen atoms as first neighbors at a mean distance of 1.95 and 1.99 Å, respectively, and by six carbon atoms. The polymer is stable with respect to polythiophene electroactivity and no demetallation or modification of the Cu oxidation state occurs over a large potential range.

In this material, we have used the conductive polymer backbone as a molecular wire or a nanocontact capable of inputting to the bis(oxamato)–Cu^{II} groups through a redox reaction. FTIR, XP, and XANES spectroscopies indicate that the properties of the copper(II)-complex center (electron density, π-donating, and π-withdrawing characters of the ligands, ligand field strength, force constant of some bonds) can be controlled, to some extent, by the potential applied to this molecular electronic device. However, there is little or no modulation of the average Cu–O,N bond length. From the viewpoint of the copper(II)-complex center, these effects are similar to those induced by introducing substituents with various electronic effects. The use of conductive polymers as "switchable molecular connectors" thus offers the possibility of generating a new class of hybrid materials in which the properties of the metal center could be adjusted, without any direct chemical modification. This work is, to our knowledge, the first in which variation of the metal electron density by means of a conducting-polymer/switching reaction is demonstrated directly. We believe that this strategy, when used on nanoscale devices and with metal centers that incorporate nervous electrons (spin transition complexes, magnetic chains), will find important applications amongst electric-field-controlled molecular electronic-switching devices.

Experimental Section

Electrochemical procedure: All voltammetric and galvanostatic experiments were performed in a one-compartment, three-electrode cell by means of an EG&G PAR Model362 potentiostat/galvanostat. The counter-electrode was a stainless steel grid, and an SCE was used as reference. The electrolyte solution consisted of either distilled water purified by a Millipore system or acetonitrile (Prolabo Chromanorm™ HPLC grade) containing 0.1M lithium perchlorate (Acros) as supporting salt. Electrochemical studies were carried out with a Pt disk (2 mm in diameter) or a glassy carbon electrode (3 mm in diameter), polished with diamond paste and rinsed in acetone with ultrasonic stirring before each experiment. For IR, XP, and selected area X-ray photoelectron spectroscopy (SAX) studies, films were deposited on an electrode consisting of a glass plate (10 mm × 30 mm) covered with a thin layer of Pt (ca. 500 nm) deposited by cathodic sputtering by using a Balzers-Sputron II device and a Pt target (Balzers, purity 99.9%). For UV/Vis measurements, transparent indium tin oxide (glass) plates were used as working electrodes.

Spectroscopic measurements: UV/Vis experiments were performed on a Perkin–Elmer lambda2 spectrophotometer. FTIR experiments were performed on a Nicolet FTIR 60-SX spectrometer. Samples were made up as KBr disks for the monomers and thin films on platinum for the polymers. ^{1}H NMR spectra were recorded on a Brüker W200 (200 MHz) spectrometer in [D$_6$]acetone, and chemical shifts are given relative to tetramethylsilane as internal standard. The XP spectra were recorded using a VG Scientific ESCALAB MKI system operating in the constant analyser energy mode. An $Mg_{K\alpha}$ X-ray source was used at approximately 10^{-9} mbar pressure. The analyzer was operated at constant pass energy (50 eV). A homemade nonlinear, least-squares curve-fitting procedure was used to analyse the spectra. These were fitted with the sum of a series of components representing individual peaks characteristic of the various chemical functionalities to unscramble the C_{1s}, N_{1s}, S_{2p}, O_{1s}, and Cu_{2p} peaks. The parameters associated with each peak were peak center, peak height, full width at half-maximum (fwhm), and the Gaussian-to-Lorentzian ratio. A Shirley baseline was chosen for peak fitting. Charge referencing was determined by setting the main C_{1s} C–C/C–H component to 285.0 eV. The surface compositions (in atom %) of the various samples were determined by considering the integrated peak areas of C_{1s}, N_{1s}, S_{2p}, O_{1s}, and Cu_{2p} and their experimental sensitivity factors. The fractional concentration of a particular element A (% A) was calculated by Equation (1):

$$\% A = \frac{(I_A/s_A)}{\sum_i (I_i/s_i)} \times 100 \quad (1)$$

in which I and s are the integrated peak areas and the sensitivity factors, respectively.

X-ray absorption data collection and processing: The XANES (X-ray absorption near-edge structures) and EXAFS (extended X-ray absorption fine structures) data were collected at LURE (Laboratoire d'Utilisation du Rayonnement Electromagnétique, Paris-Sud University) on the XAS13 beam line of the storage ring DCI (positron energy 1.85 GeV; mean current 300 mA). The spectra were recorded at copper K edge polymers using the channel-cut monochromator (Si111 for EXAFS and Si331 for XANES). The energy was calibrated by using Cu metallic foil and fixed at 8979 eV for the first inflection point of the metallic foil spectrum. The measurements were performed at room temperature in the transmission mode for the monomer with two air-filled ionization chambers, and at 80 K in the total-electron-yield mode for the polymers.

The XANES spectra were recorded step-by-step, every 0.3 eV with a 1 s accumulation time per point. The spectrum of a 5 μm copper foil was recorded just before an unknown XANES spectrum to check the energy calibration, thus ensuring an energy accuracy of 0.25 eV. The EXAFS spectra were recorded over 1000 eV, with 2 eV steps, from 8900 to 9900 eV. Data analysis was performed by means of the "EXAFS pour le Mac" package.[34] The $\chi(k)$ functions were extracted from the data with a linear pre-edge background, a combination of polynomials and spline atomic-absorption background, and normalized by using the Lengeler–Eisenberger method.[35] The energy threshold, E_o, was taken at the maximum of the absorption edge. E_o was corrected for each spectrum in the fitting procedure. The k^3 weighted $\chi(k)$ function was Fourier transformed from $k = 2-13$ or $2-11$ Å^{-1}, by means of a Kaiser–Bessel window with a smoothness parameter equal to 3 (k is the photoelectron wavenumber). In this work, all Fourier transforms were calculated and presented without phase correction. The peaks corresponding to the two first-coordination shells were then isolated and back-Fourier transformed into k space to determine the mean coordination number, N, the bond length, R, and the Debye–Waller factor, σ, by a fitting procedure realized in the framework of single scattering. Before this, we used the FEFF7 code[29] to check against a compound of known crystallographic structure[28] similar to ours ([MnCu(opba)(dmso)$_3$]) that the multiple scattering is negligible in the 0–2.7 Å range (see text) and to calculate the ab initio amplitude and phase functions, $|f_i(k,R_i)|$ and $|\phi_i(k,R_i)|$, respectively.

Preparation of the ligand and the mononuclear copper(II) precursor materials: Ethoxalyl chloride (Acros), anhydrous $SnCl_2$ (Aldrich) and $Cu(NO_3)_2 \cdot 3H_2O$ (Acros) were used without further purification. 2,5-dibromo-3,4-dinitrothiophene was prepared according to the previously published procedure.[36]

3′,4′-Diamino-2,2′:5′,2″-terthiophene (1): [PdCl$_2$(PPh$_3$)$_2$] (432 mg, 1 mol %) was added to a solution of 2,5-dibromo-3,4-dinitrothiophene (20.04 g, 60.4 mmol) and tributyl(thien-2-yl)stannane (46 mL, 144.4 mmol) in THF (400 mL).. The mixture was heated under reflux for 16 h. After cooling, the reaction mixture was concentrated under reduced pressure. Hexane was added to the residue, and the resulting yellow precipitate filtered off, washed with hexane, and collected (14.1 g, 69 %). ^{1}H NMR (200 MHz, [D$_6$]acetone, 25 °C): $\delta = 7.62$ (d, 2H), 7.56 (d, 2H), 7.19 (dd, 2H). The dinitro compound (11.7 g, 35.2 mmol) was suspended in ethanol (120 mL) and concentrated HCl (240 mL).A solution of anhydrous $SnCl_2$ (205 g, 1080 mmol) in EtOH (240 mL) was added to the mixture. The mixture was stirred at 30 °C for 18 h and poured into cold 25 % NaOH (800 mL). Toluene (400 mL) was added to the above mixture, which was then shaken vigorously and filtered through Celite. The phases were separated, and the aqueous layer was extracted with toluene. The combined organic layer was washed with brine and dried over $MgSO_4$. After removal of the solvent under reduced pressure, recrystallization from ethanol afforded the title compound **1** (6 g, 61 %) as yellowish brown needles. ^{1}H NMR (200 MHz, [D$_6$]acetone, 25 °C): $\delta = 7.36$ (d, 2H), 7.15 (d, 2H), 7.09 (dd, 2H), 4.54 (s, 4H); IR (KBr): $\tilde{\nu} = 3322, 3296, 3095, 1622, 1489, 1444, 795, 689$ cm^{-1} (strong bands only); elemental analysis calcd (%) for $C_{12}H_{10}N_2S_3$ (278): C 51.80, H 3.60, N 10.07, S 34.53; found: C 52.00, H 3.54, N 10.00, S 34.84.

3′,4′-Bis(*N*,*N*′-ethyloxamyl)-2,2′:5′,2″-terthiophene (2): The diethyl ester EOAT was obtained by adding ethoxalyl chloride (2.3 mL) dropwise to a solution of **1** (3 g, 10.8 mmol) dissolved in THF (50 mL). The resulting mixture was heated under reflux for 30 min and then filtered to eliminate the solid residue. The THF solution was evaporated, which afforded an oily residue. Slow addition of water resulted in the formation of a white polycrystalline powder that was collected by filtration, washed with water, and dried under vacuum (4.6 g, 89 %). ^{1}H NMR (200 MHz, [D$_6$]acetone, 25 °C): $\delta = 9.59$ (s, 2H), 7.57 (d, 2H), 7.39 (d, 2H), 7.15 (dd, 2H), 4.34 (m, 4H), 1.34 (m, 6H); IR (KBr): $\tilde{\nu} = 3307, 3251, 3110, 1760, 1717, 1683, 1489, 1444, 795, 713$ cm^{-1} (strong bands only); elemental analysis calcd (%) for $C_{20}H_{18}N_2O_6S_3$ (478): C 50.20, H 3.76, N 5.86, O 20.08, S 20.10; found: C 50.09, H 3.94, N 5.88, O 19.62, S 19.53.

3′,4′-Bis(*N*,*N*′-oxamato)-2,2′:5′,2″-terthiophenecopper(II) (3): The copper(II) precursor salt, OAT-Cu, was synthesized as follows: an aqueous solution of NaOH (1.26 M, 25 mL, 31.5 mmol) was added to a suspension of EOAT (3.58 g, 7.5 mmol) in amixture of water/ethanol (9:1, 50 mL). The mixture was heated at 70 °C for 30 min. A solution of $Cu(NO_3)_2 \cdot 3H_2O$ (1.81 g, 7.5 mmol) in water (25 mL) was then added slowly with stirring. The resultant mixture was filtered to eliminate the solid residue. After addition of ethanol (25 mL), it was allowed to evaporate for a week at room temperature. The polycrystalline precipitate was collected by centrifugation, washed with ethanol and dried under vacuum (2.4 g, 56 %). IR (KBr): $\tilde{\nu} = 3410, 3105, 1700, 1614, 1500, 823, 687$ cm^{-1} (strong bands only); elemental analysis calcd (%) for $C_{16}H_6CuN_2Na_2O_6S_3 \cdot 2.5H_2O$ (572.5): C 33.54, H 1.92, Cu 11.09, N 4.89, Na 8.03, S 16.76; found: C 33.92, H 2.07, Cu 10.98, N 4.82, Na 7.38, S 16.22.

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