5986 J. Am. Chem. Soc. 1992, 114, 5986-5994

Electroactive Films of Polypyrroles Containing Complexing Cavities Preformed by Entwining Ligands on Metallic Centers

Gérard Bidan,[*,†] Bernadette Divisia-Blohorn,[*,†] Mieczyslaw Lapkowski,[†] Jean-Marc Kern,[*,‡] and Jean-Pierre Sauvage[*,‡]

Contribution from the Equipe d'Electrochimie Moléculaire, Service d'Etudes des Systèmes Moléculaires, Département de Recherche Fondamentale sur la Matière Condensée, Centre d'Etudes Nucléaires de Grenoble, 85 X - F-38041 Grenoble Cédex, France, and Laboratoire de Chimie Organo-Minérale, UA du CNRS 422, Institut de Chimie, Université Louis Pasteur, F-67000 Strasbourg, France. *Received May 28, 1991. Revised Manuscript Received March 30, 1992*

Abstract: New functionalized polypyrrole films containing transition metal complexes have been prepared and studied. The strategy is based on the three-dimensional template effect of a metal center (Cu^{I}, Co^{II}, Zn^{II}, Ag^{I}) able to entwine two end-functionalized chelating ligands before polymerization (Figure 2). The ligands used consist of a 2,9-diphenyl-1,10-phenanthroline subunit (dpp) bearing two pyrrole nuclei. The pseudotetrahedral geometry of the precursor complex is such that after polymerization of the N-anchored pyrrole rings, a highly entangled network is obtained. The rigidity of the polymer matrix is sufficient to allow demetalation of the template center (by CN^- or SCN^-) without collapse of the three-dimensional structure. Such a property is related to the expected complex topology of the material prepared. The organic backbone certainly contains interlocking rings and various network substructures. The free ligand polymer film can be recomplexed using an appropriate metal source. The polymer matrix thus keeps a memory of the templating metal used for building it. Copper(I) turned out to be the most convenient template during the polymer electrosynthesis and seemed to lead to the most structured network. The various complexes obtained using the electrosynthesis method display electrochemical properties analogous to those of the corresponding catenates in solution. Here again, low oxidation states like copper(I), cobalt(I), formal zinc(I), and silver(0) are remarkably stabilized by the entwined and entangled system. Conductivity measurements and detailed electrochemical and spectroelectrochemical studies on several films have been carried out.

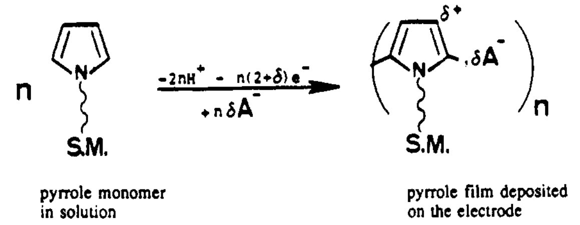
I. Introduction

One of the challenges of molecular engineering is the construction of functionalized materials that exhibit predetermined chemical and physical properties which are not simply just the sum of the individual properties of each of the component moieties, but are uniquely characteristic of the overall integrated molecule. Electronic conducting polymers, ECP, are ideal candidates[1a-c] in such a molecular construction field. Firstly, their structure allows free interaction with ions and electrons, and secondly the synthesis of such polymers is relatively easy since they are usually obtained as a film electrodeposited on the electrode surface (see Scheme I).

The functionalization of electronic conducting polymers has turned out to be a powerful tool for the modification of electrode surfaces. This new approach to the immobilization of functional groups has moved from the inclusion of a suitable doping anion[2a-k] toward the covalent grafting of a specific molecule (SM) to the ECP backbone through a spacer arm. Ferrocyanide,[2a] RuO_4^{2-},[2b] and sulfonated[2c,d] and carboxylated[2e] porphyrins of cobalt, iron, and manganese, as well as phthalocyanines of cobalt[2f,g] and iron,[2h,i] sulfonated dyes,[2j] and heteropolyanions,[2k] have been incorporated as dopants. To accomplish the covalent grafting, a suitable monomer is synthesized and subsequently electropolymerized,[1a] as illustrated in Scheme I.

The pioneering electrosynthesis of *N*-phenyl- and *N*-alkyl-substituted polypyrroles has been reported by Diaz and coworkers.[3] In addition, the synthesis of poly(*N*-(*p*-nitrophenyl)-pyrrole), which exhibits the redox properties added by the *p*-nitrophenyl group, has also been carried out.[4] However, the use of an alkyl chain spacer arm[1a] leads to a more tunable product than a phenyl spacer arm. The length of this alkyl arm can be tailored in such a fashion so as to control the steric hindrance[5] and the mobility required for the optimum activity of the SM group. In this way, large and reactive molecules such as derivatives of viologens,[6] nitroxide radical groups,[7] and anthraquinones[8] have been easily immobilized at the electrode surface using one-step electrochemical processes. Special attention has been turned on the grafting of transition metal complexes since they are well known catalysts for homogeneous organic reactions. Recent works along these lines include the grafting of 2,2′-bipyridine complexes of ruthenium(II),[9a,b] rhenium(I),[9c] and nickel(II),[9d] manganese,[9e]

Scheme I



S.M. : specific molecule with the desired property
∿ covalently bound spacer arm
δ : doping level
A^- : doping anion

[†] Centre d'Etudes Nucléaires de Grenoble.
[‡] Institut de Chimie de Strasbourg.

(1) (a) Audebert, P.; Bidan, G.; Lapkowski, M.; Limosin, D. *Springer Series in Solid-State Sciences*; Kuzmany, H., Ed.; Springer: Berlin, 1987; Vol. 76, pp 366-384. (b) Garnier, F. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 513. (c) Deronzier, A.; Moutet, J. C. *Acc. Chem. Res.* **1989**, *22*, 249.

(2) (a) Miller, L. L.; Zinger, B.; Zhou, G.-X. *J. Am. Chem. Soc.* **1987**, *109*, 2267. (b) Noufi, R. *J. Electrochem. Soc.* **1983**, *130*, 2126. (c) Ikeda, O.; Okabayashi, K.; Yoshida, N.; Tamura, H. *J. Electroanal. Chem.* **1985**, *191*, 157. (d) Okabayashi, K.; Ikeda, O.; Tamura, H. *J. Chem. Soc., Chem. Commun.* **1983**, 684. (e) Bedioui, F.; Bongars, C.; Devynck, J.; Bied-Charreton, C.; Hinnen, C. *J. Electroanal. Chem.* **1986**, *207*, 87. (f) Skotheim, T. A.; Velazquez Rosenthal, M.; Linkous, C. A. *J. Chem. Soc., Chem. Commun.* **1985**, 612. (g) Velazquez Rosenthal, M.; Skotheim, T. A.; Linkous, M. *Synth. Met.* **1986**, *15*, 219. (h) Bull, R. A.; Fan, F.-R.; Bard, A. J. *J. Electrochem. Soc.* **1984**, *131*, 687. (i) Bull, R. A.; Fan, F.-R.; Bard, A. J. *J. Electrochem. Soc.* **1983**, *130*, 1636. (j) Shimidzu, T. *React. Polym.* **1987**, *6*, 221. (k) Bidan, G.; Genies, E.; Lapkowski, M. *J. Electroanal. Chem.* **1988**, *251*, 297.

(3) Diaz, A.; Castillo, J.; Kanazawa, K.; Logan, J.; Salmon, M.; Fayardo, O. *J. Electroanal. Chem.* **1982**, *133*, 2.

(4) Velazquez Rosenthal, M.; Skotheim, T. A.; Melo, A.; Florit, M.; Salmon, M. *J. Electroanal. Chem.* **1985**, *185*, 297.

(5) Bidan, G.; Guglielmi, M. *Synth. Met.* **1986**, *15*, 49.

(6) Bidan, G.; Deronzier, A.; Moutet, J. C. *J. Chem. Soc., Chem. Commun.* **1984**, 1185.

(7) Bidan, G.; Limosin, D. *Ann. Phys.* **1986**, *11*, 5.

(8) Audebert, P.; Bidan, G. *J. Electroanal. Chem.* **1987**, *238*, 18.

0002-7863/92/1514-5986$03.00/0

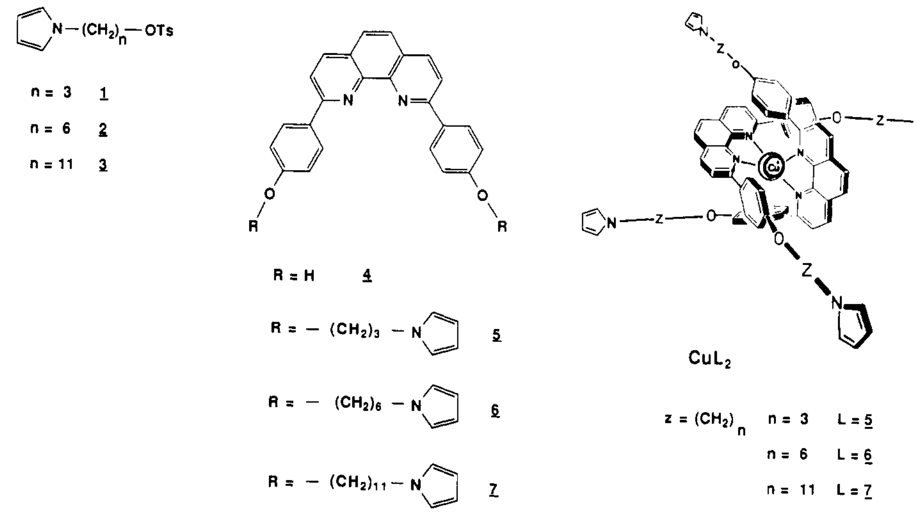


Figure 1. Precursors of 1,10-phenanthroline derivatives and schematic view of the entwined copper(I) complexes used as monomers.

nickel,[9f] and cobalt[9g] metalated porphyrins, nickel(II) cyclam[9h,i] and macrocyclic compounds,[9j] or terpyridyl complexes[9k] of iron(II), ruthenium(II), and cobalt(II). The electrode so modified exhibits the redox, electrochromic, or catalytic properties of the immobilized moiety joined to the electronic properties of the conducting polymer matrix.

Furthermore it was recently shown that the *electropolymerization of ECPs* can be exploited to *form or freeze certain molecular shapes*. Skotheim et al.[10] have formed Langmuir–Blodgett films of polypyrrolic materials which increase the mechanical stability of these materials, with the films being electronically conducting.

By further increasing the functional complexity of the molecular devices belonging to the ECP family, we have taken advantage of the relative rigidity of the polymer matrix to incorporate preformed complexing cavities into the material. We now report that this special arrangement leads to N-interlinked polypyrrole (poly($[M(L)_2]^{n+}$)) products containing transition metal complex moieties dispersed in the matrix. In addition, we will describe the various metal-containing materials obtained after demetalation of the copper(I) system and incorporation of another transition metal (Co^{II}, Zn^{II}, Ag^{I}, Li^{I}). The films so produced are characterized by spectrophotometric, voltammetric, and EPR experiments. A brief communication describing some preliminary results on the preparation of the poly($[Cu(\mathbf{6})_2]^+$) and some of its properties has recently been published.[11] The pyrrole-bearing ligands and the corresponding copper(I) complexes used in the present study are indicated in Figure 1.

II. Experimental Section

A. Synthetic Procedures. Melting points were measured with a Reichert Micro melting point apparatus (uncorrected). Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded at 200 MHz on a Bruker WP 200 SY spectrometer. NMR data are reported in the following order: chemical shift (ppm), spin multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and integration.

All reagents were the best commercially available. Chromatographic columns were filled with Merck silica gel 60 (70–230 mesh). Merck Fertigplatten F-254 were used for TLC. 2,9-Bis(*p*-hydroxyphenyl)-1,10-phenanthroline **4**[12] and the tosylates **1**, **2**, and **3**[5] of 3-(pyrrol-1-yl)propan-1-ol, 6-(pyrrol-1-yl)hexan-1-ol, and 11-(pyrrol-1-yl)undecan-1-ol, respectively, were prepared as previously reported.

Synthesis of 2,9-Bis[*p*-[[6-(pyrrol-1-yl)hexyl]oxy]phenyl]-1,10-phenanthroline (6). To a degassed solution of 182 mg (0.5 mmol) of **4** and 345 mg (2.5 mmol) of potassium carbonate in 45 mL of anhydrous DMF (60 °C) was slowly added a solution of **2** (353 mg, 1.1 mmol, in 8 mL of DMF). After the solution was stirred for 24 h at 60 °C, the mixture was evaporated to dryness, and the residue was dissolved in CH_2Cl_2 and washed with H_2O. The crude material was purified by column chromatography (CH_2Cl_2–MeOH; the concentration of methanol was progressively increased from 0 to 3% v/v): yield, 238 mg (71%), mp 115–116 °C; ^{1}H NMR (CD_2Cl_2) 1.4–1.9, m, 16 H; 3.90, t (J = 7.1 Hz), 4 H; 4.09, t (J = 6.4 Hz), 4 H; 6.09, t (J = 2.1 Hz), 4 H; 6.67, t (J = 2.1 Hz), 4 H; 7.12, d (J = 9 Hz), 4 H; 7.79, s, 2 H; 8.12, d (J = 8.5 Hz), 2 H; 8.31, d (J = 8.5 Hz), 2 H; 8.42, d (J = 9 Hz), 4 H. Anal. Calcd for $C_{44}H_{46}O_2N_4\cdot{}^1/_2H_2O$: C, 78.64; H, 7.05; N, 8.33. Found: C, 78.66; H, 6.92; N, 8.32.

Synthesis of 2,9-Bis[*p*-[[3-(pyrrol-1-yl)propyl]oxy]phenyl]-1,10-phenanthroline (5). The same procedure as above was used, but with a solution of **1**: yield, 67%, mp 209–210 °C; ^{1}H NMR (CD_2Cl_2) 2.28, m, 4 H; 4.04, t, 4 H; 4.17, t, 4 H; 6.11, t (J = 2.2 Hz), 4 H; 6.70, t (J = 2.2 Hz), 4 H; 7.13, d (J = 9 Hz), 4 H; 7.80, s, 2 H; 8.12, d (J = 8.2 Hz), 2 H; 8.31, d (J = 8.2 Hz), 2 H; 8.42, d (J = 9 Hz), 4 H. Anal. Calcd for $C_{38}H_{34}O_2N_4\cdot{}^1/_2H_2O$: C, 77.66; H, 6.00; N, 9.58. Found: C, 77.56; H, 5.76; N, 9.57.

Synthesis of 2,9-Bis[*p*-[[11-(pyrrol-1-yl)undecyl]oxy]phenyl]-1,10-phenanthroline (7). The same procedure as above was used, but with a solution of **3**: yield, 91%; ^{1}H NMR (CD_2Cl_2) 1–2, m, 36 H; 3.86 t, 4 H; 4.10, t, 4 H; 6.07, t (J = 2.2 Hz), 4 H; 6.64, t (J = 2.2 Hz), 4 H; 7.13, d (J = 9 Hz), 4 H; 7.70, s, 2 H; 8.11, d (J = 8.5 Hz), 2 H; 8.27, d (J = 8.5 Hz), 2 H; 8.42, d (J = 9 Hz), 4 H. Anal. Calcd for $C_{54}H_{66}O_2N_4$: C, 80.76; H, 8.28; N, 6.98. Found: C, 80.93; H, 8.29; N, 6.65.

Preparation of the Copper(I) Complex $Cu(\mathbf{6})_2^+$. $Cu(CH_3CN)_4BF_4$ (15.8 mg, 0.05 mmol, 1 equiv) in 5 mL of CH_3CN was added under an argon atmosphere to 66.2 mg (0.1 mmol) of **6** (2 equivs) dissolved in 50 mL of CH_2Cl_2. A deep red color appeared immediately. After 1 h of stirring, the solvents were evaporated, and the crude complex was purified by column chromatography, the product eluting with MeOH–CH_2Cl_2 (7:93 v/v): yield, 95%; ^{1}H NMR (CD_2Cl_2) 1.3–1.8, m, 16 H; 3.51, t (J = 6.4 Hz), 4 H; 3.92, t (J = 7 Hz), 4 H; 6.02, d (J = 8.7 Hz), 4 H; 6.10, t (J = 2.1 Hz), 4 H; 6.69, t (J = 2.1 Hz), 4 H; 7.41, d (J = 8.7 Hz), 4 H; 7.83, d (J = 8.4 Hz), 2 H; 7.92, s, 2 H; 8.39, d (J = 8.5 Hz), 2 H.

Preparation of Acetonitrile Solutions of $Co(\mathbf{5})_2^{2+}$, $Co(\mathbf{6})_2^{2+}$, $Co(\mathbf{7})_2^{2+}$, $Zn(\mathbf{6})_2^{2+}$, and $Ag(\mathbf{6})_2^+$. In a typical run, 100 μL (10^{-2} mmol) of a 10^{-1} mol L^{-1} $Co(ClO_4)_2\cdot 6H_2O$ solution in CH_3CN stored over 3-Å molecular sieves was added to a suspension of 13.2 mg (2×10^{-2} mmol) of **6** in 10 mL of CH_3CN. Immediately, the characteristic color of the cobalt complex[20] appeared, and after 10 min of stirring the solution was homogeneous. In the case of $Zn(\mathbf{6})_2^{2+}$ and $Ag(\mathbf{6})_2^+$, the complexes were

---

[9] (a) Bidan, G.; Deronzier, A.; Moutet, J. C. *New J. Chem.* **1984**, *8*, 501. (b) Ochmanska, J.; Pickup, P. *J. Electroanal. Chem.* **1989**, *271*, 83. (c) Cosnier, S.; Deronzier, A.; Moutet, J. C. *J. Electroanal. Chem.* **1986**, *207*, 315. (d) Labbe, E.; Bedioui, F.; Devynck, J. *J. Electroanal. Chem.* **1989**, *274*, 271. (e) Moisy, P.; Bedioui, F.; Robin, Y.; Devynck, J. *J. Electroanal. Chem.* **1988**, *250*, 191. (f) Deronzier, A.; Latour, J.-M. *J. Electroanal. Chem.* **1987**, *224*, 295. (g) Bettelheim, A.; White, B. A.; Raybuck, S. A.; Murray, R. W. *Inorg. Chem.* **1987**, *26*, 1009. (h) Collin, J. P.; Sauvage, J. P. *J. Chem. Soc., Chem. Commun.* **1987**, 1075. (i) Bartlett, P.; Chung, L. Y.; Moore, P. *Electrochim. Acta* **1990**, *35*, 1051. (j) Bartlett, P.; Chung, L. Y.; Moore, P. *Electrochim. Acta* **1990**, *35*, 1273. (k) Collin, J. P.; Jouaiti, A.; Sauvage, J. P. *J. Electroanal. Chem.* **1990**, *286*, 75.

[10] Rahman, A.; Samuelson, L.; Minehan, D.; Clough, S.; Tripathy, S.; Inagaki, T.; Yang, X.; Skotheim, T. A.; Okamoto, Y. *Synth. Met.* **1989**, *28*, C237.

[11] Bidan, G.; Divisia-Blohorn, B.; Kern, J. M.; Sauvage, J. P. *J. Chem. Soc., Chem. Commun.* **1988**, 723.

[12] Dietrich-Buchecker, C. O.; Sauvage, J. P. *Tetrahedron Lett.* **1983**, *46*, 5091.

isolated after evaporation of the solvent and identified by ^{1}H NMR. $Zn(\mathbf{6})_2(ClO_4)_2$ (CD_3CN): 1.2–1.9, m, 16 H; 3.49, t ($J = 6.3$ Hz), 4 H; 3.95, t ($J = 6.9$ Hz), 4 H; 6.06, t ($J = 2.1$ Hz), 4 H; 6.20, d ($J = 8.7$ Hz), 4 H; 6.74, t ($J = 2.1$ Hz), 4 H; 7.30, d ($J = 8.7$ Hz), 4 H; 8.07, d ($J = 8.6$ Hz), 2 H; 8.25, s, 2 H; 8.80, d ($J = 8.6$ Hz), 2 H. $Ag(\mathbf{6})_2BF_4$ (CD_2Cl_2): 1.2–1.9, m, 16 H; 3.51, t ($J = 6.3$ Hz), 4 H; 3.89, t ($J = 7$ Hz), 4 H; 6.08, t ($J = 2.1$ Hz), 4 H; 6.16, d ($J = 8.7$ Hz), 4 H; 6.66, t ($J = 2.1$ Hz), 4 H; 7.48, d ($J = 8.7$ Hz), 4 H; 7.89, d ($J = 9.8$ Hz), 2 H; 7.91, s, 2 H; 8.42, d ($J = 8.3$ Hz), 2 H.

B. Electrochemical Instrumentation and Procedures. Film studies were performed in a dry box under an argon atmosphere. Acetonitrile (BDH, HiPer Solv) was distilled once from P_4O_{10}, and propylene carbonate was doubly distilled from sodium, in the dry box. Tetrabutylammonium tetrafluoroborate, $TBABF_4$ (Fluka Purum), and tetraethylammonium tetrafluoroborate, $TEABF_4$ (Fluka Purum), were dried at 100 °C, and lithium perchlorate (G.F. Smith Chemical Co.) was dried at 150 °C for 1 day under vacuum prior to use.

The electrochemical device was made of PAR 173, 175, and 179 units from EG & G Princeton Applied Research connected to a SEFRAM TGM 164 recorder. All potentials are relative to the 10^{-2} mol L^{-1} Ag^+/Ag reference electrode.

C. Elaboration of the Films. Electrochemical syntheses of the N-substituted ECP films were performed either by repeated potential linear scanning or by electrolysis at a controlled potential of 0.850 V on a platinum electrode (diameter, 2 mm) or glassy carbon electrode (diameter, 3 mm) using a conventional three-electrode cell. The electrolyte was acetonitrile with 0.1 mol L^{-1} $TEABF_4$ (except if contrary indications are given), and the concentration of the substrate was 10^{-3} mol L^{-1}. The growing polymerization was pursued until the desired charge was passed. The films were then carefully washed before further analytical experiments.

1. Conductivity. Conductivity measurements on the N-interlinked polypyrrole films were performed using the four-probe technique on free-standing films. The films were synthesized on a 2 × 2 cm^2 indium tin oxide (ITO) coated glass electrode in a one-compartment cell, using a stainless steel electrode as the counter electrode.

2. Spectroelectrochemical Apparatus. The spectroelectrochemical cell has already been described.[13] The optically transparent electrodes were in ITO-coated glass, with a surface area $S = 1$ cm^2. The solvent, electrodes, reference electrode, and electrochemical apparatus were the same as those used in the electroanalytical studies. Spectrophotometric data were obtained from EG & G Princeton Applied Research equipment, including an optical multichannel analyzer OMA III Model 1460, equipped with a high-performance gateable intensified diode array detector, Model 1420 B, and a monochromator, Model 1229. The spectra were plotted on an HP 7474A plotter. Cell filling and film preparations were carried out inside the dry box.

3. In Situ EPR Electrochemical Experiment. The EPR apparatus was a Varian E4 and the electrochemistry apparatus was the same as that used in the electroanalytical experiments. The films were synthesized on a platinum wire (diameter, 1 mm), passing the indicated charge using the usual three-electrode system. The coated Pt wire was then transferred with thorough washing to an electrochemical cell containing fresh solvent and supporting electrolyte, which was located in the cavity of the EPR spectrometer. This cell has been previously described.[14] Film preparations and cell filling were carried out inside the dry box.

D. Ion Exchange Experiments. All experiments were performed under argon, in an oxygen-free ($O_2 < 5$ ppm) glove box. After electrodeposition of the polymers, the coated electrodes were briefly rinsed with a 0.1 mol L^{-1} collidine solution in acetonitrile. Demetalation processes, cation re-incorporation, and ion exchange experiments were monitored by cyclic voltammetric, CV, measurements in the potential range of the $M(L)_2^{n+}/M(L)_2^{(n-1)+}$ redox couples. Before each measurement, the films were thoroughly rinsed with fresh solvent.

For the demetalation of poly($[Cu(L)_2]^+$), the films were immersed for 30 min in a Bu_4NCN (0.1 mol L^{-1}) acetonitrile solution. For demetalation of poly($[Zn(L)_2]^{2+}$) and poly($[Co(L)_2]^{2+}$), the films were immersed in a KSCN (0.1 mol L^{-1}) acetonitrile solution.

Cation re-incorporation was performed on previously demetalated poly($[Cu(L)_2]^+$) or partially demetalated poly($[Co(L)_2]^{2+}$) and poly($[Zn(L)_2]^{2+}$) films. The coated electrodes were dipped into $[Cu(CH_3CN)_4]BF_4$ (0.1 mol L^{-1}), $Zn(ClO_4)_2$ (0.1 mol L^{-1}), or $Co(ClO_4)_2$ (0.1 mol L^{-1}) acetonitrile solutions.

For cation exchange, substitution of Cu^+ or Co^{2+} by Li^+ was conducted on films synthesized by electrodeposition of $Cu(L)_2^+$ or $Co(L)_2^{2+}$ in $LiClO_4$ (0.1 mol L^{-1}) propylene carbonate solutions. The electrodes were immersed, after coating, into LiSCN (0.1 mol L^{-1}) propylene carbonate solutions. Here again, CV measurements performed in fresh $LiClO_4$ (0.1 mol L^{-1}) propylene carbonate solutions allowed the observation of progressive cation replacement in the complexing cavities.

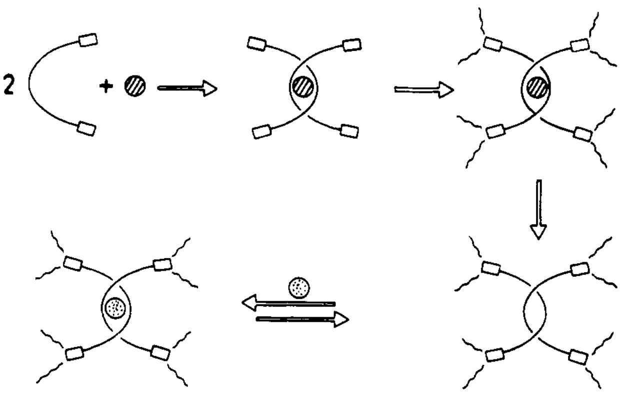


Figure 2. Synthetic strategy toward polypyrrole films containing complexes of entwined ligands based on a three-dimensional template effect induced by a transition metal. After demetalation, the preformed cavity is maintained in the polymer matrix. The dashed circle represents the gathering metal center used in the course of the template synthesis. This metal can be exchanged for another coordinated species (dotted circle).

III. Results and Discussion

A. Design and Synthesis of the Precursors. 1. Strategy toward Polypyrrole Films Containing Complexes of Entwined Ligands That Are Precursors to Preformed Complexing Cavities.

The principle of this polymer synthesis is different from that used since 1984 by others to make polypyrrole films covalently anchored to a transition metal complex.[9a-l,15a-j] Classically, an electroactive group chemically linked as a pendant moiety to a pyrrole ring was used as a polymer precursor. In our approach, two end-functionalized chelating fragments are coordinated to a potentially easily removable transition metal prior to electropolymerization, so as to entwine the complexing moieties. The material obtained in this way must be highly "entangled" in nature, this characteristic being kept even after demetalation. The strategy favors the formation of immobilized cavities ready for complexing any transition metal species provided the geometrical agreement between the coordination site and the metal is good enough, since the polymer matrix is built around the complexing metal during the electropolymerization process. The general "entangling" approach for constructing polypyrrole-based polymers is represented in Figure 2.

The strategy described in Figure 2 is reminiscent of the template synthesis of coordinating interlocked macrocyclic systems (catenates and catenands) developed by some of us a few years ago.[16-18] However, in the present work, each vertex or connecting point (squares of Figure 2) is of the third order, i.e., it can form three bonds, one already present in the ligand and potentially two more to other complexes during polymerization. The products are much more complex from a topological view point than catenands.

2. Design of the Ligands. As shown in Figure 1, two highly rigid coordinating fragments built on 2,9-diphenyl-1,10-phenanthroline (dpp) units can be held in an entwined geometry

---

(13) Genies, E.; Santier, C. French Patent 8516805, 1985.

(14) Genies, E.; Lapkowski, M. *J. Electroanal. Chem.* **1987**, *236*, 199.

(15) (a) Eaves, J. G.; Munro, H. S.; Parker, D. *Synth. Met.* **1986**, *16*, 123. (b) Deronzier, A.; Marques, M. J. *J. Electroanal. Chem.* **1989**, *265*, 341. (c) Cosnier, S.; Deronzier, A.; Moutet, J. C. *J. Electroanal. Chem.* **1987**, *198*, 187. (d) Eaves, J. G.; Munro, H. S.; Parker, D. *J. Chem. Soc., Chem. Commun.* **1985**, 684. (e) Eaves, J. G.; Munro, H. S.; Parker, D. *Inorg. Chem.* **1987**, *26*, 644. (f) Daire, F.; Bedioui, F.; Devynck, J.; Bied-Charreton, C. *J. Electroanal. Chem.* **1986**, *205*, 309. (g) Daire, F.; Bedioui, F.; Devynck, J.; Bied-Charreton, C. *Electrochim. Acta* **1988**, *33*, 567. (h) De Gregori, I.; Bedioui, F.; Devynck, J. *J. Electroanal. Chem.* **1987**, *238*, 197. (i) Deronzier, A.; Essakali, M.; Moutet, J. C. *J. Electroanal. Chem.* **1988**, *244*, 163. (j) Cosnier, S.; Deronzier, A.; Roland, J. F. *J. Electroanal. Chem.* **1990**, *285*, 133.

(16) Dietrich-Buchecker, C. O.; Sauvage, J. P.; Kintzinger, J. P. *Tetrahedron Lett.* **1983**, *24*, 5095.

(17) Dietrich-Buchecker, C. O.; Sauvage, J. P.; Kern, J. M. *J. Am. Chem. Soc.* **1984**, *106*, 3043.

(18) Dietrich-Buchecker, C. O.; Sauvage, J. P. *Chem. Rev.* **1987**, *87*, 795.

Table I. Electrochemical Properties of the Various Monomers: $E_{1/2}$ Values (V) Determined by Cyclic Voltammetry[a]

	monomers						
	$[Cu(\mathbf{6})_2]^{2+}$	$[Zn(\mathbf{6})_2]^{2+}$	$[Ag(\mathbf{6})_2]^{+}$	$[Co(\mathbf{5})_2]^{2+}$	$[Co(\mathbf{6})_2]^{2+}$	$[Co(\mathbf{7})_2]^{2+}$	**6**
medium	CH_3CN Et_4NClO_4	CH_3CN Et_4NBF_4	CH_3CN Et_4NBF_4	CH_3CN Et_4NBF_4	CH_3CN $LiClO_4$	CH_3CN Et_4NBF_4	CH_3CN Et_4NBF_4
charge of metal complex +2/+1	0.420[b]	−1.4[c]		−0.9[c]	−0.870[c]	−0.840[c]	
charge of metal complex +1/0	−2.0[b]	−1.5[c]	0.0[b]	−1.7[c]	−1.6[c]	−1.580[c]	
charge of pyrrole unit $Py^{\bullet+}/Py$	1.0(ir)[b]	0.9(ir)[c]	0.9(ir)[b]	0.7(ir)[c]	0.6(ir)[c]	0.7(ir)[c]	0.9(ir)[b]

[a] All potentials refer to Ag^+ (10^{-2} mol L^{-1})/Ag reference. The systems are reversible except in cases indicated by ir (irreversible). [b] The potentials have been determined by CV on a Pt electrode. [c] Potentials were determined by CV on a glassy carbon electrode.

by copper(I). In such a situation, the strategy given in Figure 2 is obvious. Each difunctionalized dpp ligand of Figure 1 bears two squares at its ends like in Figure 2, with $[Cu(\mathbf{6})_2]^+$ being the complex precursor to the entangled polymer. In our particular approach, the pyrrole nucleus (square of Figure 2) is indeed able to form three chemical connections, assuming that the two positions ortho to the nitrogen atom will lead to coupling products by electrochemical oxidation.

The electrochemistry of the copper complex of 1,10-phenanthroline substituted in the 2,9-positions by two electropolymerizable *N*-methylenepyrrole groups has been investigated by Bartlett et al.[9j] They reported that repeated cycling of a solution of the copper[2,9-bis[(pyrrol-1-yl)methyl]-1,10-phenanthroline]$_2$ complex produced only the passivation of the electrode surface. Compared to our results, this failure can be attributed to monomethylene spacing arms that are too short.

3. Synthesis of the Precursors: Substituted Chelates and Entwined Complexes. The pyrrole units and the polymethylene linkers were attached to the chelate center by reacting a tosylate derivative of an ω-(pyrrol-1-yl) aliphatic alcohol (**1–3**) with 2,9-bis(*p*-hydroxyphenyl)-1,10-phenanthroline in the presence of potassium carbonate (yields: 67, 71, 91% for n = 3, 6, 11, respectively).

The corresponding copper(I) complexes $Cu(L)_2^+$ (Figure 1) were prepared and isolated. They were obtained by addition of a stoichiometric amount of $Cu(CH_3CN)_4BF_4$ to the ligands dissolved in methylene chloride. They showed intense absorption bands in the visible range (red colored), corresponding to a metal-to-ligand charge transfer (MLCT) transition.[19]

Other bis-chelates $Co(L)_2^{2+}$, $Zn(L)_2^{2+}$, and $Ag(L)_2^+$ were only prepared in solution by mixing stoichiometric amounts of ligands and metal salts before electrochemical measurements. Their formation was evidenced by UV–visible spectrometry. The electronic absorption bands and electrochemical properties (Table I) are close to those of the corresponding complexes containing the 2,9-di(*p*-anisyl)-1,10-phenanthroline moiety.[20a] Furthermore, ^1H NMR spectroscopy of the diamagnetic Zn(II) and Ag(I) complexes fully confirmed their structure.[20b]

B. Synthesis and Characterization of the N-Interlinked Polypyrrole Poly($[M(L)_2^{n+}]$): Voltammetric Behavior of Poly($[M(L)_2^{n+}]$). Oxidative electropolymerization of the various substituted pyrroles was carried out either by repeated potential scanning or by electrolysis at a fixed potential by analogy with previously reported works.[3-9] The species resulting from oxidation of the precursor monomers polymerized and led to a film deposited on the electrode. This process could easily be followed visually (appearance of a colored deposit coating the electrode surface). In addition, formation of the film was monitored by CV. The modified electrodes so obtained could be washed, dried, and stored in air for some time. In particular, the copper(I)-containing materials turned out to be stable for weeks without significant modification of their electrochemical response. However, most of the results discussed below were obtained in an inert atmosphere.

The cyclic voltammetry studies were performed on poly($[Cu(\mathbf{6})_2]^+$), poly($[Zn(\mathbf{6})_2]^{2+}$), poly($[Co(\mathbf{5})_2]^{2+}$), poly($[Co(\mathbf{6})_2]^{2+}$), poly($[Co(\mathbf{7})_2]^{2+}$), and poly($[Ag(\mathbf{6})_2]^+$). Cobalt-containing systems were used to study the effect of the spacing arm on redox properties.

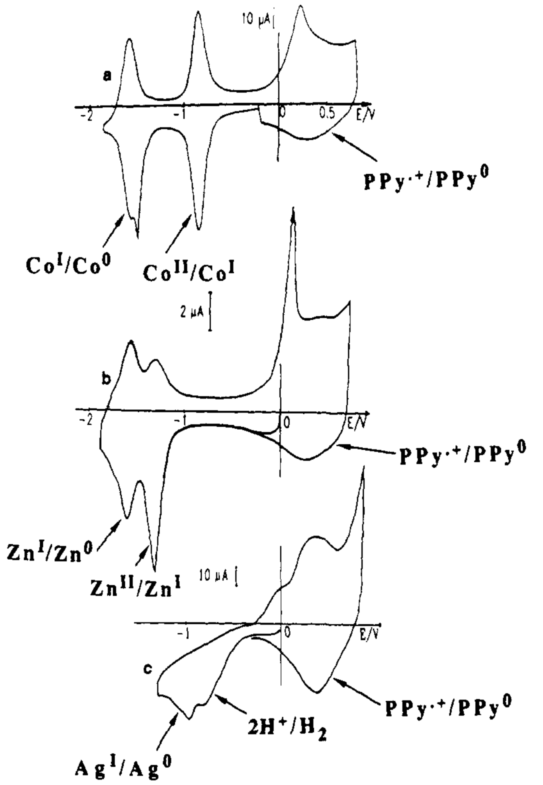


Figure 3. Cyclic voltammetry of (a) poly($[Co(\mathbf{6})_2]^{2+}$) on glassy carbon (diameter, 3 mm) in CH_3CN/0.1 mol L^{-1} $LiClO_4$, v = 100 mV s^{-1}, synthesis of the film performed at 0.825 V in CH_3CN/0.1 mol L^{-1} $TEABF_4$ by passing 1.41 × 10^{-2} C cm^{-2}; (b) poly($[Zn(\mathbf{6})_2]^{2+}$) on glassy carbon (diameter, 3 mm) in CH_3CN/0.1 mol L^{-1} $TEABF_4$, v = 10 mV s^{-1}, synthesis of the film performed at 0.830 V in CH_3CN/0.1 mol L^{-1} $TEABF_4$ by passing 2.83 × 10^{-2} C cm^{-2}; (c) poly($[Ag(\mathbf{6})_2]^+$) on Pt (diameter, 2 mm) in CH_3CN/0.1 mol L^{-1} $TEABF_4$, v = 10 mV s^{-1}, synthesis of the film performed by repetitive scans between 0.3 and 0.850 V in CH_3CN/0.1 mol L^{-1} $TEABF_4$.

All of these modified electrodes have the characteristic electrochemical response of both the redox centers and the polypyrrole matrix (Figure 3). It is not surprising that the potential values of the different redox systems are very close to those observed for the corresponding monomeric complexes in solution. The only exception is poly($[Ag(\mathbf{6})_2]^+$). For this system, the redox potential of the Ag^I/Ag^0 couple is strongly shifted (900 mV) toward cathodic values as compared to the corresponding solution species $[Ag(\mathbf{6})_2]^+$. A similar shift has been observed in solution between the electrochemical response of the silver(I) entwined complex and the silver(I) catenate.[20a] This effect, and in particular the strong analogy between the electrochemical behavior of poly($[Ag(\mathbf{6})_2]^+$) and the silver(I) catenate, suggests that the metal environment is very similar in both systems. In other words, the topological effect found in catenates is equally important in the present polymeric systems. It is thus possible to obtain topological and geometrical characteristics in a polypyrrole matrix which will lead to the same kind of stabilization of low formal oxidation states,

---

(19) Gushurst, A. K. I.; McMillin, D. R.; Dietrich-Buchecker, C. O.; Sauvage, J. P. *Inorg. Chem.* **1989**, *28*, 4070.

(20) (a) Dietrich-Buchecker, C. O.; Sauvage, J. P.; Kern, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 7791. (b) Dietrich-Buchecker, C. O.; Marnot, P. A.; Sauvage, J. P.; Kintzinger, J. P.; Maltese, P. *Nouv. J. Chim.* **1984**, *8*, 573.

Table II. Doping Levels δ and Accessibility Coefficient α of N-Substituted Polypyrroles, According to Equations 1 and 4

	poly([Cu(**6**)$_2$]$^+$)	poly([Zn(**6**)$_2$]$^{2+}$)	poly([Ag(**6**)$_2$]$^+$)	poly([Co(**5**)$_2$]$^{2+}$)	poly([Co(**6**)$_2$]$^{2+}$)	poly([Co(**7**)$_2$]$^+$)	poly(**6**)
δ	a,c,e,i,k	0.2[b,c,f,i]	0.17[a,c,f,j]	0.24[a,c,f,i]	0.17[b,d,e,i]	0.27[a,c,f,i]	0.20[b,c,g,h]
α		0.48		0.61	0.70	0.38	

[a] Determined by CV (see text). The values are calculated from the average charge measurement of 10 potential scans on the same film. Monomer concentration in the film, 1.7×10^{-8} mol cm^{-2}. [b] Determined by CV (see text). The values are calculated from the average charge measurement of 10 potential scans on the same film. Monomer concentration in the film, 3.4×10^{-8} mol cm^{-2}. [c] Solvent, CH_3CN. [d] Solvent, propylene carbonate. [e] Supporting electrolyte, $LiClO_4$ (0.1 mol L^{-1}). [f] Supporting electrolyte, $TEABF_4$ (0.1 mol L^{-1}). [g] Supporting electrolyte, $TEAClO_4$ (0.1 mol L^{-1}). [h] Platinum electrode. [i] Glassy carbon electrode. [j] ITO. [k] See section III.B1.

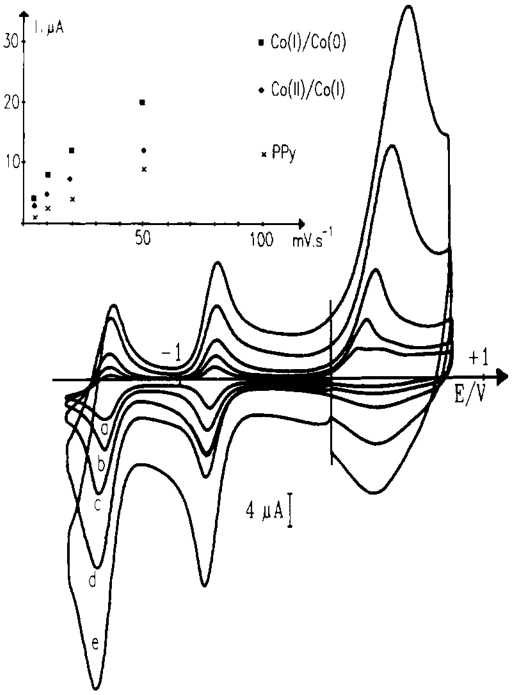


Figure 4. Cyclic voltammetry of poly([Co(**6**)$_2$]$^{2+}$) film on glassy carbon (diameter, 3 mm) in propylene carbonate/0.1 mol L^{-1} $LiClO_4$; v: (a) 5; (b) 10; (c) 20; (d) 50; (e) 100 mV s^{-1}. Synthesis of the film was performed at 0.850 V in CH_3CN/0.1 mol L^{-1} $TEABF_4$ by passing 3.18×10^{-2} C cm^{-2}.

such as Cu^I, Co^I, Co^0, Ag^0, Zn^I, and Zn^0, as that found in the corresponding catenates. Two successive perfectly reversible one-electron reduction steps are observed for poly([Co(**6**)$_2$]$^{2+}$) and poly([Zn(**6**)$_2$]$^{2+}$), corresponding to the formal couples Co^{II}/Co^I, Co^I/Co^0 and Zn^{II}/Zn^I, Zn^I/Zn^0, respectively, in the potential range where the polymer matrix is normally insulating. For each reduction step the ΔE_p ($E_{pc} - E_{pa}$) is small (~30 mV). The i_{pa} and i_{pc} values for the polypyrrole matrix electroactivity vary linearly with sweep rate (5–20 mV s^{-1}). At higher sweep rates, limitations arise due to ion migration within the film (see Figure 4 for poly([Co(**6**)$_2$]$^{2+}$). Such a linear variation cannot be observed for the successive electron transfers corresponding to the complexed metallic cores.

There is no change in the two successive reduction potential values of the cobalt centers when the length of the spacer varies (3–11 methylene groups in poly([Co(L)$_2$]$^{2+}$)). This indicates that the aliphatic arm does not lead to significant steric hindrance able to modify the coordination site geometry of the metal ion and thus does not alter the redox potential values.

1. Doping Levels, Accessibility, Yields. The doping level, δ, is an important characteristic of conducting polymers, representative of their ability to reversibly store positive charges by delocalization along the polymer backbone. δ is expressed as charge by monomer unit. This extractable charge is classically calculated by integration from the charge under the cyclic voltammogram of the electrochemical response of the polymer matrix, Q_r. In our case, the additional electroactivity of the metallic centers, Q_{rm}, with the stoichiometry of monoelectronic transfers by complexes bearing four pyrrolic units allows the use of this internal redox reference as another way to calculate the doping level. The two methods do not give the same result. An accessibility coefficient of the metallic centers, α, thus has to be introduced. This is developed below. The special case of copper complexes, doubly complicated by an overlap of the electroactivities of the Cu^{II}/Cu^I complex and of the polypyrrole matrix and by the redox mediation of the Cu^{II}/Cu^I complex during the electropolymerization process, is presented as ref 21.

In a first approach, we assume that the electrodeposition is 100% efficient ($\rho = 1$), so that the measured charge Q_t during the synthesis is equivalent to the synthesis charge, $Q_s = \rho Q_t$ and $Q_s = n(2 + \delta)F$ (see Scheme I), with n being the number of polymerized monomeric units, δ the doping level, and F the Faraday constant. The polymeric matrix electrochemical response, Q_r, is defined as one-half of the total charge for oxidation and reduction of the pyrrolic matrix, i.e., $Q_r = n\delta F$. This is measured by integration of the cyclic voltammetry curve and allows determination of the doping level from the classical equation:

$$\delta = \frac{2Q_r}{Q_s - Q_r} \tag{1}$$

In the case of poly([M(L)$_2$]$^{n+}$) studied here, there are four pyrrole units for one redox metal center. The comparison of the doping charge to the one-electron reduction charge of the metal center, Q_{rm} ($Q_{rm} = nF/4$), yields another way to calculate the doping level:

$$\delta' = \frac{Q_r}{4Q_{rm}} \tag{2}$$

When the calculations are made, it is found that the two methods give different values for the doping levels ($\delta' > \delta$), which means that either Q_{rm} is lower or ρQ_t is higher than the stoi-

---

(21) In the particular case of the copper N-interlinked polypyrrole, the oxidation of Cu^I to Cu^{II} occurs at a potential below the electropolymerization potential and moreover is superimposed on the electrochemical response of the polymeric matrix. Therefore, in eq 1 (see text), Q_s and Q_r contain both the oxidation and the reduction charge of the copper center, and their definition should be modified as follows:

$$Q_{rCu} = n(1/4 + \delta)F \text{ and } Q_{sCu} = n(2 + 1/4 + \delta)F$$

and eq 1 becomes

$$\delta = \frac{9/4 Q_{rCu} - 1/4 Q_{sCu}}{Q_{sCu} - Q_{rCu}} = \frac{2Q_{rCu}}{Q_{sCu} - Q_{rCu}} - 1/4 \tag{3}$$

According to eq 3, the δ value found for poly([Cu(**6**)$_2$]$^+$) is equal to 0.03. This is very low. A more reasonable hypothesis is thus that the interlinked copper center acts as a redox mediator during the electropolymerization, so that Q_{sCu} again equals $n(2 + \delta)F$ but Q_{rCu} remains equal to $n(1/4 + \delta)F$, and δ is given by

$$\delta = \frac{2Q_{rCu}}{Q_{sCu} - Q_{rCu}} - 1/4\left(\frac{Q_{sCu}}{Q_{sCu} - Q_{rCu}}\right) \tag{4}$$

According to eq 4, the δ value for poly([Cu(**6**)$_2$]$^+$) is still low and in a very unusual range for a conducting polymer. Consequently, the most reasonable hypothesis is that the polymerization yield ρ is not equal to 1 as expected, but lower. A low value of the polymerization yield was previously observed in the case of the electropolymerization of N-substituted pyrroles bearing a redox nitroxide group[1a] which can act as a redox mediator. Electron transfer from photogenerated Cu^{II}(dpp)$_2^{2+}$ to the pyrrole monomer, leading to polypyrrole, has already been seen.[23] A redox mediation in the case of poly([Cu(**6**)$_2$]$^+$) has been confirmed by EPR (see section III.D1). A possible explanation for ρ being less than 1 in the case of a mediated oxidation is that the diffusion of the mediator allows formation of the pyrrole radical cation in the bulk solution, affording oligomers which do not participate in the growing of the film. If δ for poly([Cu(**6**)$_2$]$^+$) is fixed at 0.20 by comparison with other poly([M(L)$_2$]$^{n+}$) compounds (see Table II), we obtain a ρ value of 0.6.

chiometric value. Since the hypothetical value of ρ has been fixed at a maximum of 1, the measured Q_{rm} must be below the theoretical value. Consequently, we introduce an accessibility coefficient, α,[22] defined as the ratio of the number of apparent electroactive metal centers to the total theoretical number of metal centers present in the film. This can be determined by $\delta = \alpha\delta'$.

For studying the influence of the metal ion or the alkyl spacing arm length on the doping level and the accessibility coefficient, the δ and α values were collected in Table II. The δ values of poly(**6**) and the different poly([M(**6**)$_2$]$^{n+}$) ($M^{n+} = Co^{2+}$, Zn^{2+}, and Ag^+) compounds are very close to 0.20, which is in good agreement with various N-substituted polypyrroles.[3] It is known that N-substitution produces a decrease in the doping level.

For different metals, it is difficult to directly compare the α values because of the very large differences in their redox potentials. However, the comparison of the α values of poly([Co(**6**)$_2$]$^{2+}$) and poly([Zn(**6**)$_2$]$^{2+}$) shows a drastic decrease, probably due to a matrix which is more insulating at the reduction potential of Zn^{2+} than for Co^{2+}.

The influence of dilution (through the polymethylene chains) of the redox metallic center on the accessibility coefficient is evidenced by the study of the Co^{II}/Co^{I} couple complexed by a ligand with a different alkyl spacing arm length. The α value also decreases drastically for $n = 11$ due to the decrease of electron hopping caused by increasing the alkyl spacing arm length.[5,24] As a matter of fact, it is well known that conducting polymers including redox centers behave as redox polymers with an electron hopping conductivity mechanism in the insulating potential range.[25] This is corroborated by the redox behavior of poly([Co(L)$_2$]$^{2+}$) in the potential range where polypyrrole becomes electroactive. For example, a prepeak appears before the polypyrrole oxidation peak in the case of the most dilute system, poly([Co(**7**)$_2$]$^{2+}$), which could correspond to reoxidation of the cobalt(I) complex by electrical wiring (inaccessible by electron hopping) in the potential range where the polypyrrolic matrix becomes conductive again.

2. Conductivity. It was difficult to obtain a large surface area for most of the films. In addition, they were extremely difficult to strip from the electrode surface. Nevertheless, it was possible to remove and study the poly([Cu(**6**)$_2$]$^+$) film. Its measured conductivity was $\sigma = 2.7 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$, in agreement with other N-substituted polypyrrole films.[1a,3] These results tend to indicate that the metal center does not contribute to the conductivity of the matrix polymer.

C. Stability to Electrochemical Cycling. The studies of the electrochemical polymer response were performed on poly(**6**), poly([Cu(**6**)$_2$]$^+$), poly([Co(**5**)$_2$]$^{2+}$), poly([Co(**6**)$_2$]$^{2+}$), and poly([Co(**7**)$_2$]$^{2+}$) by cycling the corresponding modified electrode in the electroactivity range of the polymeric matrix activity at 100 mV s^{-1}.

During the electrooxidative polymerization process, protons are liberated from pyrrole (Scheme I). Since the metal-free polymers described in the present work contain basic sites (phenanthroline nitrogen atoms), the protons generated in the course of film growth can be trapped in the material. It is therefore necessary to perform a careful neutralization by dipping the film in a basic solution (2,4,6-collidine (0.1 mol L^{-1}) in CH_3CN) prior to further studies.

The poly(**6**) shows a lesser stability than polypyrrole itself, in accordance with the observed stability of other N-substituted pyrroles. The electroactivity decreases by 51% after 2400 cycles while the anodic and cathodic peaks are slightly shifted. The last voltammogram shows again the reduction peak at -1 V characteristic of proton reduction, showing that overoxidation of the organic matrix causes the release of protons which are easily trapped in the film.

In the case of the cobalt films, the electroactivity of the polymeric matrix decreases drastically. After 2800 cycles, the electroactivity is only capacitive (Figure 5B). Interestingly, the electroactivity disappearance of the polymeric matrix does not alter the electroactivity of the complexed cobalt moiety as previously observed in similar experiments performed with *N*-nitroxide-substituted polypyrroles.[7]

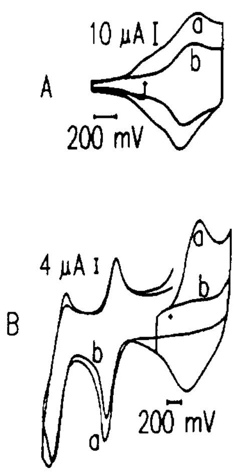


Figure 5. Stability to electrochemical cycling of (A) a poly([Cu(**6**)$_2$]$^+$) film and (B) a poly([Co(**6**)$_2$$^+$]$^{2+}$) film. In voltammogram A, curve a is cyclic voltammetry on glassy carbon (diameter, 3 mm) in propylene carbonate/0.1 mol L^{-1} $LiClO_4$, v = 100 mV s^{-1}. Synthesis of the film was performed at 0.825 V in CH_3CN/CH_2Cl_2 (CH_2Cl_2 10% v/v), 0.1 mol L^{-1} $LiClO_4$ by passing 2.12×10^{-2} C cm^{-2}. Curve b is cyclic voltammetry of the same film after 2700 electrochemical cycles between -0.5 and 0.7 V at 100 mV s^{-1}. In voltammogram B, curve a is cyclic voltammetry on glassy carbon (diameter, 3 mm) in propylene carbonate/0.1 mol L^{-1} $LiClO_4$, v = 100 mV s^{-1}. Synthesis of the film was performed at 0.850 V in CH_3CN/CH_2Cl_2 (CH_2Cl_2 10% v/v), 0.1 mol L^{-1} $LiClO_4$, by passing 2.85×10^{-2} C cm^{-2}. Curve b is cyclic voltammetry of the same film after 2800 electrochemical cycles between -0.2 and $+0.7$ V at 100 mV s^{-1}.

Table III. Redox Orbital Character of Poly([M(L)$_2$]$^{n+}$)

redox state of polymers	oxidation	first reduction	second reduction
poly([Cu(**6**)$_2$]$^+$)	$PPy^{\bullet +}$		
poly([Co(**6**)$_2$]$^{2+}$)	$PPy^{\bullet +}$	d^8	$L^{\bullet -}$
poly([Zn(**6**)$_2$]$^{2+}$)	$PPy^{\bullet +}$	$L^{\bullet -}$	$L^{\bullet -}$
poly([Ag(**6**)$_2$]$^+$)	$PPy^{\bullet +}$	$d^{10}s^1$	

The apparent great stability of the poly([Cu(**6**)$_2$]$^+$) films (Figure 5A) comes from the fact that the electroactivity of the copper(I) complex and that of the polymeric matrix strongly overlap. In reality, after 2700 cycles only copper electroactivity is observed. This is suggested by the shape of voltammogram curves and the absence of peak shift in the course of the cycling process.

D. Spectroelectrochemistry and/or EPR Spectrometry. In situ spectroelectrochemistry and/or EPR spectrometry studies were performed at different redox states of the films in order to characterize the different units responsible for the visible absorption properties and magnetic properties (Table III).

1. Poly([Cu(6)$_2$]$^+$). When scanning the poly([Cu(**6**)$_2$]$^+$) film electrodeposited on a platinum electrode between 0.2 and 0.65 V versus the pseudoreference Ag^+/Ag[14] in an EPR cavity, only the signal due to the polaron of the pyrrolic matrix $PP^{\bullet +}$ was observed. On the first part of the anodic scan, the characteristic signal of the polaron increases (Figure 6A). Afterward the signal decreases in accordance with the formation of the bipolaron, inactive in EPR, as observed in polypyrrole itself (Figure 6B).[26] But surprisingly, no signal of the paramagnetic Cu^{II} is detected. However, an exhaustive electrolysis at 1.2 V leads to destruction of the pyrrolic matrix, and signals for the Cu^{II} and $PP^{\bullet +}$ residues are observed. The EPR observations are in accordance with the redox mediator role of the entwined copper complexes during the

---

[22] Audebert, P.; Bidan, G.; Lapkowski, M. *J. Electroanal. Chem.* **1987**, *219*, 165.

[23] Kern, J. M.; Sauvage, J. P. *J. Chem. Soc., Chem. Commun.* **1989**, 657.

[24] Enkelman, V.; Rühe, J.; Wegner, G. *Synth. Met.* **1990**, *37*, 79.

[25] Andrieux, C.; Audebert, P.; Salou, C. *J. Electroanal. Chem.*, in press.

[26] Nechtschein, M.; Devreux, F.; Genoud, F.; Vieil, E.; Pernaut, J. M.; Genies, E. *Synth. Met.* **1986**, *15*, 59.

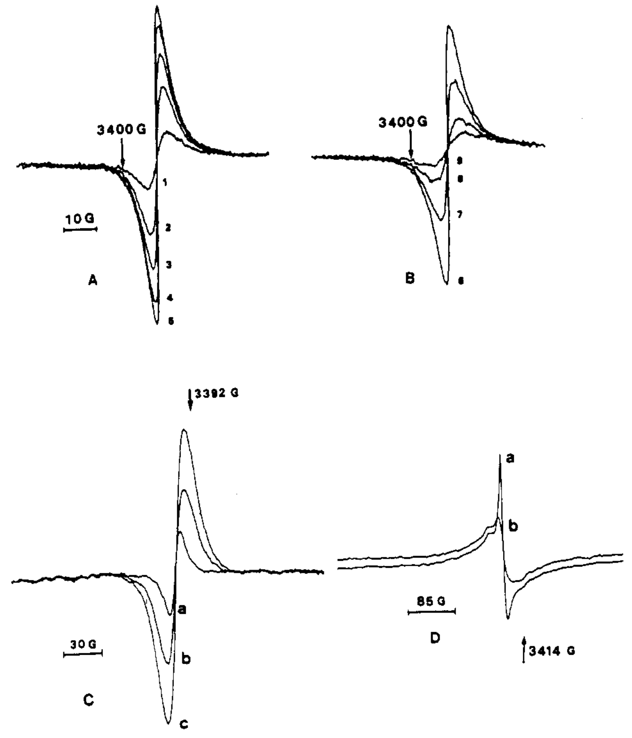


Figure 6. EPR spectra of a poly([Cu(**6**)$_2$]$^+$) film (A) deposited on a platinum wire by passing 6.4 10^{-2} C cm^{-2} at 0.8 V vs 10^{-2} mol L^{-1} Ag$^+$/Ag in CH$_3$CN/0.1 mol L^{-1} TEABF$_4$ and 10^{-3} mol L^{-1} [Cu(**6**)$_2$]$^+$. Polaron formation at various potentials vs Ag$^+$/Ag: (1) 0.2 V; (2) 0.3 V; (3) 0.35 V; (4) 0.4 V; (5) 0.45 V. Spectrum B is a continuation of A, with bipolaron formation increasing the potentials: (6) 0.5 V; (7) 0.55 V; (8) 0.6 V; (9) 0.65 V. EPR spectra C are of a poly([Zn(**6**)$_2$]$^{2+}$) film deposited on a platinum wire by passing 6.4 × 10^{-2} C cm^{-2} at 1.14 V vs Ag$^+$/Ag in CH$_3$CN/0.1 mol L^{-1} TEABF$_4$ and 10^{-3} mol L^{-1} in [Zn(**6**)$_2$]$^{2+}$ (a), after exhaustive electrolysis at −1.2 V (b), and after exhaustive electrolysis at −1.3 V (c). EPR spectra D are of a poly([Ag(**6**)$_2$]$^+$) film deposited on a platinum wire by passing 6.4 × 10^{-2} C cm^{-2} at 1.15 V vs Ag$^+$/Ag in CH$_3$CN/0.1 mol L^{-1} TEABF$_4$ and 10^{-3} mol L^{-1} in [Ag(**6**)$_2$$^+$] at +0.5 V (a) and −0.75 V (b).

polymerization previously discussed in section III.B1.[27]

2. Poly([Co(6)$_2$]$^{2+}$). In the case of the poly([Co(**6**)$_2$]$^{2+}$) film, the redox potentials of the complexed cobalt centers are located in the potential range where the polypyrrolic matrix is electroinactive. Consequently, changes in the UV–visible spectrum cannot be assigned to a process involving the polymer matrix. In addition, the two potentials of the successive reduction steps are separated by 730 mV, which is sufficient to allow clear observation of the modification of the UV–visible spectrum of the film by spectroelectrochemistry (Figure 7).

When scanning the poly([Co(**6**)$_2$]$^{2+}$) film across the potential of the first reduction step, the UV–visible absorption decreases significantly. In contrast, the scan at the second reduction potential causes a strong increase in the absorption near 520 nm, characteristic of the formation of a radical anion localized on the phenanthroline entity. The different nature of the redox orbitals involved (metal or ligand) between the two reduced species is in accordance with the large difference of reduction potential between the two redox couples.[28]

3. Poly([Zn(6)$_2$]$^{2+}$). In contrast to the case of poly([Co(**6**)$_2$]$^{2+}$), the two successive one-electron reduction potential values are close to each other. Scanning the two successive one-electron reductions of poly([Zn(**6**)$_2$]$^{2+}$) causes a strong absorption between 500 and 600 nm, analogous to the spectra obtained by exhaustive electrolysis of the monomer in solution. The EPR spectra recorded in the same potential range show only an increase in the characteristic signal of organic radicals (Figure 6C). Consequently, it seems reasonable to propose that the two one-electron reductions observed occur in ligand-localized orbitals in accordance with the low and close potential values of the redox site.[28]

4. Poly([Ag(6)$_2$]$^+$). The spectroelectrochemical studies performed on poly([Ag(**6**)$_2$]$^+$) do not show formation of the ligand radical anion when the film is reduced between 0 and −1.3 V. As a matter of fact, no new absorption peak appears in the expected wavelength range. This is in accordance with the EPR spectra where only an intensity decrease of the polymeric matrix polaron is observed (Figure 6D). This allows us to suggest the formation of a formal Ag^0 complex. However, it has not been possible to observe the paramagnetism of the Ag^0 species. Cyclic voltammetry shows that this hypothetical zero-valent state is very unstable.

E. Ion Exchange within the Film Polymer Matrix. 1. Complexing Properties of Catenands in Solution. By complexation to a metal, the coordinating fragments which form the complexing core lock together, adopting an entwined geometry. If the two coordinating subunits are interlocked, complexation of metal ions leads to highly rigid caged systems. The shapes of the free catenand and its copper(I) complex are dramatically different.[29] In the free ligand (catenand), the two diphenylphenanthroline units are far away from each other. Complexation occurs by the gliding of the two interlocked rings through one another, leading to a metallic complex species (catenate) where the metal atom is bonded to the two phenanthrolines via four nitrogen atoms. The catenate complexes and their noninterlocking analogues can be easily demetalated in solution by reaction with cyanide ions. Yet, the kinetics of this reaction is highly dependent on the shape and topology of the complexes.[30]

2. Demetalation of Poly([M(L)$_2$]$^{n+}$). In previous research,[11] it was shown that poly([Cu(**6**)$_2$]$^+$) films could be demetalated by the action of cyanide ions by simply dipping the polymer films into an acetonitrile–water–potassium cyanide solution. Loss of electrochemical activity due to the removal of the Cu(dpp)$_2$$^+$ electrophores was clearly observed. After demetalation, the polymeric matrix displayed nearly the same electroactivity as *N*-alkyl polypyrrole films.

In the same way, but using potassium thiocyanate instead of cyanide, demetalation of various polymeric films built around Co^{II} or Zn^{II} dpp complexes can be performed, as shown in Figure 8 illustrating the electrochemical behavior of a poly([Zn(**6**)$_2$]$^{2+}$) film before and after treatment with the decomplexing agent.

3. Metalation of Polypyrrole Films Containing Coordinating Moieties. Incorporation of the cations in the polymeric matrix can be followed electrochemically by measurements effected in the potential range of the M(L)$_2$$^{n+}$/M(L)$_2$$^{(n-1)+}$ redox couples. After dipping a film of poly(**6**) into a [Cu(CH$_3$CN)$_4$]BF$_4$ solution in acetonitrile, rinsing, and carrying out cyclic voltammetry measurements in fresh electrolyte, no change in the electrochemical activity of the film was observed. Cu$^+$ ions were not complexed by the polymeric matrix. The coordinating dpp units covalently linked to the nitrogen atoms of the polymeric network could not reorient themselves in order to adopt an appropriate geometry to complex the Cu$^+$ ions. Devynck et al.[9d] have reported the complexation of Ni^{2+} by a poly(pyrrole-2,2′-bipyridine) film dipped into a DMSO–NiCl$_2$ solution. However, it must be noted that spontaneous demetalation occurs after 40 repeated potential scans, due to the weak stability of the Ni^{II} monoligand complex.

In contrast, the behavior of the polymeric film obtained after demetalation of poly([M(L)$_2$])$^{n+}$ is very different with respect to metalation processes as compared to poly(**6**). Cu$^+$ ions are rapidly incorporated in the network after a few minutes of dipping the film in a [Cu(CH$_3$CN)$_4$]BF$_4$–acetonitrile solution. These successive exclusion–inclusion steps can be performed with several different films. Curve c on Figure 8 shows the inclusion of Zn^{2+}

---

[27] The spectroelectrochemical studies are not very informative with respect to the formation of Cu^{II} owing to the fact that the difference of ϵ_{max} and λ_{max} between the Cu^I and Cu^{II} entities is too small in the UV–visible range where the polypyrrolic matrix absorbs.

[28] De Armond, M. K.; Carlin, C. M. *Coord. Chem. Rev.* **1981**, *36*, 325.

[29] Cesario, M.; Dietrich-Buchecker, C. O.; Guilhem, J.; Pascard, C.; Sauvage, J. P. *J. Chem. Soc., Chem. Commun.* **1985**, 244.

[30] Albrecht-Gary, A. M.; Dietrich-Buchecker, C. O.; Saad, Z.; Sauvage, J. P. *J. Am. Chem. Soc.* **1988**, *110*, 1467.

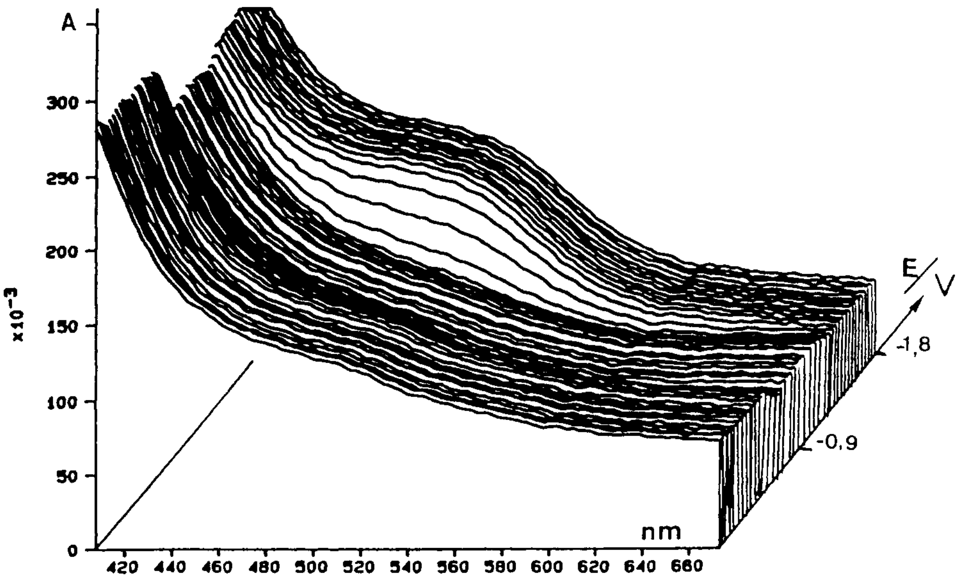


Figure 7. Visible spectroelectrochemistry for a poly($[Co(6)_2]^{2+}$) film deposited on ITO in CH_3CN/0.1 mol L^{-1} $TEABF_4$ and 10^{-3} mol L^{-1} $[Cu(6)_2]^{2+}$ passing 2 × 10^{-2} C cm^{-2}. Various spectra were taken during scanning from 0 to −1.8 V at 2 mV s^{-1} in CH_3CN/0.1 mol L^{-1} $LiClO_4$.

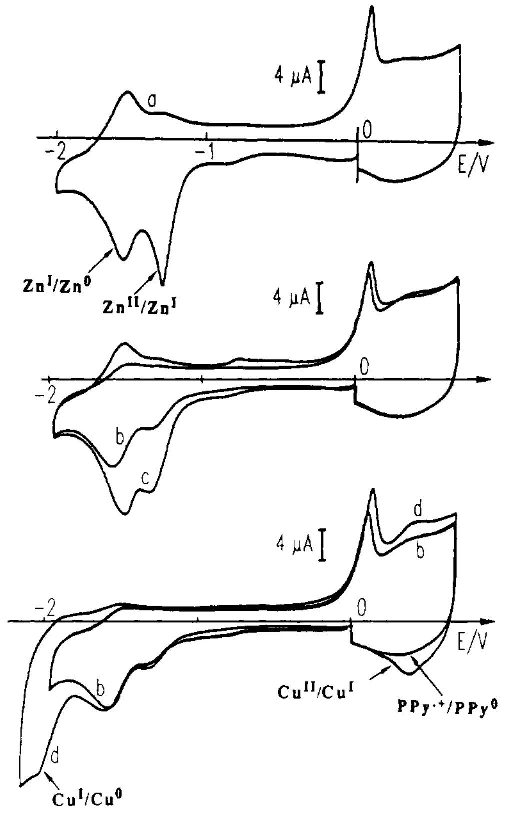


Figure 8. Cyclic voltammetry of a poly($[Zn(5)_2]^{2+}$) film (a) on a glassy carbon (diameter, 3 mm) electrode in CH_3CN/0.1 mol L^{-1} $TEABF_4$, v = 20 mV s^{-1}. Synthesis of the film was performed at 0.85 V in CH_3CN/0.1 mol L^{-1} $TEABF_4$ by passing 2.83 × 10^{-2} C cm^{-2}. Cyclic voltammetry of the same film (b) after 75 min of dipping in a CH_3CN/0.1 mol L^{-1} KSCN solution. Cyclic voltammetry after dipping (19 h) the film (c) obtained in b in a CH_3CN/0.1 mol L^{-1} $ZnClO_4$ solution. Cyclic voltammetry after dipping (1 h) the film (d) obtained in b in a CH_3CN/0.1 mol L^{-1} $CuBF_4$ solution.

cations into a partially demetalated poly($[Zn(6)^{2+}]$) film. These observations tend to indicate that the rigidity of the polymeric matrix is sufficient to conserve the structure of the coordination sites, thus allowing further incorporation and complexation of metallic cations.

4. Ion Exchange. Successive demetalation of poly($[M(L)_2]^{n+}$) films and inclusion of different metallic cations should allow the modulation of the electroactivity range of the film.

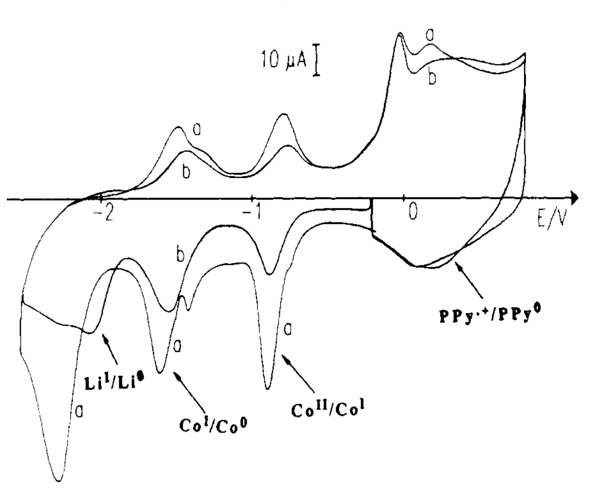


Figure 9. Cyclic voltammetry of a poly($[Co(6)_2]^{2+}$) film (a) on a glassy carbon (diameter, 3 mm) electrode in propylene carbonate/0.1 mol L^{-1} $LiClO_4$, v = 100 mV s^{-1}. Synthesis of the film was performed at 0.73 V in CH_3CN/0.1 mol L^{-1} $TEABF_4$ by passing 1.41 × 10^{-2} C cm^{-2}. Cyclic voltammetry of the same film (b) after dipping (5 min) in a propylene carbonate/0.1 mol L^{-1} LiSCN solution.

Figure 8d illustrates the inclusion of Cu^+ species into a partially demetalated poly($[Zn(6)_2]^{2+}$) film. In the same manner, Co^{2+} can be replaced in the polymeric network by Cu^+. However, it must be mentioned that, in some cases, complete demetalation of the films inhibits further recomplexation. This is particularly true with Co^{2+} and Zn^{2+} cations, which are less easily incorporated into the complexing film than Cu^+. This is in accord with the fact that the stability constant for the monomeric dpp or catenate complexes is lower for Co^{2+} and Zn^{2+} than for Cu^+.[31] In addition, anion effects may also be of some importance. In fact, prolonged decomplexation experiments would permit exchange of the perchlorate or tetrafluoroborate counterion by the decomplexing agent in the polymeric matrix and prevent further remetalation processes.

Complexation of Li^+ by the dpp units in the polymeric matrix underscores the effect of the topology of the coordinating sites. Whereas bis(2,9-dianisyl-1,10-phenanthroline) Li^+ has never been observed in solution, the existence of Li(cat-30)$^+$ can be shown either by NMR spectroscopy or by electrochemistry.[20] The dipping of poly($[Cu(6)_2]^+$) or poly($[Co(6)_2]^{2+}$) into a lithium thiocyanate

---

(31) Arnaud-Neu, F.; Marques, E.; Schwing-Weill, M. J.; Dietrich-Buchecker, C. O.; Sauvage, J. P.; Weiss, J. *New J. Chem.* **1988**, *12*, 15.

solution in propylene carbonate leads to films where exchange of the transition metal by lithium cation has occurred (Figure 9). The similar $\mathrm{Li^+}$ and $\mathrm{Ag^+}$ complexing ability of the catenand cat-30 and of the preorganized bis(2,9-diphenyl-1,10-phenanthroline) coordination sites covalently incorporated in the polypyrrole films is striking. This effect may be attributed to the particular rigidity of the complexing core, resulting from cross-linking of the coordinating moieties in an analogous manner as in the catenates.

IV. Conclusion

In conclusion, a new type of functionalized polypyrrole has been made and studied. It is synthesized by entwining two chelates around a transition metal, with each chelate being end functionalized by a pyrrole. This strategy provides a means of intertwining the molecular fragments, which are converted to a highly entangled polymer after electropolymerization of the N-bonded pyrrole units. The coordinating moieties used in the present work are 2,9-diphenyl-1,10-phenanthroline derivatives. The pyrrole nuclei are connected to the chelate via polymethylene chains of various lengths (3, 6, or 11 methylene fragments). It is shown that copper(I) is an ideal templating metal center, leading to an electroactive complex acting as an electron relay during electropolymerization. The same procedure can be applied with other metallic species (cobalt(II), zinc(II), or silver(I)), although no electron relay process takes place in these cases during electropolymerization and film growth. By electrochemical methods, it is shown that each metal complex subunit incorporated in the film is very similar in nature to the corresponding homogeneous species, the catenate.

The conductivity properties of the materials are reminiscent of those of the previously prepared and studied N-substituted polypyrroles, with no particular contribution of the transition metal complex.

Demetalation of the various systems was carried out using either $\mathrm{CN^-}$ (for copper(I)) or $\mathrm{SCN^-}$ (for cobalt(II) and zinc(II)). Interestingly, the material retains partial memory of its complex precursor. This property leads in some cases to relatively easy re-incorporation of a metal into the coordinating cavity. The highly entangled nature of the polymeric material helps to maintain the relatively rigid complexing cavities of the film.

Acknowledgment. The authors thank CNRS PIRSEM (ARC "Electrodes modifiées par des polymères conducteurs organiques fonctionnalisés") for partial financial support. Prof. D. K. Mitchell is gratefully acknowledged for a critical reading of the manuscript.

Registry No. 1, 100890-92-4; **2**, 104104-93-0; **3**, 104104-94-1; **4**, 88498-43-5; **5**, 141484-30-2; **6**, 115748-16-8; **6** (homopolymer), 141484-32-4; **7**, 141484-31-3; $[\mathrm{Cu}(\mathbf{6})_2]^+$, 116141-15-2; $[\mathrm{Cu}(\mathbf{6})_2]^+$ (homopolymer), 141484-38-0; $[\mathrm{Zn}(\mathbf{6})_2]^{2+}$, 141484-33-5; $[\mathrm{Zn}(\mathbf{6})_2]^{2+}$ (homopolymer), 141484-39-1; $[\mathrm{Ag}(\mathbf{6})_2]^+$, 141484-34-6; $[\mathrm{Ag}(\mathbf{6})_2]^+$ (homopolymer), 141484-40-4; $[\mathrm{Co}(\mathbf{5})_2]^{2+}$, 141484-35-7; $[\mathrm{Co}(\mathbf{5})_2]^{2+}$ (homopolymer), 141484-41-5; $[\mathrm{Co}(\mathbf{6})_2]^{2+}$, 141484-36-8; $[\mathrm{Co}(\mathbf{6})_2]^{2+}$ (homopolymer), 141484-42-6; $[\mathrm{Co}(\mathbf{7})_2]^{2+}$, 141484-37-9; $[\mathrm{Co}(\mathbf{7})_2]^{2+}$ (homopolymer), 141484-43-7.

ESR of the Cationic Triradical of 1,3,5-Tris(diphenylamino)benzene

Kazunari Yoshizawa,[†] Akihisa Chano,[†] Akihiro Ito,[†] Kazuyoshi Tanaka,*,[†] Tokio Yamabe,[†] Hideo Fujita,[‡] Jun Yamauchi,[‡] and Motoo Shiro[§]

Contribution from the Department of Hydrocarbon Chemistry and Division of Molecular Engineering, Faculty of Engineering, Kyoto University, and College of Liberal Arts and Sciences, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan, and Research Section, Rigaku Corporation, 3-9-12 Matsubara-cho, Akishima-shi, Tokyo 196, Japan. *Received January 2, 1992. Revised Manuscript Received April 17, 1992*

Abstract: The ESR spectrum of the cationic triradical of 1,3,5-tris(diphenylamino)benzene (TDAB) is discussed. The tricationic state of TDAB was observed by means of cyclic voltammetry. The orange cationic triradical was prepared by oxidation of TDAB with trifluoroacetic anhydride in the presence of tetra-*n*-butylammonium tetrafluoroborate in $\mathrm{CH_2Cl_2}$. The ESR spectrum of the randomly oriented radicals in the $\mathrm{CH_2Cl_2}$ glass agrees well with the theoretical prediction of a quartet ($S = {}^3/_2$) spin state with a zero-field splitting parameter D' of 13.1 G (0.0012 $\mathrm{cm^{-1}}$). This is the first observation of a high-spin state of a cationic radical.

Introduction

Previously observed cases of ferromagnetism usually involve the spins of either d or f electrons, which presumably play an essential role in magnetic interactions. In recent years, several groups have launched efforts toward the preparation of organic ferromagnets based on molecular crystals and polymers.[1-9] In particular, ferromagnetic intramolecular interaction has been clearly observed in carbenes[3,10] and nitrenes.[6,11] However, the goal of obtaining bulk ferromagnetism in organic solids has been elusive.[12,13] Recently, however, an organic ferromagnet, the β-phase crystal of *p*-nitrophenyl nitronyl nitroxide, with a Curie temperature of 0.60 K was reported by Kinoshita et al.[9]

[†] Department of Hydrocarbon Chemistry and Division of Molecular Engineering, Kyoto University.

[‡] College of Liberal Arts and Sciences, Kyoto University.

[§] Rigaku Corp.

(1) Torrance, J. B.; Oostra, S.; Nazzal, A. *Synth. Met.* **1987**, *19*, 709.

(2) Awaga, K.; Sugano, T.; Kinoshita, M. *J. Chem. Phys.* **1986**, *85*, 2211.

(3) (a) Sugawara, T.; Bandow, S.; Kimura, K.; Iwamura, H.; Itoh, K. *J. Am. Chem. Soc.* **1986**, *108*, 368. (b) Teki, Y.; Takui, T.; Itoh, K.; Iwamura, H.; Kobayashi, K. *J. Am. Chem. Soc.* **1986**, *108*, 2147.

(4) Miller, J. S.; Calabrese, J. C.; Rommelmann, H.; Chittipeddi, S. R.; Zhang, J. H.; Reiff, W. M.; Epstein, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 769.

(5) Kahn, O.; Pei, Y.; Verdaguer, M.; Renard, J. P.; Sletten, J. *J. Am. Chem. Soc.* **1988**, *110*, 782.

(6) Iwamura, H.; Murata, S. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 33.

(7) Chiang, L. Y.; Upasani, R. B.; Goshorn, D. P.; Tindall, P. *Mater. Res. Soc. Symp. Proc.* **1990**, *173*, 15.

(8) Awaga, K.; Maruyama, Y. *J. Chem. Phys.* **1989**, *91*, 2743.

(9) Tamura, M.; Nakazawa, Y.; Shiomi, D.; Nozawa, K.; Hosokoshi, Y.; Ishikawa, M.; Takahashi, M.; Kinoshita, M. *Chem. Phys. Lett.* **1991**, *186*, 401.

0002-7863/92/1514-5994$03.00/0