Electroactive polymer films of silver complexes with intertwined and interlocked ligands: the Ag^I–Ag^0 redox couple as a topological probe†

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The electrochemical properties of bis(2,9-diaryl-1,10-phenanthroline)silver complexes are reported. The redox potentials of the coordinated metal centre are strongly dependent on the topology of the organic backbone surrounding the metal centre and its set of ligands. This particular property can be used for the evaluation of the topological characteristics of different polypyrrole matrices built around entwined 2,9-diaryl-1,10-phenanthroline moieties.

Although the functionalization of electronic conducting polymers (ECP) with a view to obtaining predetermined chemical or physical properties has been extensively studied,[1] there are very few results on the topological properties of these materials, probably owing to the diversity of possible connections, and consequently, the difficulties in characterising the relation between the particular properties of the material and their topological features. To our knowledge, the only studies reported concern the thermodynamic properties of specific types of polymers such as polyrotaxanes and polycatenanes.[2] Elaborations of conducting polymetallorotaxanes using supramolecular approaches, with the aid of transition metals as templating agents, have been recently described.[3]

At present, there is a growing interest in topology in molecular chemistry due to the challenge to build supramolecular edifices displaying new topological properties.[4] Over the last few years, interesting topology related properties have been observed for certain molecular structures such as interlocked macrocycles, especially the enhancement of basicity,[5] kinetic effects,[6] NMR properties[7] and photochemical and photophysical properties.[4f,8] Recently, interesting electrochemical properties have been reported for purely organic catenanes or rotaxanes formed by a self-assembly process.[9] They display cathodic or anodic shifts of the half-wave potentials of the redox subunits included in the host complexing macrocycle, reflecting either the intensity of the interaction between aromatic units or the steric hindrance imposed by the rotaxane structure. Different behaviour has been observed[10] for catenands synthesized by the template effect of a transition metal coordinated to 2,9-diphenyl-1,10-phenanthroline (dpp) units [Scheme 1(A)].They exhibit stabilization of the low oxidation states of the metal ion concerned, this being due to the pseudo-tetrahedral geometry imposed by the phenanthroline units around the metal centre. As a matter of fact, transition-metal complexes of entwined phenanthroline-containing ligands show very similar electrochemical properties. Particular electrochemical characteristics arising from the topological properties of interlocked macrocyclic complexes have been reported[11] and include the emergence of reversibility of the one-electron reduction of the formal Cu^I–Cu^0 redox couple and a cathodic shift of the reduction potential between a Ag^I–Ag^0 catenate and its analogous entwined complex. It should be noted that the index 0 in Cu^0 or Ag^0 does not imply that the metal is zerovalent. It simply means that the monovalent complex has been reduced in a one-electron process to afford a neutral species (overall charge = 0) with no indication of whether this process is metal- or ligand-localized. More recently, electrochemical hysteresis properties have been observed for catenates where one of the macrocyclic subunit contains both di- and ter-dentate ligands[12] Our previous work[13] has demonstrated the electropolymerisation of different metallic complexes with acyclic chelating fragments (end-functionalized dpp) covalently linked to either the nitrogen[13a] atom or the 3-carbon[13b] of the pyrrole unit, through a polymethylene spacer. Removal of the gathering metal centre allows the anchoring of preformed sites in a rigid polymeric conducting network [Scheme 1(B)]. These coordinating sites are able to complex other transition-metal species. An increase in the topological complexity of the precursor for electropolymerisation, by the substitution of one acyclic ligand by the coordinating macrocycle m-30 (a 30-membered 2,9-dpp-containing ring) [Scheme 1(C)], leads to the ECP films deposited on the electrodes exhibiting an enhancement of the electronic accessibility of the redox metal centres.[3a] These electropolymerisations produce random connections, which can be inter- or intramolecular, between pyrrole units. Processes B and C allow the elaboration of ECP-modified electrodes with varying topological properties. Thus, electropolymerisation according to process B produces a multi-entangled criss-cross of molecular wires with possible ring formation leading to ECP films containing local catenane- and rotaxane-like structures, whilst electropolymerisation of preformed rotaxanes produces, after demetallation, a polyrotaxane [Scheme 1(C)]. Consequently, it appears to be interesting to investigate and to compare the topological properties of these different materials.

Here, we report the electrochemical properties of the three silver complexes **1**, **2** and **3**; with the same topographical features but different topologies, by increasing the number of macrocyclic ligands around the metal centre (Scheme 2). The entwined system **1**, the threaded complex **2** and the silver catenate **3** exhibit different electrochemical behaviour for the reduction process of the metal. Hence the formal Ag^I–Ag^0 redox centre can be used as an electrochemical probe to evaluate the topological properties of the differently functionalized ECP films elaborated by utilizing different starting materials. The electrochemical response of the cobalt centre in cobalt-containing films (poly-**5**) prepared with cobalt(II) as a templating centre is not sensitive to the topological properties of the polymeric network. However, this resulting polyrotaxane

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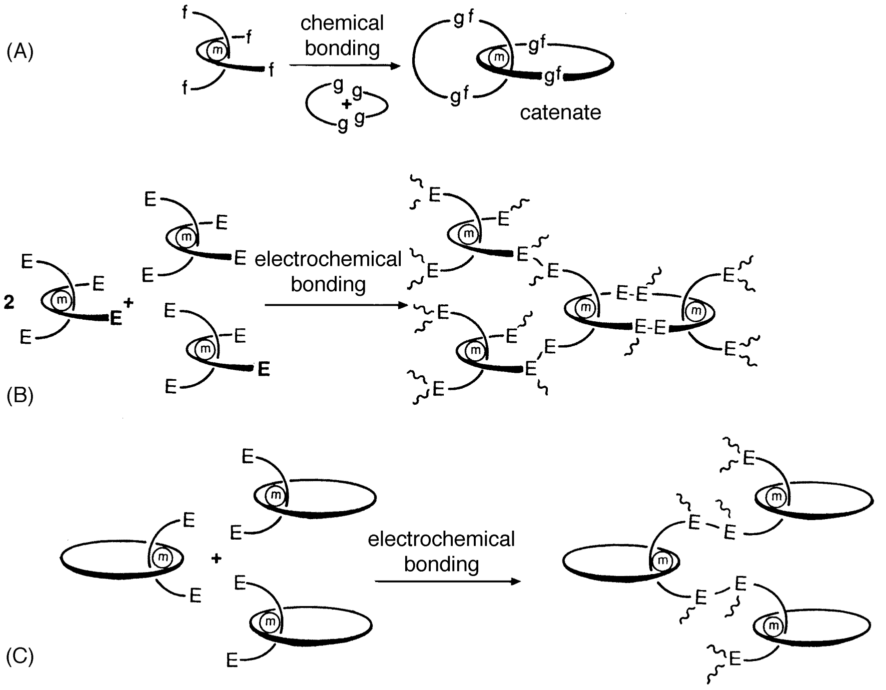
† Dedicated to Professor H. J. Schäfer on the occasion of his 60th birthday.



Scheme 1 Synthetic strategy used for constructing: (A) a [2]catenate, by means of a strategy based on the three-dimensional template effect induced by a transition metal on the molecular fragment represented by f—f; f and g represent functional groups which are able to react to form a covalent bond; (B) multi-entangled criss-cross molecular wires produced by electropolymerisation of preformed entwined complexes; (C) polyrotaxanes, by means of electropolymerisation of suitable rotaxane monomers, where E represents the electropolymerisable unit

like system is able to undergo a reversible complexing–decomplexing process.[3a] Cobalt–silver exchange has therefore been monitored by voltammetric measurements in order to observe the sensitive electrochemical response of silver and to use it as a probe of the topological properties of the network matrix.

Experimental

Chemicals

The synthetic procedures for the synthesis of the macrocycle m-30,[14] the different ligands[13] and the catenate[11] **3** have been previously reported. The complexes **1**, **2**, **4** and **5** were formed in solution immediately prior to the electrochemical experiments by addition of slightly less than the stoichiometric amount of Ag^+ ($AgBF_4$) or Co^{2+} [$Co(BF_4)_2$] to the linear and macrocyclic ligands.

Reagents, electrochemical apparatus and procedure

Electrochemical studies were performed in a dry-box under an argon atmosphere. Acetonitrile (MeCN) (BDH, HiPer Solv) was distilled over P_4O_{10}. Tetraethylammonium tetrafluoroborate (Et_4NBF_4) (Fluka purum) was dried at 100 °C under vacuum for 1 day prior to use. The concentration of the pyrrole units was 4×10^{-1} mol l^{-1} for complexes **1**, **2**, **4** and **5**.

The electrochemical apparatus consisted of PAR 273A from EG&G Princeton Applied Research, monitored by a Hewlett Packard 9836C computer ensuring data acquisition and connected to a Kipp & Zonen recorder. All potentials are relative to a 10^{-2} mol l^{-1} Ag^+–Ag reference electrode. The working electrodes were made of carbon felt ($s = 3$ cm^2).

Elaboration of the films

Anodic electropolymerisation of the functionalized ECP films was performed in MeCN either by repeated potential linear scanning or by electrolysis at a controlled potential of 0.850 V *vs.* the Ag^+–Ag reference electrode, $[Ag^+] = 10^{-2}$ mol l^{-1} in MeCN. The film growth was monitored by anodic cyclic voltammetry. The modified electrodes were washed in pure solvent before further analytical experiments.

As the electrochemical study of the silver complexes turned out to be especially difficult due to non-reproducible adsorption poisoning phenomena on the platinum electrode, electropolymerisation experiments were performed on carbon felt electrodes. The results reported herein concern the first cathodic CV made after electrodeposition of the film.

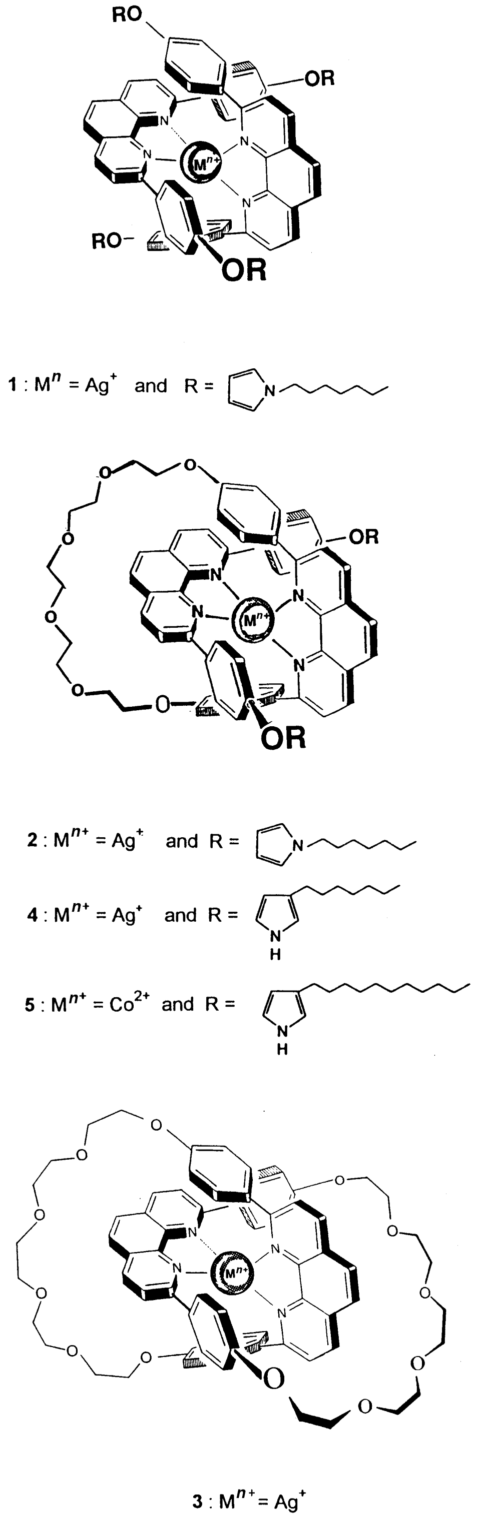
Results and Discussion

Electrochemical properties of free Ag^+ and complexes 1, 2 and 3

The voltammograms of the free Ag^+ ion and complexes **1**, **2** and **3** exhibit the same shape and are characteristic of thin-layer electrochemical behaviour due to the nature of the working electrode (carbon felt) and the low scan rate used. They exhibit an irreversible one electron reduction attributed to the Ag^I–Ag^0 redox centre leading to formal Ag^0 complexes. In addition, the complexes **1** and **2** show irreversible oxidation of the pyrrole units at 0.80 V. The relative intensities of the peaks associated with the silver redox process and the oxidation of the pyrrole units are consistent with the stoichiometry of each complex (number of pyrrole nuclei per metal) and the number of electrons transferred for each electrochemical process. The half-potential values $E_{1/2}$, defined as $(E_{pc} + E_{pa})/2$ (E_{pc} and E_{pa} are the cathodic and anodic peak potentials respectively), and the difference between the cathodic and the anodic peak potential values DE_p for the three complexes **1**, **2** and **3** and for the free silver ion are reported in Table 1.

The redox potential of free Ag^+ at carbon felt determined in CH_3CN is in good agreement with previous published data at a dropping mercury electrode.[15] Only a slight irreversibility of the electron transfer process is observed due to silver desorption during the anodic scan.

As the three complexes **1**, **2** and **3** exhibit the same voltammogram shape as the free Ag^+ ion, it is not possible to determine if their reoxidation occurs with or without partial silver



Scheme 2 Structural formulae of the catenate **3** and of the precursors of the polymers

Table 1 Cyclic voltammetry data for $AgBF_4$ and complexes **1**, **2** and **3**. All potentials refer to Ag^+ (10^{-2} mol l^{-1})/Ag reference in $MeCN–Et_4NBF_4$ (0.1 mol l^{-1}), $v = 5$ mV s^{-1}; potentials were determined by CV on a carbon felt electrode

complex	c/mol l^{-1}	E_{pc}/V	E_{pa}/V	$E_{1/2}$/V	DE_p/V
$AgBF_4$	10^{-2}	−0.07	0.00	−0.04	0.07
1	10^{-3}	−0.24	−0.05	−0.15	0.20
2	2×10^{-3}	−0.40	−0.12	−0.26	0.33
3	10^{-3}	−0.94	−0.44	−0.69	0.50

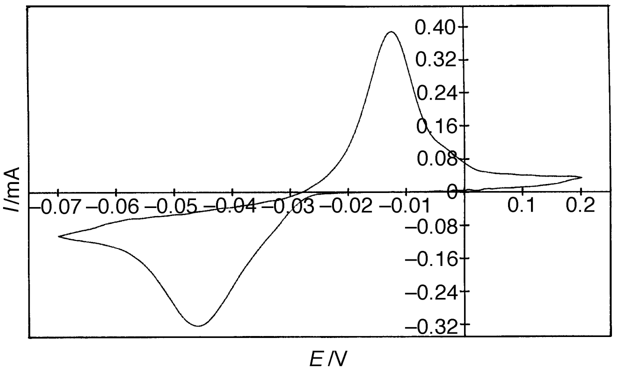


Fig. 1 Cyclic voltammetric response of the silver redox centre of **2**. 2×10^{-3} mol l^{-1} in $MeCN–Et_4NBF_4$ (0.1 mol l^{-1}), sweep rate $v = 5$ mV s^{-1} on a carbon felt electrode, Ag^+ (10^{-2} mol l^{-1})/Ag as reference.

desorption, free silver possibly being formed from the complexes by demetallation during the reductive scan.

The $E_{1/2}$ and DE_p values for the silver redox centre of complex **1** are in agreement with those reported by El Hajbi *et al.*[16] for several phenanthroline complexes of silver which undergo an irreversible one-electron reduction at −0.17 V *vs.* SCE with low DE_p.

Surprisingly, concerning the metal redox response, a relatively strong cathodic shift (0.21 V) of the E_{pc} values is observed between **1** and **2**, together with a remarkable cathodic shift (0.70 V) between **1** and **3** (Table 1). In addition, DE_p increases slightly (0.13 V) between **1** and **2** but increases drastically (0.30 V) between **1** and **3**. This observation shows that each successive substitution of an acyclic phenanthroline ligand by a macrocyclic one induces a strong stabilization of the corresponding silver complex. This remarkable topological effect on the redox properties of the complexed $Ag^I–Ag^0$ centre led us to use it as an electrochemical probe for evaluating the topology of complexes linked to different polypyrrole matrices, *i.e.* their degree of interlocking and entanglement.

Electrochemical properties of silver(I) complexes covalently linked to polypyrrole matrices

The polypyrrole films modified by **1** and **2** display very similar cyclic voltammograms composed of both the characteristic anodic and cathodic response of the N-substituted polypyrrole matrix centred at 0.30 V and, in the cathodic potential range, an irreversible one-electron transfer attributed to the reduction of the metal centre (Fig. 2). Further scans produce main changes in the metal centre response, indicating silver electrodeposition. As the formal zerovalent silver complexes are very unstable, all reported results concern the first scan. The

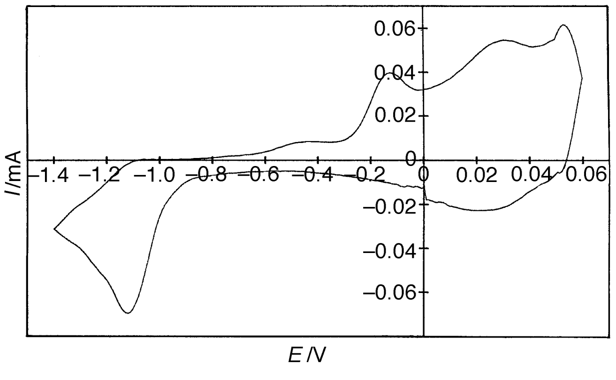


Fig. 2 Cyclic voltammetry of poly-**2** on a carbon felt electrode ($s = 3$ cm^2) in $MeCN–Et_4NBF_4$ (0.1 mol l^{-1}), $v = 5$ mV s^{-1}, Ag^+ (10^{-2} mol l^{-1})/Ag as reference. Synthesis of the film performed at 0.85 V in $MeCN–Et_4NBF_4$ (0.1 mol l^{-1}), at a monomer concentration of 2×10^{-3} mol l^{-1}, by passing 14 mC cm^{-2}.

Table 2 Cyclic voltammetry data of the substituted polypyrroles determined by CV on a carbon felt electrode *vs.* Ag^+ (10^{-2} mol l^{-1})/Ag reference in MeCN–Et_4NBF_4 (0.1 mol l^{-1}), $v = 5$ mV s^{-1}

polymer	metal centre E_{pc}/V	E_{pa}/V	ppy matrix $E_{1/2}$
poly-**1**[a]	−1.10	−0.35	+0.30
poly-**2**[b]	−1.10	−0.20	+0.30
poly-**5** after Co^{2+}–Ag^+ exchange[c]	−1.10	−0.10	−0.20
free-ligand film	< −2.0		−0.20

[a,b]Synthesis of the film performed at 0.85 V in MeCN + Et_4NBF_4 0.1 mol l^{-1} + 4×10^{-3} mol l^{-1} pyrrole units by passing 14 mC cm^{-2}, [a]$s = 4$ cm^2, [b]$s = 3$ cm^2. [c]Synthesis of the film by ion exchange within an analogous film polymer with cobalt as the complexing transition metal (see text).

cathodic peak is situated at −1.1 V for the two films while, on the anodic scan, the associated reoxidation peak is observed in the potential range where the polymer matrix is conductive (Table 2). These reduction peaks are not due to the reduction of protons which are formed during electropolymerisation and which could be trapped by the polymer matrix and/or initiate partial decomplexation of silver, despite the relative stabilities of silver catenates and proton [2]catenates. Indeed, dipping of the modified electrodes into a basic 10^{-3} mol l^{-1} solution of 2,4,6-trimethylpyridine in MeCN before the first voltammetric measurement led to no significant modification of the voltammogram. For each film, the ratio of the metal centre reduction peak area to the area of the polypyrrole matrix redox peak is in agreement with its own stoichiometry, the number of electrons transferred for the electrochemical process concerned and the doping level values (*ca.* 0.2).[13a]

As the reoxidation of the zerovalent complex occurs in the conducting matrix potential range, DE_p has no significance and it is not possible to determine $E_{1/2}$. So the discussion will concern only the E_{pc} values of the one-electron transfer of the Ag^I–Ag^0 centre. Both polymers exhibit the same one-electron reduction potential value of the silver centre, −1.1 V, corresponding respectively to a cathodic potential shift of 0.86 and 0.70 V between the precursors **1** and **2** and their polymers. This potential is measured for a solid-phase species, in a potential range in which the polymer matrix is electrically insulating, which is expected to create an overpotential as compared to the same redox species in solution. Nevertheless, this strongly negative value of the silver(I) complex reduction potential E_{pc} for the polymers is remarkable. It reflects the pronounced stabilization of the complex as compared to the monomer in solution and is likely to originate from the highly entangled nature of the matrix. The fact that this reduction occurs in all the polymers at the same potential values suggests that the two films poly-**1** and poly-**2** have very similar multicatenate-like network structures.

To take advantage of these observations and of the special relationship between the topological properties of the matrix backbone and the reduction potential of the silver(I) complex used as a probe, it can be useful to substitute any metal of a polymer to be tested by silver(I). To demonstrate the usefulness of the technique, ion-exchange experiments have been performed on analogous 3-substituted polypyrroles covalently linked to Co(dpp,m-30)$^{2+}$. The successive cobalt exclusion–silver inclusion reactions have been performed on a poly-**5** modified electrode. The poly-**5** is demetallated by action of thiocyanate ions by dipping the polymer film into an MeCN–H_2O/KSCN (0.1 mol l^{-1}) solution and subsequently metallated by silver ion by dipping in an MeCN–$AgBF_4$ (0.1 mol l^{-1}) solution. Cobalt demetallation and silver metallation were monitored by cyclic voltammetry. After treatment, the film always displays the characteristic electroactivity of 3-substituted polypyrrole which occurs near −0.20 V, loss of electrochemical activity as a result of the removal of cobalt and the appearance of a reduction process located, here again, at −1.10 V and assigned to the complexed Ag^I–Ag^0 electrophore. This identical reduction potential value for the complexed silver ion in three films issued from three different precursors, the entwined complex **1**, the thread and ring complex **2** and the thread and ring **5**, after silver–cobalt exchange, suggests that these films have very similar polyrotaxane network structures. Consequently, in the specific case of the poly-**1**, inter- or intra-molecular ring formation must occur during electropolymerisation. The linkage position of the silver complex through the alkyl chain on the pyrrole ring, *i.e.* 3-substituted or N-substituted pyrrole, has no influence on the topological properties of the films.

Conclusion

We had previously noticed that the redox potential of the Ag^I–Ag^0 couple was strongly dependent on the topology of its 2,9-diphenyl-1,10-phenanthroline based ligands, being more negative in the case of the catenate structure than in the case of the entwined one by 700 mV. In this study we took advantage of this particular property to characterise the topology of bis(2,9-diaryl-1,10-phenanthroline)silver(I) based complexes covalently linked to polypyrrole matrices. In the case of coordinating polymers built around other metallic templates, the topology could be evidenced by exchanging the metallic centre for Ag^I and determining the redox potential of the corresponding electroactive polymer. This observation is of course valid for the present family of coordinating polymers only.

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