Letter

Electrode-deposited films of polyrotaxanes: electrochemically induced gliding motion

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Using the three-dimensional template effect of copper(I) or copper(II), a macrocycle incorporating two different chelating units was threaded by a coordinating molecular fragment whose two ends bear pyrrole nuclei; after electropolymerization, an electroactive film was obtained that clearly showed pirouetting of the ring induced by reducing the five-coordinate copper(II) complex to copper(I). The motion is driven by the difference in the stereoelectronic preferences of copper(I) and copper(II). The present system allows motions of the monovalent complex only.

If the notion of molecular rearrangement is clear, that of controlled molecular motions in multi-component systems[1] is more ambiguous, since no fixed reference can be found easily. When a ring moves along a string on which it is threaded,[2] it is of course identical to the movement of the string inside the ring. One way to solve the problem of what is moving and what is not, is to immobilize physically one component of the system or to attach it onto a surface, so that 'motionless' points or fragments will be clearly identified.

In this communication, it is shown that the molecular motions ('gliding') of a hetero-bis-chelating macrocycle threaded by a coordinating polymer string can be triggered electrochemically, the process being confined to the electrode surface onto which the multicomponent system was electrodeposited.

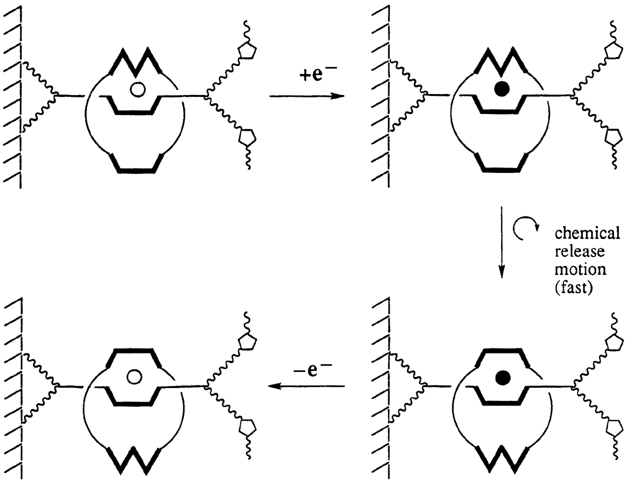
Indeed, we showed recently[3] that it is possible to imprison coordinating macrocycles in a polypyrrole network. These electroactive films were prepared by oxidation on a carbon felt electrode of a rotaxane-like transition metal complex, consisting of a 3-functionalized pyrrole covalently linked to a 2,9-diaryl-1,10-phenanthroline fragment threaded through a coordinating macrocycle using the metal [cobalt(II) in this case] as templating agent. It is noteworthy that, after demetallation of the template, the rings were still entrapped in the entangled structure, and could be used to bind again either the initial template agent [cobalt(II)] or another transition metal such as copper(I).

In this work, we have synthesized analogous electroactive films, built on a polyrotaxane organic backbone, in which the wheel of the rotaxane is now a hetero-bis-chelating macrocycle (**2**). The thread remains a 2,9-diaryl-1,10-phenanthroline complexing core functionalized by electropolymerizable pyrrole rings, the metal being copper. By varying the electrochemical potential of these electroactive films, gliding of the ring around the polymer string was expected.

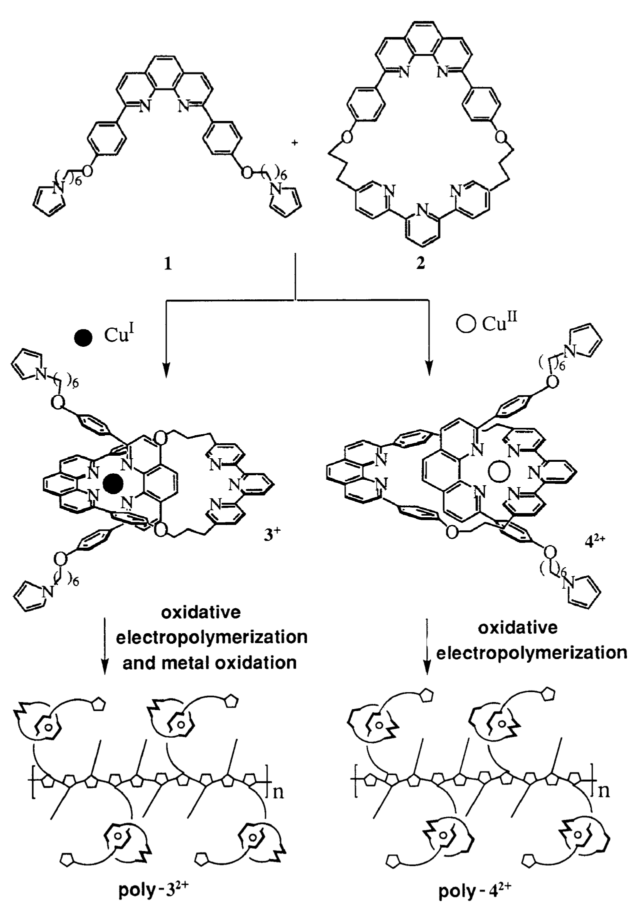
The principle of the molecular motions[4] is shown in Scheme 1. It is based on the difference of preferred coordination number for the two different redox states of the coordinated metal: 4 for Cu^I and 5 for Cu^{II}. It was observed, in homogeneous solutions, in the case of a [2]-catenane built on the same complexing sub-units as our system, that the rate of rotation of the cycles is highly dependent, among other factors, on the initial coordination number and oxidation state of the metal. Thus, reduction of pentacoordinated Cu^{II} ($Cu^{II}N_5$) to pentacoordinated Cu^I (Cu^IN_5) was rapidly followed by formation of tetracoordinated Cu^I (Cu^IN_4) whereas the interconversion of tetracoordinated Cu^{II} ($Cu^{II}N_4$) into pentacoordinated Cu^{II} ($Cu^{II}N_5$) was much slower.

In order to observe potential ring motions, we studied two different kinds of films, synthesized from either tetracoordinated Cu^I or pentacoordinated Cu^{II} structures.

The syntheses of $\mathbf{3}^+$ and $\mathbf{4}^{2+}$ (Scheme 2) uses the same preassembly principle as for the syntheses of catenates.[5] The thread **1** contains the 2,9-diphenyl-1,10-phenanthroline coordinating core functionalized at both ends by a pyrrole ring.



Scheme 1 Principle of the electrochemically triggered gyration of a hetero-bis-chelating macrocycle entrapped on a polymer coordinating thread. The stable five-coordinate divalent complex (top left, the white circle represents Cu^{II}) is reduced to an intermediate five-coordinate monovalent species (top right, the black circle represents Cu^I). This compound undergoes a slow reorganization process to afford the stable four-coordinate Cu^I complex (bottom right). Upon oxidation, the four-coordinate divalent state is formed (bottom left). Due to the presence of a polypyrrole matrix, the conformational change that regenerates the starting complex is too slow to be observed with the present system



Scheme 2 Prerotaxanes 3^+ and 4^{2+} are prepared by mixing stoichiometric amounts of acyclic ligand **1**, bis-coordinating macrocycle **2** and Cu^I (black circle) or Cu^{II} (white circle). Conversion of 3^+ or 4^{2+} to polypyrrolic networks is performed by anodic oxidation

The ring **2** is a 33-membered macrocycle containing bidentate and terdentate chelating sites: 2,9-diphenyl-1,10-phenanthroline (dpp) and 2,2′;6′,6″-terpyridine (terpy) moieties. **1** is threaded through **2** using copper as a templating agent.[5] Copper(I) leads to $\mathbf{3}^+$ and copper(II) to $\mathbf{4}^{2+}$. The syntheses of $\mathbf{1}^6$ and $\mathbf{2}^{4,7}$ have been reported previously. The complex $\mathbf{3}\cdot BF_4$ was obtained by mixing stoichiometric amounts of **1**, **2** and $[Cu(MeCN)_4]BF_4$ in CH_2Cl_2–MeCN under argon at room temperature. Evaporation of the solvent and column chromatography (alumina, CH_2Cl_2–2% MeOH as eluent) afforded the desired threaded complex as a dark-red solid in 50% yield. The light green complex $\mathbf{4}\cdot(BF_4)_2$ was prepared following the same procedure but using $Cu^{II}(BF_4)_2$ instead of $[Cu(MeCN)_4]BF_4$ and has not been purified.

Electropolymerization of $\mathbf{3}^+$ and $\mathbf{4}^{2+}$ actually led to the deposition of electroactive films, as earlier demonstrated for different metal complexes of 2,9-diaryl-1,10-phenanthroline complexing moities linked at both ends to pyrrole units. In our case, for both $\mathbf{3}^+$ and $\mathbf{4}^{2+}$, after electropolymerization the Cu was in the divalent oxidation state (white circle on Scheme 2). Depositions of poly-$\mathbf{3}^{2+}$ and poly-$\mathbf{4}^{2+}$ onto carbon felt electrodes were performed by repetitive scans of the electrode potential between −0.200 and 0.850 V for $\mathbf{3}^+$ and 0.000 and 0.850 V for $\mathbf{4}^{2+}$. Concentrations of the monomers were 2×10^{-3} and 1.4×10^{-3} mol L^{-1} for $\mathbf{3}^+$ and $\mathbf{4}^{2+}$, respectively, the electrolytic medium itself consisted of a 10^{-1} mol L^{-1} solution of tetraethylammonium tetrafluoroborate in acetonitrile.

The redox potentials of the reference couples $Cu^{II}N_5/Cu^IN_5$[4] and $Cu^{II}N_4/Cu^IN_4$,[8] as well as that of the doping-undoping process of *N*-substituted polypyrrole matrices,[6] have already been measured in previous work and are now known accurately. The reversible reduction of pentacoordinated Cu^{II}—the higher oxidation state of the metal being stabilized both by a dpp fragment and a terpy derivative—occurs at a relatively cathodic potential around −0.3 V *vs.* Ag^+ (10^{-2} mol L^{-1})/Ag. On the other hand, the overlapping of the oxidation signal of the strongly stabilized tetracoordinated Cu^I—the lower oxidation state of the metal complexed by two dpp units—with the response of the polymer matrix has been clearly shown in previous work for poly-$[Cu\cdot\mathbf{1}_2{}^+]$.[6] It occurs at a relatively high potential, around 0.3–0.4 V *vs.* Ag^+/Ag. Thus, electrochemical analysis of the behaviour of the polymer films represents a versatile tool for the observation of the coordination isomers present in the matrix, if any, and their possible interconversion.

Fig. 1 represents the cyclic voltammetry (CV) response of a poly-$\mathbf{4}^{2+}$ electrode surface film in a fresh conducting acetonitrile solution. The first anodic scan (dotted line) shows the characteristic signal of the poly-*N*-substituted pyrrole (0.35 V). The cathodic scan (full line) shows the presence of a nearly reversible redox system whose potential value ($E^0 = -0.31$ V) identifies the presence of a pentacoordinated Cu^{II} moiety. Since the CV wave around −0.3 V is reversible (Cu^{II}/Cu^I), no geometrical changes occur during the scan (0 to −0.56 V; −0.56 to −0.05 V; scan rate = 5 mV s^{-1}). The absence of any gliding motion within the few tens of seconds of the experiment is confirmed by the persistance of the anodic peak after the cathodic scan. In this CV a peak near 0.0 V is detected, which probably corresponds to an electroactive impurity formed during the film growth process; it may originate from partial dethreading of the copper(II) complex precursor, $\mathbf{4}^{2+}$.

After polarizing 60 min at −600 mV, a spectacular modification of the electrochemical response was observed [compare Fig. 2(*b*) to Fig. 2(*a*)]. The intensity of the $CuN_5{}^{2+/+}$ redox system decreased noticeably whereas the peak localized at 0.35 V increased and sharpened. This variation could be explained by the disappearance of Cu^IN_5 and its transformation into a Cu^IN_4 system whose redox signal is concomitant with that of the *N*-polypyrrole matrix. A longer polarization (24 h) at the same potential completed this modification [Fig. 2(*c*)]. The isomerization of the five-coordinate Cu^I complex into a more stable tetrahedral Cu^I complex is achieved by the gliding of the macrocycle around the polymer-coordinating thread.

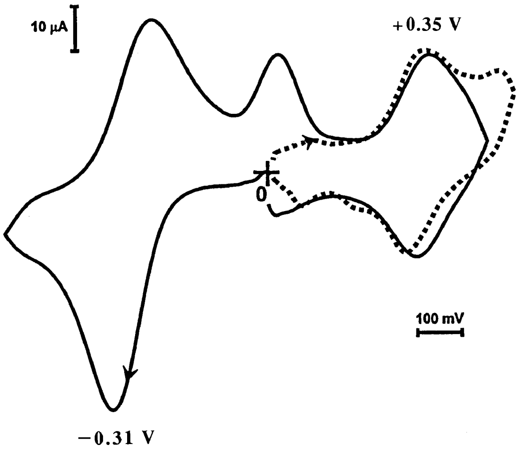


Fig. 1 Cyclic voltammetry (5 mV s^{-1}) of the [poly-$\mathbf{4}\cdot(BF_4)_2$] film deposited on carbon felt (9.6 cm^2), by scanning the electrode potential between 0 and +0.850 V *vs.* Ag^+ (10^{-2} mol L^{-1})/Ag until 7 mC cm^{-2} were consumed. Initial concentration of $\mathbf{4}\cdot(BF_4)_2$: 2×10^{-3} mol L^{-1}. Dotted line: first anodic scan after electropolymerization (0 to +0.52 to 0 V). Full line: first cathodic scan after electropolymerization. The potential was swept successively from 0 to −0.56 V, from −0.56 to 0.47 V, from +0.47 to 0 V

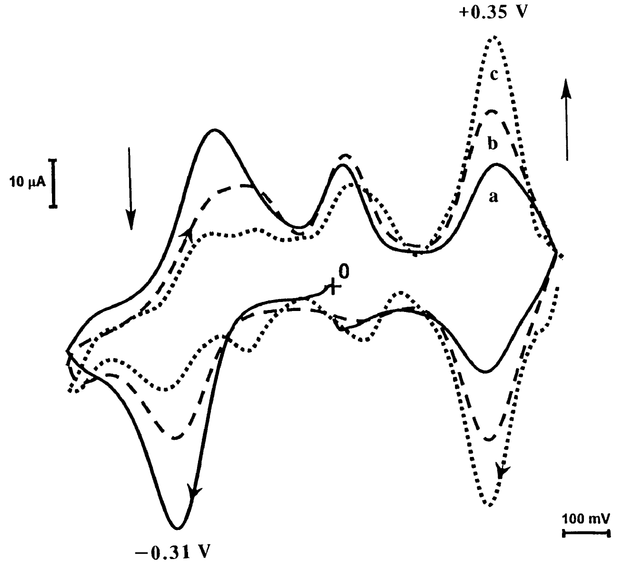


Fig. 2 Cyclic voltammetry of the same film as in Fig. 1. (*a*) Full line: as in Fig. 1; (*b*) dashed line: CV after polarization (60 min) of the film at −0.6 V; (*c*) dotted line: CV after 24 h polarization at the same potential

The reverse phenomenon, that is the $Cu^{II}N_4$ to $Cu^{II}N_5$ transition, could be expected when oxidizing the $Cu^{I}N_4$ state (poly-**3**$^+$, obtained from poly-**4**$^{2+}$ by reduction followed by molecular motion) to Cu^{II}. Nevertheless, on the timescale of our experiments (24 h), no rearrangement of $Cu^{II}N_4$ could be evidenced by CV. This inertia was confirmed by the following analogous experiment. Poly-**3**$^{2+}$ was elaborated by electropolymerization of the tetrahedral **3**$^+$ monomer and simultaneous oxidation of the monovalent copper. For poly-**3**$^{2+}$, only one redox system appeared at +0.38 V, corresponding again to the simultaneous $Cu^{I/II}N_4$ and doping/undoping redox processes. Moreover, even after a long polarization time (24 h) at +0.5 V, no signal corresponding to a $Cu^{I/II}N_5$ (poly-**4**$^+$/poly-**4**$^{2+}$) system appeared at −0.3 V.

For molecular species in solution, the gliding of coordinating macrocycles one within the other, induced by changing the redox state of the metal, has already been observed. In the present work, we could demonstrate the pirouetting of imprisoned macrocycles in a polymeric matrix, stimulated again by a redox change. Moreover, it could be observed that the ease ($Cu^{I}N_5$ to $Cu^{I}N_4$) or difficulty ($Cu^{II}N_4$ to $Cu^{II}N_5$) of molecular motions parallel those of analogous systems in solution.

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