Redox-Responsive Metallo-Supramolecular Polymers and Gels Containing bis-Terpyridine Appended Cyclam Ligand

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This manuscript is dedicated to our colleagues from the Department of Chemistry in Conception (Chile) who were recently affected by the earthquake.

Summary: Soluble coordination polymers and gels built from a polytopic ligand containing two terpyridine units linked by a azamacrocyclic group are presented. This system originally incorporates two different types of metal complexes in the same polymer chain which induces remarkable electrochromic properties and a rare redox triggered reversible sol-gel transition.

Keywords: coordination polymers; electrochromism; gels

Introduction

One of the greatest challenges facing physics, chemistry, and materials science is to find a way to structure molecules in functional superlattices, molecular devices or responsive materials.[1] In this context, the domain of soluble coordination polymers, *i.e.* supramolecular architectures spontaneously obtained in solution through self-assembly of metal ions and polytopic bridging ligands is of particular interest.[2] Such systems are expected to exhibit essential properties of conventional organic polymers (viscosity, processability). The presence of metal-ligand interactions in the structure gives access to a wide range of redox, magnetic, spectroscopic and dynamic properties particularly suited to the development of *stimuli*-responsive and intelligent materials.[2–4]

The properties and potential applications of these soluble organic/inorganic hybrid systems greatly depend on the nature of the binding sites and metal ions but also on the *spacer* (linker between the terminal coordinating units), which might confer original structural and physico-chemical properties (viscoelasticity, solubility) to the final material. Various linkers (*e.g.* rigid, flexible, linear, curved or chiral) have yet been experimented,[2] but soluble coordination polymers incorporating coordinating groups as spacer are scarcer.

Experimental Part

All reagents were commercial grade and used without further purification. Tetra-*n*-butylammonium perchlorate (TBAP) was purchased from Fluka. Ligand **L** and the corresponding coordination polymers were prepared following the procedure reported in ref. [2g]. Electrochemical experiments were done on millimolar solutions of complexes (or millimolar equivalent of monomer complex) in DMF containing 0.1 M TBAP, in a conventional three-

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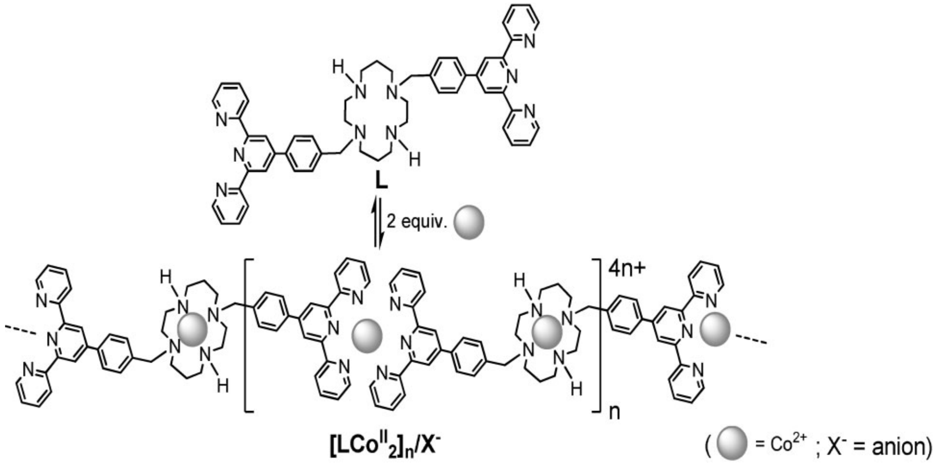

Scheme 1.
Structure of ligand **L** and **$[L(Co^{II})_2]_n/X^-$** polymers.

electrode cell at 298 K using a CH Instrument potentiostat (CHI 660B). The reference electrode was $Ag/AgNO_3$ (10 mM in CH_3CN containing 0.1 M TBAP) and the regular ferrocene/ferrocenium ($E_{1/2} = +0.054V$ *vs* Ag/10 mM $AgNO_3$ under our experimental conditions) redox couple was used as internal reference. *All potentials given in the text are referred to the ferrocene/ferrocenium couple*. The counter electrode was a large area platinum gauze in DMF + 0.1 M TBAP isolated from the working compartment by a glass frit. Cyclic voltammetry (CV) curves were recorded at a scan rate of 0.1 V s^{-1} using a platinum disc (2 mm in diameter) electrode, polished with 1 μm diamond paste. Electrolyses were performed at controlled potential using a platinum plate ($\sim 2 \text{ cm}^2$) as the working electrode. Due to the polyelectrolytic nature of the polymers, electrolyses of the gel phases were done without addition of supporting electrolyte. UV-vis spectra were recorded on a Varian Cary 100 spectrophotometer using quartz cells (l = 1 cm). Viscosimetry measurements have been performed on a Ostwald viscosimeter (Prolabo) using a capillary of 0.42 mm diameter appropriate for Newtonian liquids undergoing a Poiseuille type flow. The temperature was regulated at $T = 19 \pm 0.3$ °C. The apparatus was calibrated using water and a standard oil (ThermoFisher Scientific, reference E7) with a 5.3 mPas dynamic viscosity. The density of the specimens was measured with a DMA 35N apparatus at the operating temperature. The measurements were repeated 5 times. Rheological measurements were performed with a controlled stress rheometer RS600 Thermo Electron equipped with a cone-plate Ti geometry (gap = 105 microns). A glass cup and a silicon oil ring were used to limit the solvent evaporation during the measurement at a regulated temperature ($T = 15.2 \pm 0.2$ °C).

Results and Discussion

Here, we report some properties of soluble metallopolymers obtained with a polytopic ligand (**L**, Scheme 1) containing two chelating terpyridine (terpy) terminal units linked through a complexing cyclam macrocycle (cyclam = 1,4,8,11-tetraazacyclotetradecane). The presence of cyclam *i*) allows the incorporation of additional metal ions in the polymeric chain[2e] and *ii*) may confer unusual structural and switching properties owing to the known ability of cyclam complexes to undergo isomerization processes under redox *stimulus*.[5] The metallopolymers described here exhibit a rare

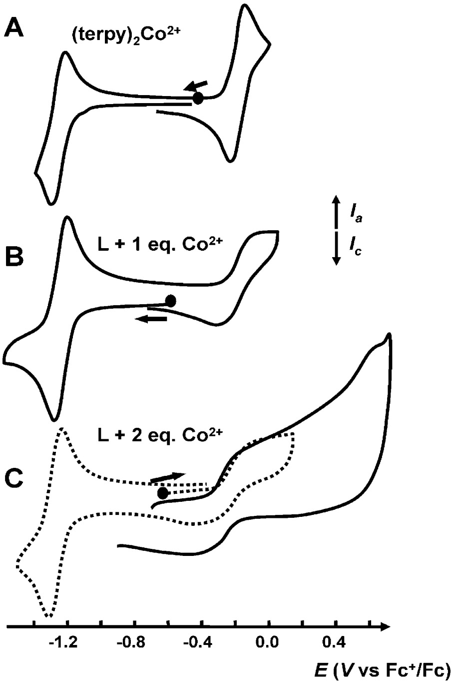

Figure 1.

Cyclic voltammograms of A) $(terpy)_2Co^{2+}$ complex , B) L + 1 molar eq. of Co^{2+} and C) L + 2 molar. eq. of Co^{2+}. Scan rate: $0.1\,V\,s^{-1}$.

redox-triggered gel-sol transition[2g] and remarkable electrochromic properties.

L was easily prepared in a three-step procedure[2g] and its metallation in DMF with $Co(ClO_4)_2$ in a 1:1 molar ratio afforded a red solution ($\lambda_{max} = 521\,nm$; $\varepsilon = 2220\,M^{-1}\,cm^{-1}$) suggesting the formation of a $(terpy)_2Co^{2+}$ derivative in which the cyclam unit remains metal-free.[3a] Analysis of this solution by cyclic voltammetry (Figure 1) confirmed this assumption since the electrochemical signature, showing three reversible reduction waves at $E_{1/2} = -1.14\,V$, $-1.95\,V$, and $-2.31\,V$ (*vs* Fc^+/Fc) and one oxidation wave at $E_{1/2} = -0.19\,V$, fully matches that of the $(terpy)_2Co^{2+}$ reference complex (Figure 1A).[6] Upon addition of a second molar equivalent of $Co(ClO_4)_2$ to the previous solution, an additional and irreversible oxidation wave appeared at $E_p = \sim +0.6V$ attributed to the oxidation of the Co^{2+} ion in the cyclam core.[7] These redox data proved the formation of both {cyclam-Co^{2+}} and {$(terpy)_2Co^{2+}$} subunits. Evidence for the formation of the metallopolymer $\mathbf{[L(Co^{II})_2]_n/X^-}$ (Scheme 1, $\mathbf{X^-} = ClO_4^-$) was given by viscosity measurements: a reduced viscosity $\eta_r = 1.85$ ($\eta_r = \eta/\eta_s$; η_s = viscosity of the solvent) was measured after addition of two molar equivalents of $Co(ClO_4)_2$ to a 13 mM solution of **L** in DMF, supporting the hypothesis of the formation of polymer-like species.[2c–d]

Electro-oxidation of the red $\mathbf{[L(Co^{II})_2]_n/ClO_4^-}$ polymer in DMF at $E = +0.4V$ afforded a stable orange-yellow solution (Figure 2). This color change was assigned to the selective oxidation of all {$(terpy)_2Co^{2+}$} to {$(terpy)_2Co^{3+}$} units in the polymer.[3a] Subsequent oxidation at $E = +1V$ led to a stable green solution ($\lambda_{max} = 666\,nm$; $\varepsilon = 500\,M^{-1}\,cm^{-1}$), attributed to the formation of {cyclam-Co^{3+}} subunits in the structure.[5a] The initial red solution was readily restored by reduction of the oxidized green solution at $E = -0.4V$. The large variety of colors obtained by straightforward redox *stimulus* clearly illustrates the advantage, for electrochromic applications, of incorporating metal ions in the spacer.

Another remarkable property of these polymers is their ability to form gels. Indeed, when the metallation of **L** was performed in DMF by addition of 2 molar equivalents of $CoCl_2$, red gels were spontaneously formed ($\mathbf{[L(Co^{II})_2]_n/Cl^-/DMF}$ system; concentration <1 wt%). Conversely, when the metallation of **L** was performed in CH_3CN, the use of $Co(NO_3)_2$ led to gels whereas a liquid phase was obtained with $CoCl_2$ was used. These results outline the important role of anions and solvents in the gelating process and are in accordance with recent studies[4d-e,8] showing that electrostatic interactions and solubility are crucial and subtle parameters controlling the formation of supramolecular gels. It should be outlined that **L** is not a gelator by itself and that no gelation was observed when only one molar equivalent of metal ion per ligand unit was added (*i.e.* when the cyclam unit remains metal-free).

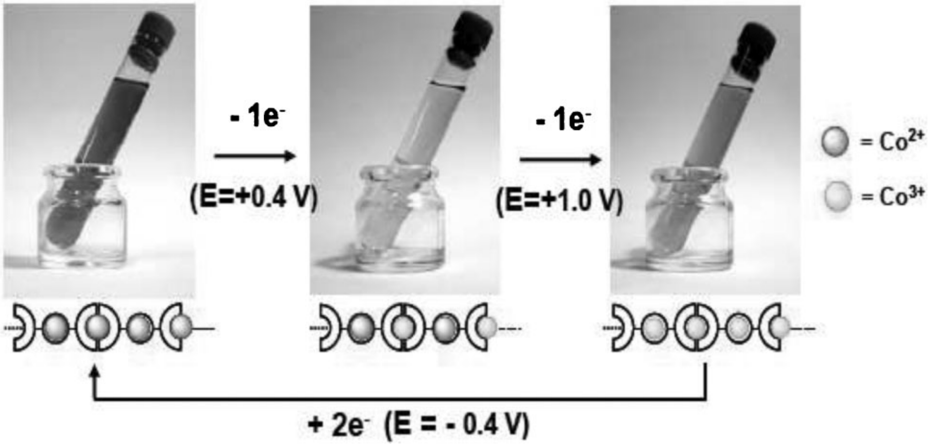

Figure 2.
Electrochromic behavior of the $[\mathrm{LCo^{II}}_2]_n/\mathrm{ClO_4^-}$ polymer (the indicated number of electrons transferred are given per unit of monomer).

Although the presence of Co^{2+} in the macrocycle is not required to form self-assembled chains, it introduces additional positive charges in the polymer that modify its solubility, and also rigidifies the spacer unit, which appears to be favourable for gelation.

Rheometry was used to characterize the gel character of the viscoelastic $[\mathrm{L(Co^{II})_2}]_n/\mathrm{Cl^-}$/**DMF** material. When submitted to a sinusoidal oscillatory shear stress, the storage *modulus G'* appears to be in-phase with the applied stress as expected with an elastic solid (Figure 3A). This behavior can

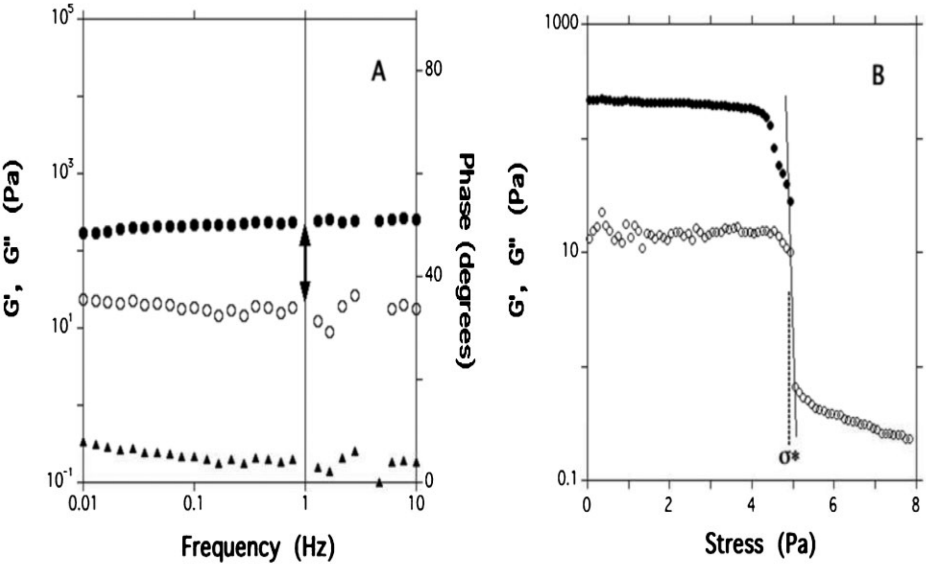

Figure 3.
A) Dynamic rheology of the $[\mathrm{L(Co^{II})_2}]_n/\mathrm{Cl^-}$/**DMF** gel at a constant applied stress (0.1 Pa). Concentration = 0.33% in mass. ● = G', ○ = G'' (the arrow illustrates a ratio $G'/G'' \approx 12$ at $\nu = 1$ Hz). **B**) Variation of the elastic and loss *moduli* as a function of an increasing oscillatory shear stress at $\nu = 1$ Hz. The yield stress is pointed at $\sigma^* = 4.8$ Pa.

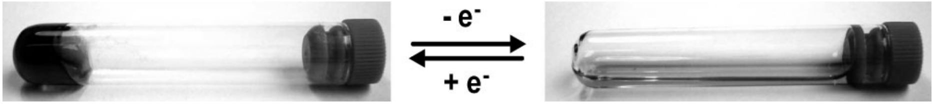

Figure 4.
Redox-controlled reversible gel-to-liquid transition.

be observed over an extended range of frequencies from 0.01 Hz to *ca.* 10 Hz. Concomitantly, the loss *modulus* G'' exhibits an amplitude about one order of magnitude lower than the elastic shear modulus G' and both G', G'' profiles are plateaus. These features are typical of gels.[9] The metallo organogel presents also a threshold value of the applied stress (σ^*) at which the solid-like network fails.

Figure 3B illustrates the relative stability of the gel up to 4 Pa beyond which a solid-to-liquid phase transition suddenly occurs. Interestingly, the absolute values of the yield stress (4.8 Pa) and elastic shear *modulus* (*ca.* 215 Pa at $\nu = 1$ Hz) that characterize respectively the brittleness and elasticity of the gel are weak. These values are concentration-dependent, frequently following a quadratic scaling law, and are much weaker than values found in ordinary molecular organogels.[9b] Nevertheless, a system of the class of metallo-supramolecular gels, made up of ditopic ligands based on modified oxypyridine and ethylene glycol moieties,[4] showed comparable values. Without going into the details of the complex rheology of self-assembled networks, it can be claimed that the connectivity of the bis-terpy-cyclam metallo-suprapolymeric network is insured through weak interactions in standard preparation conditions, contrasting with the high affinity of the metal ions with the two coordinating sites. Moreover, when increasing the temperature of the **$[L(Co^{II})_2]_n/Cl^-/DMF$** gel up to 100 °C, the gel phase was maintained.

Gel formation using organic molecules has been widely reported in the literature,[9] but the use of metal-coordination to assist gelation is much less frequent.[10] A particular interest of metallo-containing gels and viscoelastic solutions are their ability to exhibit *stimuli*-responsive performances.[4,8a,11] The **$[L(Co^{II})_2]_n/Cl^-/DMF$** gel was thus electrolyzed at +1V using a conventional three-electrode device. In addition to the expected red to green color change (electrochromic behavior), a remarkable gel-to-liquid transition was observed (Figure 4). The reverse process was obtained by exhaustive reduction at −0.4 V of the Co^{3+} to Co^{2+} units. This gel-to-liquid transition may be accounted for the introduction of supplementary positive charges in the polymer chains upon oxidation, which possibly affects the solubility of the system and destabilizes the gel. Modification of the coordination modes and topological reorganization of the cyclam metal core upon electron transfer[5] certainly also contribute to this process.

Conclusion

In conclusion, we report here a novel class of *stimuli*-responsive coordination polymers and gels that incorporate metal ions in the cyclam spacer units of a terpyridine-based network. A three colors electrochromic system and a remarkable redox-triggered sol-gel transition have been achieved. These versatile systems, whose structural characterizations are under progress, are promising candidates for the elaboration of heterometallic and organized architectures.

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