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Soluble Heterometallic Coordination Polymers Based on a Bis-terpyridine-Functionalized Dioxocyclam Ligand

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Soluble homo- and heterometallic coordination polymers containing transition metal cations (Cu^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+} ions) were prepared in a two-step procedure using a polytopic bis(terpyridine)dioxocyclam ligand **1**H_2 (dioxocyclam = 1,4,8,11-tetraazacyclotetradecane-5,7-dione). These supramolecular systems incorporate two different metal complexes, the metal cations being located both between two terpyridine units and in the macrocyclic framework. The characterization of these soluble architectures was investigated by cyclic voltammetry, mass spectrometry, viscosimetry, and UV–vis absorption and electron paramagnetic resonance (EPR) spectroscopies. Our results clearly indicate the formation of well-organized heterometallic polymers in which two different metal ions alternate in the self-assembled structure. These investigations furthermore brought to light an original acid-controlled disassembling process of the homometallic copper(II) polymer into dinuclear complexes.

Introduction

Supramolecular polymers fabricated by self-assembly processes represent an interesting class of materials because of their potential applications in material science and functional devices.[1] In particular, metal coordination has been used to prepare a wide range of supramolecular polymers. However, if there is an extensive literature about coordination polymers in the solid state,[1d] the number of metallopolymers that has been characterized in solution is much less extensive. Recent research is now devoted to the conception of soluble one-dimensional (1D) to three-dimensional (3D) metallo-polymers in which supramolecular chains are spontaneously built-up in solution through the formation of coordination bonds between metal ions and polytopic bridging ligands (Scheme 1).[2]

In these macromolecular metal-containing systems, the relation between concentrations, binding constants, and chain trajectory can be exploited to elaborate materials with specific behaviors. Importantly, these materials may exhibit the properties of standard organic polymers (viscosity, processability, etc.), but the incorporation of metallic species in the polymer chain opens new perspectives giving access to magnetic, redox, optical, electrochromic, or specific mechanical properties. In addition, the use of kinetically labile metal complexes may provide to the coordination polymers dynamic features relevant to the construction of environment-adaptable materials.[2,3] These dynamic coordination polymers are thus promising systems for the development of smart stimuli-responsive molecular materials, and a major challenge in this emerging domain is to design and elaborate functional self-organized architectures with tunable properties.

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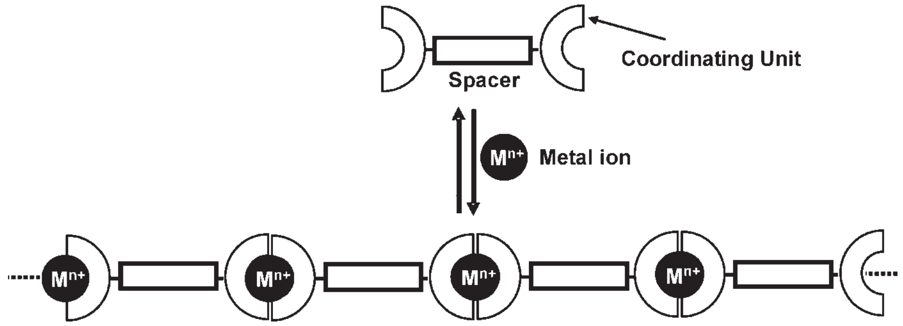
Scheme 1. Schematic Formation of a 1D Coordination Polymer



Because of its ability to form strong and well-defined 2:1 (L:M^{n+}) octahedral complexes with a range of transition metal cations,[4,5] the tridentate 2,2′:6′,2″ terpyridine is certainly one of the most popular building block for the preparation of coordination polymers.[2,4] On the other hand, the design of the spacer itself (i.e., the bridge between the coordinating units, see Scheme 1) is also essential since it might introduce a great variety of structural arrangements and/or physicochemical properties (e.g., viscosity, optical, mechanical properties, etc.) to the targeted metallo-polymer. Numerous organic spacers exhibiting various shapes, rigidities, and conjugations have already been reported[2] but a promising and almost unexplored route to build-up multiresponsive coordination polymers relies on the use of complexing spacers. This strategy may especially allow the introduction of additional metal ions in the polymer chain to produce homo- or heterometallic coordination polymers with a wider range of properties and potential applications.

Recently we have demonstrated that cyclam derivatives (cyclam = 1,4,8,11-tetraazacyclotetradecane) are particularly suited as spacers because of their exceptional coordination properties and the abundant available literature describing efficient and straightforward *N*- or *C*- substitution strategies.[6] Metal complexes of cyclam have furthermore been shown to exhibit switching properties[7] that can be advantageously exploited to produce redox responsive coordination polymers. For example, we have reported a novel class of such responsive polymers.[8,9] In these systems, the nature and redox state of the metal ions located in the macrocyclic spacer units drastically influences the properties (length, shape, solubility, color, etc.) of the polymeric materials as exemplified by a rare reversible redox controlled gel to liquid transition.[8] An original acid−base driven interconversion between a mononuclear copper(II) complex and coordination polymers was also presented.[9]

Another particular interesting property of polytopic ligands having two chemically different coordination sites is their ability to form heterometallic coordination polymers, that is, polymers that incorporate two kinds of ions or metal complexes in the same chain. Advanced molecular materials could be obtained by the integration in the same polymer architecture of different metal complexes presenting complementary functions, for example, a photosensitive metal complex could activate a close catalytic metal center.

Here we describe the preparation and the characterization of organized homo- and heterometallic coordination polymers based on the dioxocyclam ligand **1**H$_2$ (dioxocyclam = 1,4,8,11-tetraazacyclo-tetradecane-5,7-dione[10]), following the synthetic strategy depicted in Scheme 2. The **1**H$_2$ "monomer" was formed by selective *trans*-disubstitution of the 1,8-dioxocyclam by two tolyl-terpyridine units. This derivative was shown to selectively bind copper(II) inside the macrocyclic framework when the metalation was conducted in the presence of a mild base (K_2CO_3), and the red stable mononuclear **1Cu** complex was readily isolated.[9] This complex features two metal free terpyridine fragments which can be advantageously used to prepare homo- and heteronuclear polymers **1CuM** by reaction with one molar equivalent of a divalent transition metal cation (**M** = Fe, Co, Ni, or Cu, Scheme 2).

Results and Discussion

Preparation of 1H$_2$ and Its Metal Complexes 1CuM. The **1CuM** complexes were prepared following the two-step strategy represented in Scheme 2. **1**H$_2$ was prepared in good yield following a previously described procedure[9] based on the reaction of 4′-(4-bromomethylphenyl)-2,2′:6′2″-terpyridine[11] with *trans*-dioxocyclam[10] in refluxing CH_3CN in the presence of base. When one molar equivalent of Cu^{2+} cations was added to a solution of **1**H$_2$ in MeOH in the presence of K_2CO_3 in excess, a pink-red species (λ_{max} = 503 nm) was formed and was isolated after precipitation by addition of diethyl ether and finally

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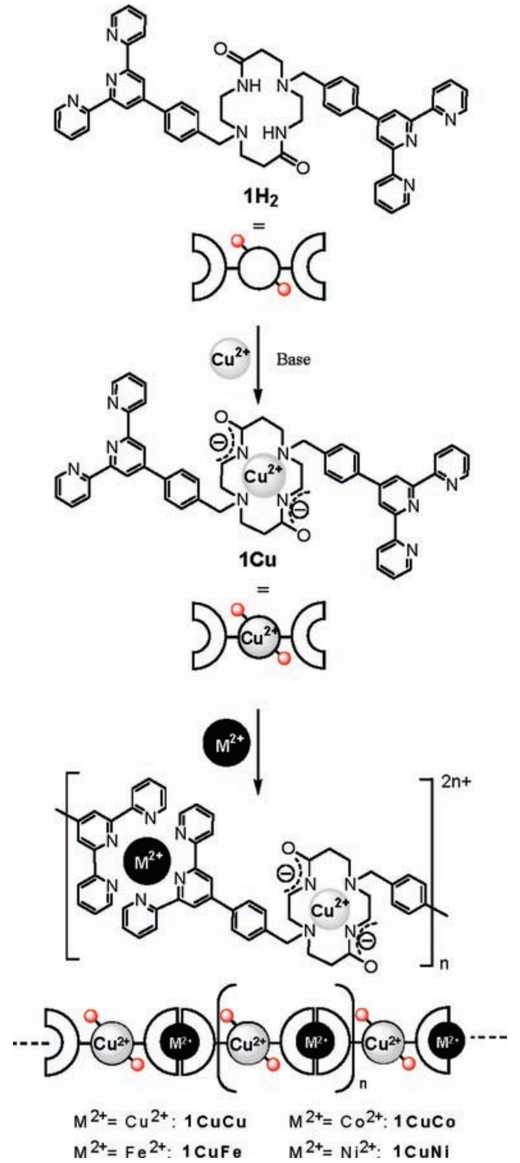
Scheme 2. Schematic Preparation of the Polynuclear Species **1CuM** (**M** = Fe, Co, Ni, or Cu)



purified by chromatography on alumina. This red compound was characterized by mass spectrometry, elemental analysis, FTIR and UV−visible spectroscopies and electrochemistry (data are given in Table 1) and was identified as the neutral square planar *trans*-dioxocyclam-Cu(II) **1Cu** complex formed by metal-assisted deprotonation of the two macrocyclic amide fragments, both terpyridine units remaining free (Scheme 2).[9] In a second step the formation of polynuclear complexes **1CuM** (Scheme 2) was achieved by addition of one molar equivalent of a transition metal ion M^{2+} (M^{2+} = Fe^{2+}, Ni^{2+}, Co^{2+}, or Cu^{2+}) to a solution of **1Cu** in methanol. In the case of Fe^{2+} and Co^{2+}, the initially light-red solution of **1Cu** turned out instantaneously purple and deep red, respectively, in agreement with the formation of the corresponding bis(terpyridine)-metal complexes. All these materials were isolated by precipitation with diethyl ether in 80−90% yields.

Characterization of the Metal Complexes. The isolated metal complexes **1CuM** were characterized by mass spectrometry, electrochemical and spectroscopic methods (see Table 1 and the Experimental Section). Bis(terpyridine)metal complexes synthesized with the 4′-phenyl-2,2′:6′6″-terpyridine were used as reference compounds (**2M**, with M = Fe, Co, Ni, Cu, Scheme 3).

(i). UV−visible and FTIR Analysis. The UV−vis absorption spectrum of the isolated **1CuCu** complex dissolved in MeOH indicated the presence of bis(terpyridine)Cu^{2+} units in the structure, featuring an absorption band at λ_{max} = 687 nm similar to that observed in the same condition with **2Cu** (Table 1). The d→d transition still seen at λ_{max} = 501 nm confirmed that copper ions remained also present in the dioxocyclam framework.[9,12] The UV−vis spectra corresponding to the heterometallic complexes also unambiguously showed the formation of bis(terpyridine)M^{2+} units (see Table 1). As an example, the band at λ_{max} = 572 nm and its molar absorptivity coefficient (ε ∼25000) recorded for the purple **1CuFe** complex were a clear signature for the quantitative formation of bis(terpyridine)Fe^{2+} complexes.

The presence of Cu^{2+} in the cyclam-based spacer of the **1CuM** self-assembled complexes was furthermore confirmed by FTIR spectra, which show a ν_{CO} stretching band around 1545 cm^{-1} against 1645 cm^{-1} in the free ligand.[9] All these results fully corroborate the presence of metal ions between the terpyridine units and in the dioxocyclam spacer.

(ii). Mass Spectrometry Analysis. Molecular weight determinations of dynamic coordination polymers still represent a real challenge.[2,13] Usually, most available methods such as gel permeation chromatography or mass spectrometry indeed turned out to generate inconclusive results because of the polyelectrolytic nature of the systems and the inherent lability of the metal−ligand interactions.[13] Actually, coordination polymers are thermally equilibrated polymers, and the molecular weight of such self-assembled species is dependent upon the concentration of the complexes, the temperature, and various thermodynamic constants of the aggregation reactions. However, in the present study, ESI-MS spectrometry (Electropray Ionization, positive mode) appeared particularly helpful to characterize the heterometallic **1CuM** species: even if only short oligomers could be identified because of fragmentation processes during the experiments, the relative position of each metal ion in the structures could be determined using isotopic patterns.

A dicationic $\{\mathbf{1}_2\mathbf{Cu}_2\mathbf{M}\}^{2+}$ fragment containing two deprotonated dioxocyclam, two Cu^{2+}, and one M^{2+} ion (M = Fe, Co, Ni, or Cu) was systematically observed on the ESI-MS spectra recorded with all the **1CuM** complexes. As an illustration, the experimental and calculated spectra corresponding to the trinuclear $\{\mathbf{1}_2\mathbf{Cu}_2\mathbf{Ni}\}^{2+}$ fragment centered at m/z = 961 are shown in Figures 1A and 1B, respectively. In addition, the calculated spectra of some hypothetical $\{\mathbf{1}_2(\mathbf{Cu})_n(\mathbf{M})_m\}^{2+}$ species ($m + n = 3$) featuring three Cu^{2+} cations or one Cu^{2+} and two Ni^{2+}

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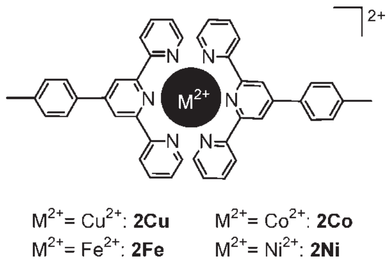
Table 1. Characteristic Visible Absorption Bands and Electrochemical Data Recorded with the Reference Complexes and **1CuM** Polymers

		electrochemical data $E_{1/2}$ $(\Delta E_p)^{b,c}$,V				
compounds	$\lambda_{\max}$, nm^a (ε, L mol^{-1} cm^{-1})	ligand centered reduction	(Tpy)M$^{II/I}$	(Cy)Cu$^{II/I}$	(Cy)Cu$^{III/II}$	(Tpy)M$^{III/II}$
2Cu	687 (73)	e	−0.733 (0.080)			d
2Fe	572 (25800)	−1.640 (0.080); −1.730 (0.080)	d			0.600 (0.080)
2Ni	793 (56)	−1.830 (0.110)	−1.625 (0.090)			d
2Co	519 (2800)	−1.990 (0.070)	−1.185 (0.080)			−0.225 (0.070)
1Cu	503 (156)	−2.465 (0.080)		−1.475 (0.085)	+0.435 (0.085)	
1CuCu	500 (170); 687 (100)	e	$E_{pc} = -0.855$	d	+0.480 (0.130)	d
1CuFe	575 (24700)	−1.600 (0.070); −1.730 (0.095)	d	−1.420 (0.080)	$E_{pa} = 0.510$	+0.650(0.080)
1CuNi	787 (45)	−1.875 (0.110)	−1.595 (0.080)	−1.425 (0.120)	+0.495 (0.060)	d
1CuCo	522 (1900)	$E_{pc} = -2.090$	−1.140 (0.090)	−1.520 (0.180)	+0.510 (0.180)	−0.225 (0.090)

[a] In MeOH. [b] Because of the low solubility of some compounds in MeOH in the presence of supporting electrolyte, experiments were conducted in DMF + 0.1 M TBAP; E (V) vs $E_{1/2}$(ferrocenium/ferrocene); (TPy)M: electron transfer centered on the metal ion located between two terpyridine units, (Cy)Cu: electron transfer centered on the copper(II) ion located in the dioxocyclam unit. [c] $E_{1/2} = (E_p{}^a + E_p{}^c)/2$ at 0.1 V s^{-1}; $\Delta E_p = E_p{}^a - E_p{}^c$. [d] Not observed under these experimental conditions. [e] Not observed because of the prior electrodeposition of Cu^0.

Scheme 3. Bis(terpyridine) Complexes (**2M**) Used As Reference Compounds



ions are shown on Figure 1C and 1D, respectively. These signals that correspond to disordered fragments containing two or three successive units based on the same metal cation would be experimentally observed if metal exchange occurred during the self-assembling process. Such fragments being not observed in the experimental spectra, these results thus corroborate the expected alternation of the metal ions in the heterometallic structures.

In the case of the **1CuFe** system, a longer fragment was observed on the ESI-MS spectrum with an isotopic pattern centered at $m/z = 727$. This signal was attributed to the tetracationic pentanuclear species $\{\mathbf{1}_3\mathrm{Cu}_3\mathrm{Fe}_2\}^{4+}$ containing three monomer units, three Cu^{2+} and two Fe^{2+} ions (Figure 1E). Here again, the comparison with spectra calculated for different stoichiometries (Figure 1F−H) unambiguously shows that the polymer is formed from alternating dioxocyclam-Cu and bis(terpyridine)Fe moieties.

(iii). Electrochemical Investigations. The electrochemical characterization of the **1CuM** complexes (**M** = Fe, Co, Ni, or Cu) was performed by cyclic voltammetry (CV) in *N*,*N*-dimethylformamide (DMF) containing tetra-*n*-butylammonium perchlorate (TBAP, 0.1 M) as the supporting electrolyte (DMF was used because of the low solubility of some complexes in MeOH in the presence of TBAP). Representative curves are shown in Figure 2, and the electrochemical data are summarized in Table 1. To assign the observed electron transfers, the reference compounds **1Cu** and **2M**[14] were studied under the same experimental conditions. For all the complexes, the oxidation processes were centered on the metal cations whereas metal and ligand-centered reductions were observed (see Table 1 for assignment). As previously reported,[9] the Cu^{2+} ion in the mononuclear **1Cu** complex was reversibly reduced at $E_{1/2} = -1.47$ V and oxidized at $E_{1/2} = +0.43$ V to form the corresponding mononuclear copper(I) and copper(III) complexes, respectively.

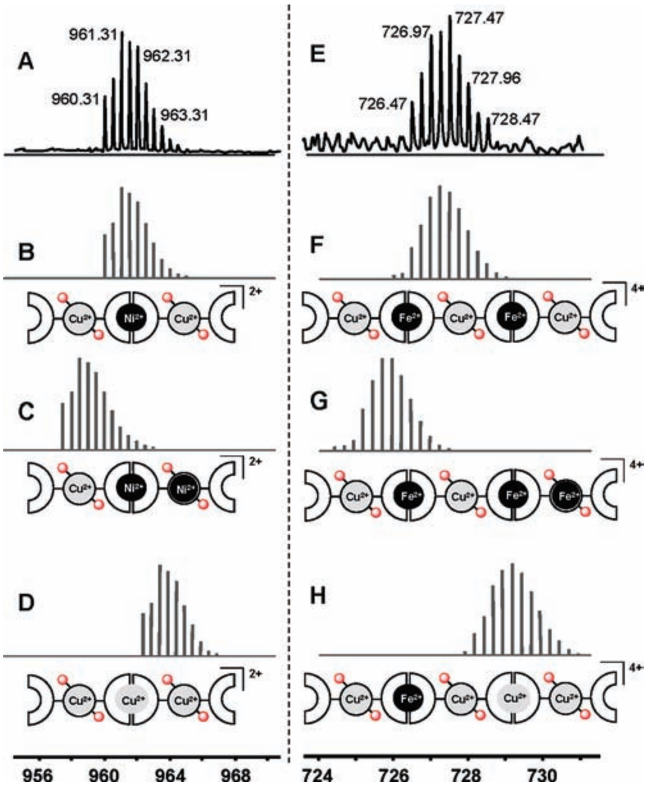


Figure 1. ESI-MS spectra of trinuclear fragments of **1CuNi** (left) and pentanuclear species of **1CuFe** (right). A and E correspond to experimental data and B, C, D, F, G, and H are calculated spectra.

Logically, the electrochemical signatures of the polynuclear **1CuM** complexes roughly correspond to the superposition of those of the reference derivatives **1Cu**

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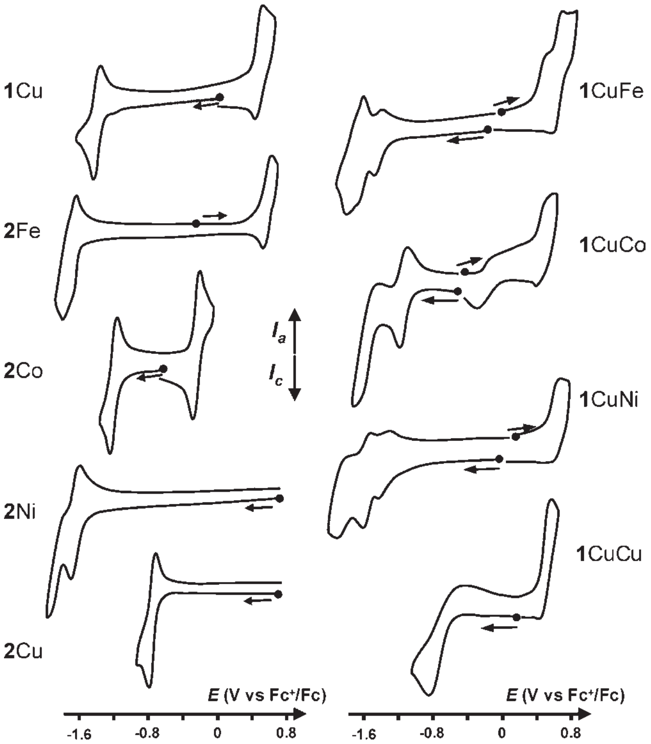

Figure 2. Cyclic voltammograms of **1Cu**, **2M**, and **1CuM** (M = Cu, Co, Ni, and Fe) species in DMF + TBAP (0.1 M). Scan rate 0.1 V s^{-1} (normalized currents).

and the corresponding **2M**. Such behavior is well-illustrated in Figure 2 that shows the cyclic voltammogram of the **1CuCo** system: copper(II) and cobalt(II) centered oxidation and reduction potentials are close to those measured with **1Cu** and bis(terpyridine)Co derivatives.[15] These data indicate that the redox active units in the polymer behave almost independently in the polymer chain, and it can be concluded that there are none or only very weak electrochemical interactions between two vicinal metallic ions. This result was expected considering the non-conjugated nature of the **1**H_2 ligand. It is also interesting to note that these macromolecules can be regarded as real electron-reservoirs since, except for **1CuCu**, at least four reversible or quasi-reversible electron-transfer processes have been observed under our experimental conditions. Depending on the nature of M^{2+} in the **1CuM** self-assembly, the first oxidation or reduction process can be centered either on the linker (macrocyclic complex) or on the terminal terpyridine connectors. For instance, Cu^{2+} cations are oxidized at a lower potential than Fe^{2+} cations in **1CuFe** but at a higher potential than Co^{2+} in **1CuCo**.

In addition, the absence of electrochemical signal corresponding to the presence of bis(terpyridine)Cu units in the **1CuM** structures is a strong indication that no metal exchange occurred during the synthesis of these complexes and that metal ions of different natures regularly follow one another in the macromolecular chain (the dioxocyclam units containing copper(II) ion and the second metal ion being pinched between two terpyridine chelates).

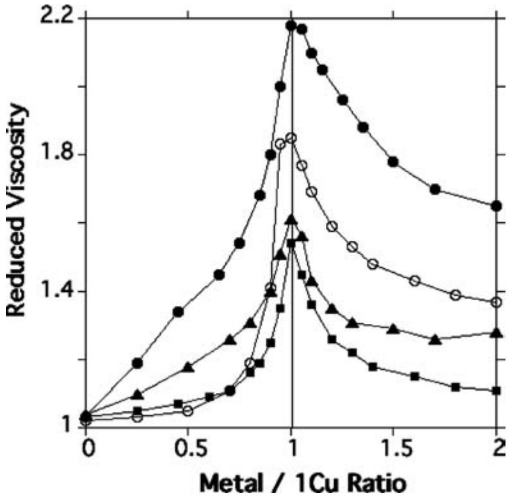

Figure 3. Viscosimetry experiments. Stepwise addition of metallic salt (II) solutions to a solution of **1Cu** (C_0 = 13 mM). Full lines are guidelines. (●), $Fe(BF_4)_2$; (○), $Co(BF_4)_2$; (▲), $NiCl_2$; (■), $Cu(OTf)_2$.

(iv). Viscosimetry Experiments. When a bridging "monomer" such as **1Cu** reacts with a stoichiometric amount of metal ion, 1D polymer/oligomer chains or rings can potentially be formed.[2h,16,17] The self-assembling of **1Cu** with transition metal ions was thus investigated by viscosimetry experiments: this technique can give good qualitative information on the polymerization degree in metallorganic aggregates[8,9,17] and can be used to establish the polymeric character of the soluble **1CuM** materials.

Figure 3 displays the variation of the reduced viscosity $\eta_r = \eta/\eta_s$ (η_s being the viscosity of the solvent) as a function of the molar ratio M^{2+}/**1Cu** in EtOH/DMF. In these experiments, the initial concentration of **1Cu** was 13 mM and the M^{2+}/**1Cu** ratio was varied from 0 to 2.

All experiments led to the same profile with an increasing reduced viscosity up to an apex for a M^{2+}/**1Cu** molar ratio of 1, followed by a decrease of the reduced viscosity for higher ratios. The presence of a maximal η_r value at a 1:1 metal on ligand ratio can be unambiguously related to an increase of the average chain contour length and is in agreement with the formation of linear coordination polymers. It is important to note that the maximal reduced viscosity value depends on the metal ion type: the apex extended in the range $1.54 < 1.60 < 1.85 < 2.2$ for the series $Cu^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+}$. These values depend on the degrees of polymerization of the supramolecular coordination polymers (i.e., longer chains are obtained with Fe^{2+}) and are essentially related to the stability constants of the mono or bis(terpyridine) complexes. At this stage, only qualitative trends of the effect of added metallic cations on the viscosity can be discussed since parameters such as the polydispersity of the aggregated species, the attractive and repulsive interactions between them, and the balance between hydrodynamic

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and Brownian forces should also be considered. These values of η_r at the apex are in full agreement with those measured by Schubert and coworkers for high molecular weight coordination polymers based on poly(ethylene oxide) spacers.[17] In addition, it is interesting to note that a maximal reduced viscosity of 1.54 was obtained for the **1CuCu** polymer, whereas a $\eta_{r_{\max}}$ of only 1.26 was measured[9] when 1 equiv of Cu^{2+} was added directly to a solution of **1**H_2 without base, leading to the polymer in which the dioxocyclam unit remains metal free. This difference suggests that the metal-containing spacer is rigidified in the **1CuCu** species compared to the metal-free macrocycle and certainly adopts a square planar geometry which promotes the formation of longer 1D polymer chains.

Beyond M^{2+}/**1Cu** = 1, the reduced viscosity decreased for all metal ions. This effect was indicative of the presence of reversible complexation processes and can be explained by the fragmentation of the 1D polymer chains into shorter species, increasing the proportion of lower molecular weight complexes with two metallic ends. It is important to note that the change in the reduced viscosity upon addition of an excess of metal ions appeared also metal-dependent. Consistently, when the M^{2+}/**1Cu** ratio approaches 2, the sequence Cu < Ni < Co < Fe was still observed, and the value of the viscosity indicated that non-negligible volume fractions of self-assembled polymeric species with significant molecular weights remained in the solutions. This behavior was related to the sequence of stability constants of two types of complexes, a first one where a metal ion is coordinated by a single terpyridine unit (stability constant K_1) and a second type, in which a metal ion is coordinated by two terpyridine units (stability constant K_2). Ideally, if $K_2 \gg K_1$ the bis-terpyridine complex (hence a polymer chain in this case) is present in solution, even at a large excess of metal ion and a stable viscosity should be observed above the ratio of 1. In the case of $K_1 \geq K_2$, beyond a M^{2+}/monomer ratio of 1, the mono-(terpyridine) complex is favored relative to the bis-(terpyridine) one, and the profile of the reduced viscosity versus stoichiometry should be roughly symmetric with weak η_r final values at stoichiometry 2. Experimentally, this last case was observed only with Cu^{2+}. This result was expected since K_1 and K_2 present similar values for this ion, and stable mono(terpyridine)-copper(II) complexes can be easily obtained when a 1:1 (metal/ligand) molar ratio is used.[9,17,18] For the other metal ions, the sequence of η_r observed at stoichiometry 2 indicates also the sequence of K_1 with respect to K_2, and logically, the higher viscosity was observed with Fe^{2+}.

(v). Electron Paramagnetic Resonance (EPR) Spectroscopy. X-band EPR spectra have been recorded for all samples including references complexes in DMF at 100 K. Since **2Fe** is diamagnetic, no signal was observed in the EPR spectrum. **2Ni** (S = 1) was also X-band EPR silent because of the large magnetic anisotropy of the complex. By contrast, **1Cu** and **2Co** presented characteristic S = 1/2 EPR spectra with observable hyperfine coupling originating from the nuclear spin $^{55}I = 3/2$ and $^{59}I = 7/2$ of the Cu^{2+} and Co^{2+} ions, respectively (Figure 4). The EPR spectrum of **1Cu** displayed an axial signature comparable to analogous tetra-coordinated Cu^{2+} complexes in square planar geometries with an electronic ground state $3d_{x^2-y^2}$.[12a] Concerning **2Co**, under our experimental conditions of temperature and concentration, only the ground spin state S = 1/2 was observed, although it has been shown that an S = 3/2 contribution can be expected at 100 K.[19] The orthorhombic symmetry indicated by the g values is consistent with a D_{2d} symmetry.

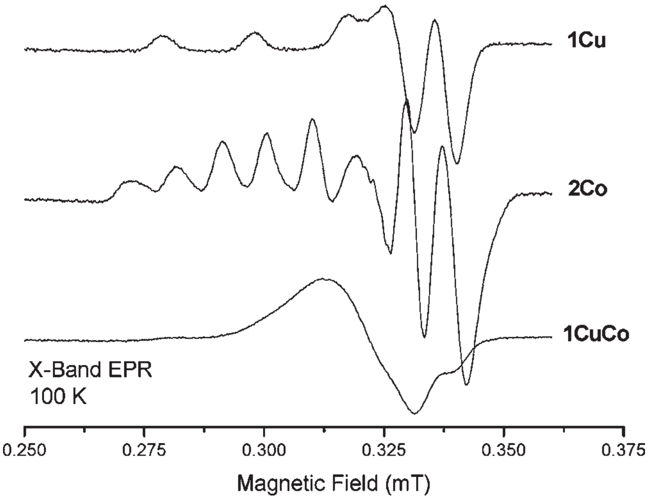

Figure 4. X-Band EPR spectra of **1Cu**, **2Co**, and **1CuCo** in DMF at 100 K (concentration = 15 mM).

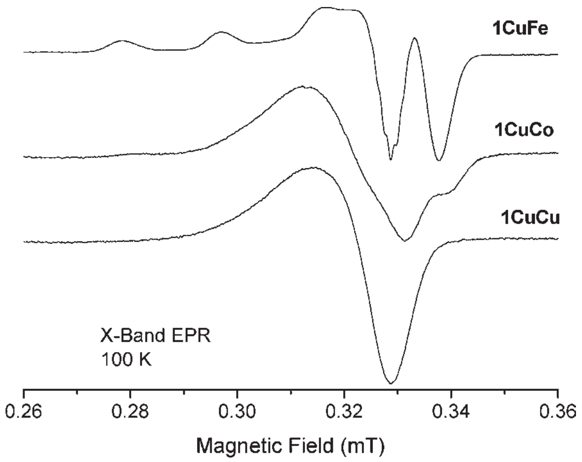

Figure 5. X-Band EPR spectra of **1CuFe**, **1CuCo**, and **1CuCu** in DMF at 100 K (concentration as monomer: 15 mM).

The EPR spectra of the **1CuM** polymers appeared to be strongly influenced by the nature and spin state, that is, the paramagnetism of the M^{2+} ion (Figures 4 and 5). The broad EPR signature recorded with **1CuCo** was clearly not a simple addition of signals attributed to the **1Cu** and **2Co** units (Figure 4). The significant line broadening especially prevented the observation of Cu and/or Co-based hyperfine interactions. In agreement with

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electrochemical results that did not present significant interactions between metal centers, this EPR spectrum was not characteristic of a strong magnetically coupled system. Two types of interactions can be taken into account, the exchange magnetic interaction, which is generally dominant, and the dipolar interaction. A strong antiferromagnetic exchange coupling would lead to a diamagnetic system, whereas a strong ferromagnetic coupling would afford additional EPR lines at least arising from the resulting $S = 1$ ground spin state. The EPR spectrum of **1CuCo** could be thus explained by the existence of weak magnetic interactions between vicinal metallic ions and/or of interchains dipolar interactions between metal ions, the latter hypothesis being less plausible since the shape of the EPR spectrum appeared to be concentration-independent.

While results similar to those obtained with the **1CuCo** polymer were observed with the **1CuCu** system, our investigations on **1CuNi** were greatly limited by the unusual line width of the EPR signal, covering few hundred gauss at a concentration of 15 mM. Because of the low solubilities of these compounds, it was thus not possible to record a spectrum at high concentration. Finally, a remarkable similarity was obtained between the signature of **1CuFe** and **1Cu**. This result unambiguously excludes magnetic interactions between chains. The signal broadening, which significantly increased with the spin state of M^{2+} ($Fe^{2+} < Cu^{2+} = Co^{2+} < Ni^{2+}$), was thus mainly attributed to weak (exchange and/or dipolar) magnetic interactions between vicinal metallic ions along the polymeric chain.

Acid-Controlled Disassembling of 1CuCu. As shown above with viscosimetry experiments, when two molar equivalents of Cu^{2+} cation are added to a solution of **1Cu**, mono(terpyridine)Cu^{2+} adducts are formed with solvent molecules or counteranions completing the coordination sphere of the metal ion. In addition, we have previously demonstrated that the Cu^{2+} ion can be readily removed from the dioxocyclam unit in the presence of acid because of the protonation of both amide groups.[9]

Taking advantage of this promising acid-responsive feature, we were keen to investigate the effect of acid on the self-assembled architectures **1CuCu**. Addition of trifluoromethanesulfonic acid (2.5 mol equiv by dioxocyclam unit) to a solution of **1CuCu** in methanol led to drastic color changes from red-brown to green. The evolution of the solution was followed by UV−visible spectroscopy (Figure 6).

The main absorption band instantaneously experienced a bathochromic shift from $\lambda_{max} = 503$ nm to $\lambda_{max} = 530$ nm (spectrum a to b, Figure 6). In agreement with previous studies,[9,12] this 530 nm absorption band was attributed to a d→d transition in the monoprotonated **1HCuCu** intermediate, wherein copper is bound to only three nitrogen atoms of the dioxocyclam unit, one amide function being protonated. This band at 503 nm then progressively disappeared, and the initial band at $\lambda_{max} = 687$ nm corresponding to the signature of the bis(terpyridine)Cu was slightly red-shifted and more intense (Figure 6, curves b to c). These changes can be attributed to a disassembling process originated by the dissociation of the dioxocyclam-Cu(II) complexes and to the progressive release of free Cu^{2+} ions promoting the formation of end-capping mono(terpyridine)Cu complexes to afford, in conclusion, the tetracationic dinuclear complex **$1H_2Cu_2$** (Scheme 4). The formation of this dinuclear monomer was confirmed by the CV study of the resulting solution, which displayed one single and poorly reversible reduction wave at $E_p = -0.65$ V in agreement with the formation of a simple mono(terpyridine)Cu^{2+} adduct.[9] The absence of redox process around +0.4 V also corroborated the absence of dioxocyclam- Cu^{2+} fragment.

In addition, a mass spectrometry analysis of the green solid obtained by precipitation with diethyl ether further supports the formation of **$1H_2Cu_2$** species through the presence of an intense signal at $m/z = 647$ corresponding to the dicationic species $\{\mathbf{1H_2Cu_2}, 2CF_3SO_3\}^{2+}$. Unfortunatly, because of precipitation phenomena, the reverse process, that is, the regeneration of the **1CuCu** polymer by

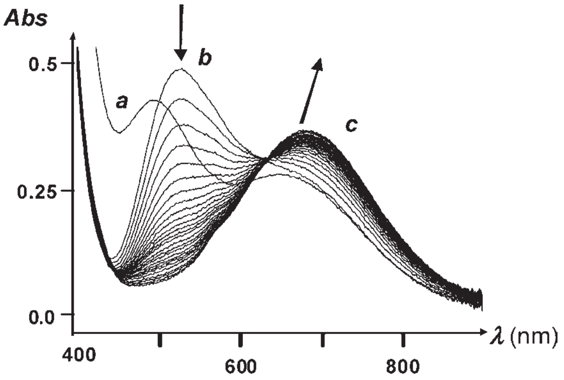
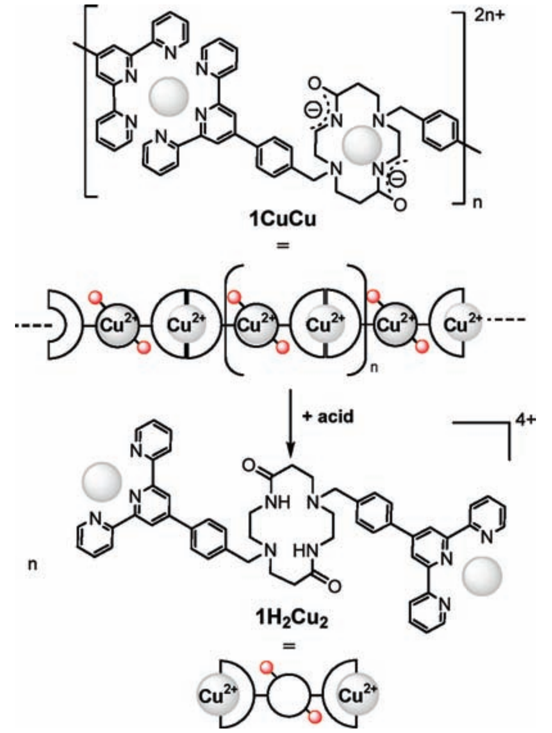


Figure 6. Evolution of the visible absorption spectrum of **1CuCu** in MeOH upon addition of 2.5 equiv of triflic acid by monomer unit, as a function of time. $T = 25$ °C, $l = 1$ cm. (a) without addition of acid, (b) immediately upon addition of acid, and (c) final spectrum. b to c: one spectrum every 90 s.

Scheme 4. Disassembling Process of **1CuCu** in Presence of Acid



addition of base to a solution of **1H$_2$Cu$_2$**, was unsuccessful.

Conclusions

Supramolecular coordination polymers were self-assembled from a polytopic bis(terpyridine)-dioxocyclam receptor. The formation of polymers was demonstrated by viscosimetry experiments. The use of a macrocyclic complexing spacer in this bridging ligand allowed the introduction of additional metal ions in the polymer chain, and thus the synthesis of both homo- and heterometallic architectures. The regular alternation of different metal ions in the structure was demonstrated by CV, mass spectrometry, and UV−vis spectroscopy. EPR experiments also revealed the existence of weak intramolecular magnetic interactions between vicinal metal ions. In addition, the homometallic Cu^{2+} polymer could be converted into dinuclear complexes in the presence of acid. This work shows that the use of polytopic bridging ligands containing complexing spacers opens perspectives for further developments of functional supramolecular materials.

Experimental Section

Reagents, Instrumentation, and Procedures. All reagents were commercial grade and used without further purification. TBAP was purchased from Fluka. Electrochemical experiments were conducted under an argon atmosphere in a conventional three-electrode cell under an argon atmosphere 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). The working electrode was a vitreous carbon disk (3 mm in diameter) polished with 1 μm diamond paste before each record. The regular ferrocene/ferrocenium ($E_{1/2} = +0.054$ V vs Ag/10 mM $AgNO_3$ under our experimental conditions) redox couple was used as internal reference. CV curves were recorded at a scan rate of 0.1 V s^{-1}. Electrochemical experiments were done on millimolar solutions of the compound in the case of the mononuclear **2M** complexes. In the case of the **1CuM** polymers, since their exact molar concentration can not be accurately determined, a mass concentration of ~1 mg of complex per milliliter of solvent was used.

Viscosimetry measurements have been performed using a Cannon-Fenske viscometer (Comecta) appropriate for Newtonian liquids undergoing a Poiseuille type flow. The temperature was regulated at $T = 18.6 \pm 0.3$ °C. The apparatus was calibrated using water and a standard oil (ThermoFisher Scientific) having a 5.3 mPas dynamic viscosity. The density of the specimens was measured with a DMA 35N densimeter. The mononuclear **1Cu** complex was dissolved in DMF (60%)-EtOH(40%) and increasing volumes of metal ions ([ ] = 260 mM in DMF) were added. All measurements were repeated 5 times. The initial concentration of the **1Cu** complex is 13 mM while at the end of the sequence of metal ion additions, the concentration at the stoichiometry 2, becomes 11.8 mM. ESI experiments were performed in the positive mode on a Bruker MicrOTOF-Q instrument of the "Centre de Spectrométrie Moléculaire de l'Université de Bourgogne" in Dijon. Methanolic solutions of 10^{-6} M concentration were introduced into the mass spectrometer at a flow rate of 4 μL/min. Nitrogen was used as nebulizer gas, and the needle voltage was set at 4500 V with a end plate offset of −500 V. FAB (positive mode) mass spectra were recorded with an AEI Kratos MS 50 spectrometer fitted with an Ion Tech Ltd. gun and using *m*-nitrobenzyl alcohol as matrix. NMR spectra were recorded on a Bruker AC 250 at 298 K. ^{1}H chemical shifts (ppm) were referenced to residual solvent peaks. UV−vis spectra were recorded on a Varian Cary 100 spectrophotometer using quartz cells (l = 1 cm). Infrared spectroscopy was carried out on a Perkin-Elmer GS 2000.

Preparation of Ligand 1H$_2$ and Metal Complexes. Preparation of Bis-(4′-phenyl-2,2′:6′,6″-terpyridine)Metal(II) Complexes. The **2M** complexes with M = Fe, Co, Ni, or Cu were prepared as BF_4^- salts ($CF_3SO_3^-$ salt was used in the case of Cu) following previously reported experimental procedures.[5b,9]

Synthesis of 1,8-Bis-(4-[2,2′;6′,2″]terpyridin-4′yl-benzyl)-1,4,8,11-tetraazacyclotetradecan-5,12-dione (1H$_2$). This ligand was prepared as previously reported: to a stirred solution of 0.876 mmol (200 mg) of 1,4,8,11-tetraazacyclotetradecane-5,12-dione,[10] in a mixture of methanol (30 mL) and acetonitrile (100 mL) containing 7.2 mmol (1.0 g) of potassium carbonate were added dropwise 2 mmol (0.805 g) of 4′-(4-bromomethylphenyl)-2,2′:6′,2″-terpyridine[11] dissolved in dichloromethane (10 mL). This solution was refluxed for 4 days, and the resulting mixture was filtered. Upon removal of the solvent under reduced pressure, the crude product was dissolved in aqueous NaOH (pH ~ 12) and extracted three times by dichloromethane. The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under vacuum. The residue was purified by column chromatography on alumina (dichloromethane-methanol, 98:2; v:v) to afford **1**H_2 as a light-yellow solid. Yield: 0.374 g (49%). ^{1}H NMR (250 MHz, $CDCl_3$, δ): 8.74−8.66 (m, 8 *H*, tpy 3-3″ and tpy 3′-,5′) ; 8.61−8.57 (m, 6 H, tpy, 6-,6″ and −CON*H*); 7.86−7.79 (m, 8 H, tpy 4-,4′ and -Ph); 7.40−7.38 (m, 4 *H*, Ph); 7.34−7.29 (m, 4 *H*, tpy 5-,5″); 3.78 (s, 4 *H*, PhC*H*$_2$); 3.51 (br, 4 H, CONHC*H*$_2$); 2.73 (t, br, J = 5.1 Hz, 8 H, $NCOCH_2CH_2$ and $CONCH_2CH_2$); 2.49 (t, br, J = 5.1 Hz, 4 H, NHCOC*H*$_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.9 ; 155.9; 155.7; 149.2; 149.0; 137.9; 137.2; 136.7; 130.1; 127.4; 123.8; 121.2; 118.5; 57.4; 52.2; 49.3; 35.8; 32.2. FAB$^+$-MS, *m*/*z*: 871 {**1**H_2 + H}$^+$. IR (KBr, cm^{-1}): 1645 ($\nu_{C=O}$) ; 1584 (δ_{N-H}). Anal. Calcd for $C_{54}H_{50}N_{10}O_2 \cdot 0.5CH_3OH$ (%): C, 73.79, H, 5.90, N, 15.79; found C, 73.64, H, 5.89, N, 15.50.

Preparation of 1Cu Complex.[9] To a solution of 0.172 mmol of **1**H_2 (150 mg) in methanol (6 mL) containing 0.342 mmol of potassium carbonate (24.0 mg) was added dropwise 0.172 mmol of $Cu(CF_3SO_3)_2$ (62.4 mg) dissolved in methanol (6 mL). Upon addition, the reaction medium turned dark-green. The mixture was refluxed for 12 h to afford a deep-purple solution. Potassium carbonate was removed by filtration, and the filtrate was evaporated under reduced pressure. Purification was carried out by column chromatography (alumina), with dichloromethane-methanol (96:4 ; v:v) as eluent to afford the expected complex as a purple solid; yield: 51.1 mg (32%). ESI-MS: *m*/*z* 932.34 [**1**H_2+H]$^+$. UV−vis (MeOH) λ_{max}, nm (ε, M^{-1} cm^{-1}): 503 (156). IR (KBr, cm^{-1}): 1544 ($\nu_{C=O}$). Anal. Calcd for $C_{54}H_{48}N_{10}O_2Cu$. Three CH_3OH (%): C, 66.55, H, 5.88, N, 13.61; found C, 66.62, H, 6.00, N, 13.28.

Preparation of 1CuM polymers with M = Fe, Co, Ni, or Cu. 1CuM complexes were prepared by mixing 15 mg of **1Cu** in 4 mL MeOH and 1 mol equiv of metal salt (as BF_4^- salts for M^{2+} = Fe^{2+}, Co^{2+}, and Ni^{2+} and as $CF_3SO_3^-$ salt for Cu^{2+}) dissolved in 1 mL MeOH under an inert atmosphere. After 1 h, the complex was precipitated by addition of diethyl ether, collected by suction filtration, washed with diethyl ether, and dried under reduced pressure. Yields: 80−90%. **1CuCu**: ESI-MS: *m*/*z* 963.81 {**1**Cu_3}$^{2+}$; IR (KBr, cm^{-1}): 1545 ($\nu_{C=O}$). **1CuFe**: ESI-MS: *m*/*z* 960.29 {**1**Cu_2Fe}$^{2+}$, 727.47 {**1**Cu_3Fe_2}$^{4+}$; IR (KBr, cm^{-1}): 1542 ($\nu_{C=O}$). **1CuCo**: ESI-MS: *m*/*z* 961.80 {**1**Cu_2Co}$^{2+}$; IR (KBr, cm^{-1}): 1544 ($\nu_{C=O}$). **1CuNi**: ESI-MS: *m*/*z* 961.31 {**1**Cu_2Ni}$^{2+}$; IR (KBr, cm^{-1}): 1543 ($\nu_{C=O}$).

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