# Inorganic Chemistry

**Communication**

# Acid–Base-Driven Interconversion between a Mononuclear Complex and Supramolecular Coordination Polymers in a Terpyridine-Functionalized Dioxocyclam Ligand

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A polytopic cyclam−bis-terpyridine ligand has been used to accomplish an acid–base-triggered formation of either a mononuclear neutral complex or metallopolymers with $Cu^{2+}$ ions. A controlled interconversion between these two forms was achieved through the reversible displacement of a $Cu^{2+}$ cation from the macrocycle to the terpyridine units.

Supramolecular architectures containing labile and reversible bonds between multifonctional ligands and transition-metal ions open large possibilities for the conception of smart molecular materials and devices.[1] In particular, remarkable coordination polymers[2] or metal-containing molecular systems acting as dynamic molecular switches[3] have been recently reported. It thus appears highly challenging to combine these two domains, i.e., to elaborate coordination polymers displaying switching properties.[1–4] Herein we report a proton-triggered self-assembling−disassembling process between mononuclear and polynuclear copper(II) complexes based on the bis-terpyridine−dioxocyclam ligand **L1** (Scheme 1).

**Scheme 1.** Complexation Routes of $Cu^{2+}$ by the **L1** Ligand (A) without and (B) with the Addition of a Base and (C) Acid–Base-Driven Interconversion
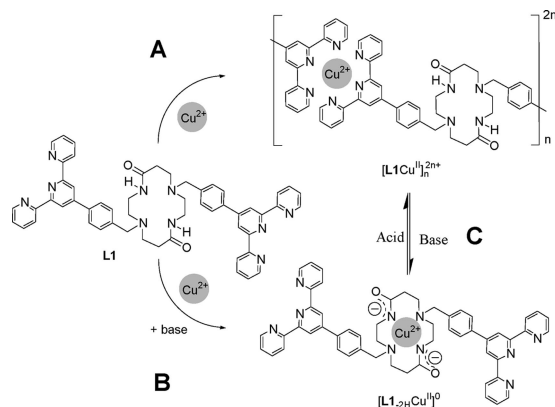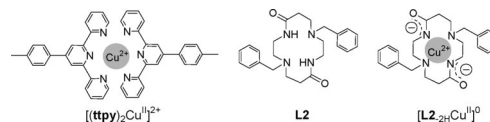


**Chart 1.** Structures of the Ligand **L2** and the $[\text{L2}_{-2H}Cu^{II}]^0$ Complex Used as Reference Compounds in This Study



The 1,4,8,11-tetraazacyclotetradecane (cyclam) is a remarkable molecular platform for the conception of elaborated architectures because it can be N- and/or C-functionalized and forms many stable complexes with a wide range of metal ions.[5,6] Here, the employed cyclam derivative **L1** comprises two types of coordination sites: (i) tridentate terpyridine groups, well-known to form octahedral 2:1 (**L/M**) complexes

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**Table 1.** Characteristic Visible Absorption, FT-IR, and Electrochemical Data of the Ligands and Copper(II) Complexes Used in This Work

| compound | $\lambda_{max}$, nm[a] ($\epsilon$, L mol$^{-1}$) | FT-IR data $\nu$ (cm$^{-1}$) | | electrochemical data $E_{1/2}$ ($\Delta E$ p)[b,c] V | | |
| | | $\nu_{CO}$ | $\nu_{CF_3SO_3^-}$ | terpyridine-centered reduction | Cu$^{II/I}$ | Cu$^{III/II}$ |
|---|---|---|---|---|---|---|
| **L1** | | 1645 | | −2.420 (0.070) | | |
| **L2** | | 1646 | | | | |
| **[L1Cu$^{II}$]$_n$$^{2n+}$** | 687 (69) | 1645 | 1259, 1033 | e | −0.719 (0.190) | |
| **[(ttpy)Cu$^{II}$]$^{2+}$** | 687 (73) | | 1262, 1031 | e | −0.733 (0.080) | |
| **[L1$_{-2H}$Cu$^{II}$]$^0$** | 503 (156) | 1544 | d | −2.465 (0.080) | −1.475 (0.085) | +0.434 (0.085) |
| **[L2$_{-2H}$Cu$^{II}$]$^0$** | 501 (115) | 1559 | d | | −1.514 (0.090) | +0.429 (0.090) |

[a] In MeOH. [b] Because of the low solubility of some compounds in MeOH in the presence of a supporting electrolyte, experiments were conducted in DMF + 0.1 M TBAP; V vs Fc/Fc$^+$ couple. [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. [e] Not observed because of the prior electrodeposition of Cu$^0$.

with transition-metal cations and (ii) a dioxocyclam (1,4,8,11-tetraazacyclotetradecane-5,7-dione) unit whose complexing properties might be turned on upon deprotonation of the amide functions.[7] **L1** was prepared by the reaction of 4′-[4-(bromomethyl)phenyl]-2,2′:6′2′′-terpyridine with *trans*-dioxocyclam in refluxing CH$_3$CN in the presence of a base. The reaction of **L1** in MeOH with Cu(CF$_3$SO$_3$)$_2$ in a 1:1 molar ratio afforded a green solution, from which a light-green powder was isolated upon precipitation by the addition of diethyl ether.

This species presents an absorption band at $\lambda_{max} = 687$ nm in MeOH, identical with that obtained with the [(**ttpy**)$_2$Cu$^{II}$]$^{2+}$ reference compound (Chart 1 and Table 1). This feature strongly suggests the formation of a copper(II) bis-terpyridine based coordination complex in which the macrocyclic dioxocyclam unit remains metal-free. This result was further demonstrated by spectrophotometric titration of **L1** during the progressive addition of Cu$^{2+}$ ions showing the formation of a structure having a 1:1 (**L1**/Cu$^{2+}$) ratio (see the Supporting Information). FT-IR studies of the green solid confirmed the presence of counteranions, in agreement with the formation of a cationic copper(II) complex ([**L1Cu$^{II}$**]$_n$$^{2n+}$; Scheme 1).

The presence of metal-free dioxocyclam in [**L1Cu$^{II}$**]$_n$$^{2n+}$ was corroborated by a $\nu_{CO}$ stretching band at 1645 cm$^{-1}$, identical in free **L1**.[7,8] Cyclic voltammetry (CV) curves of the complex displayed a reversible reduction wave at $E_{1/2} = -0.719$ V, close to the wave obtained with [(**ttpy**)$_2$Cu$^{II}$]$^{2+}$ and attributed to the Cu$^{II/I}$ system (Figure 1A,B and Table 1).[9]

All of these experimental data proved the formation of copper (II) bis-terpyridine units when **L1** is mixed with 1 mol equiv of metal cations, but the exact nature of the species remained unclear because linear chains (oligomers/polymers) or [**L1**$_n$M$_n$]$^{2n+}$ cyclic structures could theoretically be formed.[10] First, the formation of a mononuclear ring in which both terpyridines of **L1** would be bound to the same Cu$^{2+}$ ion was excluded because the dioxocyclam spacer in **L1** is
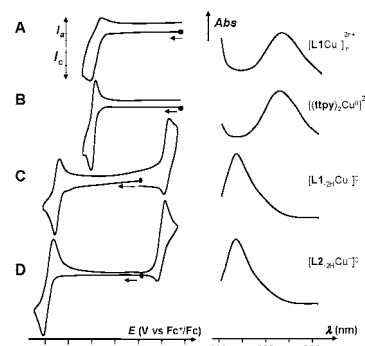


**Figure 1.** (left) CV curves in DMF + TBAP 0.1 mol L$^{-1}$ solutions and (right) visible absorption spectra in MeOH of millimolar solutions of (A) [**L1Cu$^{II}$**]$_n$$^{2n+}$, (B) [(**ttpy**)$_2$Cu$^{II}$]$^{2+}$, (C) [**L1$_{-2H}$Cu$^{II}$**]$^0$, and (D) [**L2$_{-2H}$Cu$^{II}$**]$^0$.

too short (<7 Å)[11a] compared to the size of the bis-(terpyridine)copper(II) unit (21 Å),[11b] preventing an intramolecular 1 + 1 coordination mode (see the Supporting Information). A mass spectrometry (MS) study (electrospray ionization mode) of the isolated species gave a signal at *m/z* = 1699.9 corresponding to the trinuclear {**L1**$_3$(Cu$^{II}$)$_3$-(CF$_3$SO$_3$)$_4$}$^{2+}$ dication. Unfortunately, certainly because of the reversibility of the metal–ligand bonds, higher molecular weight structures could not be observed.

The potential formation of coordination polymers was then investigated by viscosimetry. Indeed, the reduced viscosity $\eta_r = \eta/\eta_s$ ($\eta_s$ is the viscosity of the solvent) can be used to trace out the variation of the concentration of particles with a given morphology in noninteracting conditions and/or the variation of the morphology of these particles in the dilute regime of concentrations. Various theoretical models have been proposed to relate the reduced viscosity to the form factor of the dispersed particles.[12] Figure 2 shows the variation of the reduced

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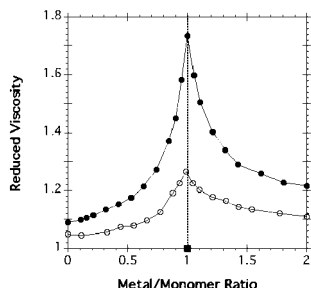
**Figure 2.** Viscosimetry experiments. Progressive addition of $Cu(CF_3SO_3)_2$ (0.52 M in DMF) to a solution of **L1** in DMF/$CH_2Cl_2$ (90:10): (●) [**L1**] = 26 mM; (○) [**L1**] = 13 mM; (■) isolated [**L1**$_{-2H}$Cu$^{II}$]$^0$ (13 mM in DMF).
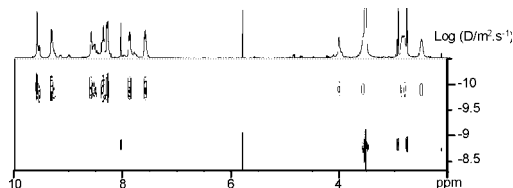


**Figure 3.** $^1$H DOSY NMR spectra of **L1** + 1 mol equiv of Zn$^{2+}$ in DMF-$d_7$ (90%)/CD$_2$Cl$_2$ (10%). (The signals at log $D$ from about −9 to −8.5 are attributed to the solvents and water molecules.)

viscosity of the media during stepwise addition of Cu$^{2+}$ ions to a solution of **L1**.

The reduced viscosity is increasing up to an apex for a Cu$^{2+}$/**L1** ratio of 1 that can be related to an increase of the average chain length of 1D assemblies. Beyond this maximum, $\eta_r$ is decreasing, which reveals the formation of extra chain ends. Such evidence for the formation of shorter entities is a good indication of the reversibility of the metal–ligand bonds. Without going into the details of the functional dependence of the viscosity of a solution of charged supramolecular polymers on the volume fraction, morphology, and balance between the hydrodynamic and Brownian forces, the increase of the reduced viscosity can be related to an increase of the molecular weight of the species. Indeed, the concentrations involved in our experiments are not very dilute, and the variation of the viscosity (between ca. 30 and 70%) is relatively important. These features, also observed for other coordination chains,[10a,b] are not in favor of the potential formation of rings but rather of linear species following the description by Jacobson and Stockmayer[12d] of the linear polycondensation of polymeric-like chains.

In order to confirm this result, NMR experiments were carried out. Because of the paramagnetic character of the copper(II) complexes, Zn$^{2+}$ was used as the metal cation. First, broad peaks and the absence of free **L1** were logically observed by $^1$H NMR after the progressive addition of 1 equiv of Zn$^{2+}$ to a solution of **L1**. The strongest chemical shifts induced by the presence of metal ions were observed in the terpyridine region, indicating that the metal insertion occurs in these units. $^1$H DOSY NMR experiments performed on a solution containing a 1:1 (Zn$^{2+}$/**L1**) molar ratio (Figure 3) showed the presence of species having a low diffusion coefficient ($D = 6.3 \times 10^{-11}$ to $2 \times 10^{-10}$ m$^2$ s$^{-1}$). These data corroborate the presence of high-molecular-weight polymers.[10b,c]

Although the formation of [**L1**$_n$M$_n$]$^{2n+}$ rings cannot be fully excluded, all of these results unambiguously confirmed the major formation of metallopolymers when a 1:1 (M$^{2+}$/**L1**) ratio is reached (Scheme 1A). In contrast, metalation of **L1** with 1 mol equiv of Cu(CF$_3$SO$_3$)$_2$ in MeOH in the presence of a mild base (2 equiv of K$_2$CO$_3$) gave a pink-red solution displaying an absorption band at 503 nm, consistent with a d → d transition in a square-planar Cu$^{2+}$ complex.[7,8] FT-IR data of the isolated red powder showed no presence of anion, indicating the neutral character of the complex, and the $\nu_{CO}$ stretching band at 1544 cm$^{-1}$ was strongly shifted compared to the free ligand (1645 cm$^{-1}$). These features are in agreement with a metal-assisted deprotonation of the two amide groups and their coordination to the metal ion, giving rise to a neutral [**L1**$_{-2H}$Cu$^{II}$]$^0$ complex (Scheme 1B).[7,8] This formula was confirmed by MS data and elemental analysis.

For comparison, the **L2** ligand and the corresponding red-pink [**L2**$_{-2H}$Cu$^{II}$]$^0$ complex were studied as reference compounds (Chart 1). The characteristics of this complex were close to those of [**L1**$_{-2H}$Cu$^{II}$]$^0$. Because **L2** has no terpyridine units, all of these data clearly demonstrate that the terpyridine groups in [**L1**$_{-2H}$Cu$^{II}$]$^0$ are not involved in the coordination mode. As expected, CV curves of [**L1**$_{-2H}$Cu$^{II}$]$^0$ and [**L2**$_{-2H}$Cu$^{II}$]$^0$ presented very similar features (Figure 1C,D and Table 1), with the two waves around −1.50 and +0.43 V attributed to the metal-centered redox processes affording the corresponding Cu$^I$ and Cu$^{III}$ complexes, respectively.[11] The presence of metal-free terpyridine in [**L1**$_{-2H}$Cu$^{II}$]$^0$ was corroborated by the observation of a reduction wave at −2.46 V, close to the signal corresponding to the reduction of the terpyridine units in free **L1** ($E_{1/2} = -2.42$ V). In addition, the relative viscosity measured for a solution of [**L1**$_{-2H}$Cu$^{II}$]$^0$ was negligible ($\eta_r = 1$; see Figure 2).

The possible interconversion (Scheme 1C) between [**L1**$_{-2H}$Cu$^{II}$]$^0$ and [**L1**Cu$^{II}$]$_n^{2n+}$ was then investigated. For solubility reasons, these experiments could not be realized in aqueous solvents, but upon the addition of K$_2$CO$_3$ to a methanol solution of [**L1**Cu$^{II}$]$_n^{2n+}$, the green solution ($\lambda_{max} = 687$ nm) turned gradually red-pink ($\lambda_{max} = 503$ nm) in accordance with the formation of the [**L1**$_{-2H}$Cu$^{II}$]$^0$ complex. Conversely, upon the addition of triflic acid to a red solution of [**L1**$_{-2H}$Cu$^{II}$]$^0$, the initial absorption at $\lambda_{max} = 503$ nm was replaced by a band at 687 nm characteristic of the polymer (see the Supporting Information). This process was also readily confirmed by electrochemical experiments because the CV curve representative of the [**L1**Cu$^{II}$]$_n^{2n+}$ complex was obtained when acid was added to a solution of [**L1**$_{-2H}$Cu$^{II}$]$^0$.

In this work, we have designed a cyclam−bis-terpyridine ligand allowing an acid–based-triggered formation of mononuclear neutral complex or metallopolymers with Cu$^{2+}$ ions. We are now exploiting these promising systems for the conception of heterometallic polymers.