Proton-controllable fluorescent switch based on interconversion of polynuclear and dinuclear copper(II) complexes†

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The first reversible interconversion process between a one-strand polymeric copper(II) complex {[$Cu_2(L1)_2(ClO_4)_2$](ClO_4)$_2$}$_n$ (1) and a dicopper(II) helicate [Cu_2(L1–2H)$_2$] (2), proceeding *via* a deprotonation–protonation process, can transduce fluorescence and function as a fluorescent switch simply by introducing a one fiftieth equivalent of coumarine 343 anion, a fluorophore.

Polydentate ligands that can assemble dinuclear and polynuclear complexes with unique structural motifs, such as rings,[1] helicates,[2] grids,[3] cages,[4] boxes,[5] *etc*, have been widely studied. Further development in this fascinating area has been directed at controllable assembling/disassembling processes by an external input (photon, electron, or proton) so as to form a molecular switch. There are a few examples of monomer and oligomer interconversions of copper(II) complexes.[6–8] However, interconversion between polynuclear copper(II) complexes and dicopper(II) helicates has not been found to date. Herein, we report on the first example of this sort of interconversion between copper(II) complexes with a pyridyl-carboxamide ligand, *N*,*N*′-bis[(2-pyridyl)methyl]isophthalamide L1, by a simple deprotonation–protonation process. The employed ligand L1 contains two amide groups and one benzene spacer and functions as a ditopic ligand due to its potential carbonyl O-donor and amido N-donor binding sites. Namely, upon the complexation of copper(II) ions, the amido-N and pyridyl-N chelating sites would be favoured in the deprotonated state, forming a planar 5-membered ring structure, whereas the carbonyl-O and pyridine-N chealting sites would be preferred in the protonated state, resulting in a puckered 7-membered metallocycle. Accordingly, such a structural rearrangement can easily be manipulated *via* a deprotonation–protonation process (Fig. 1). These two complexes can be detected by UV-Vis spectrometry and their bonding modes around the copper(II) centers have been confirmed by X-ray diffraction analysis. The spatial rearrangement on a fluorescent switch is described herein.

Ligand L1 was readily prepared by the reaction of 2-aminomethylpyridine and isophthaloyl chloride in the presence of NEt_3 to give a 90% yield. The reaction of L1 with [$Cu(H_2O)_6$](ClO_4)$_2$ in acetonitrile generated the polymeric complex **1** [eqn (1)]. For complex **1**, the presence of the ν(N–H) at 3343 cm^{-1} and the red shift of the carbonyl ν(C=O) at 1617 cm^{-1} in the IR spectrum indicate that the carbonyl O-atom is the coordination site.[9] The electronic spectrum of **1** is characterized by a broad d–d absorption band at 708 nm in the CH_3OH–CH_3CN (1 : 1) solution and in the solid state, indicative of a square pyramidal stereochemistry around the copper(II) ion. A single crystal X-ray diffraction analysis further supports the square pyramidal geometry.‡

$$2n[\mathrm{Cu(H_2O)}]_6(\mathrm{ClO_4})_2 \xrightarrow{+2n\mathbf{L1}} \{[\mathrm{Cu_2}(\mathbf{L1})_2(\mathrm{ClO_4})_2](\mathrm{ClO_4})_2\}_n \quad (1)$$

$$\underset{\text{Polymer}}{\{[\mathrm{Cu_2}(\mathbf{L1})_2(\mathrm{ClO_4})_2](\mathrm{ClO_4})_2\}_n} \underset{+4n\,\mathrm{H^+}}{\overset{-4n\,\mathrm{H^+}}{\rightleftharpoons}} \underset{\text{dimer(helicate)}}{n[\mathrm{Cu_2}(\mathbf{L1{-}2H})_2]} \quad (2)$$

Upon the addition of 4 equivalents of [$(CH_3)_4N$]OH to a CH_3OH–CH_3CN (1 : 1) solution of complex **1**, dimeric helicates **2** are nearly quantitatively formed [eqn (2)]. The absence of ν(N–H) and the uncoordinated carbonyl ν(C=O) at 1552 cm^{-1} suggest that the amide ligand binds to the copper through the amido N-atom.[10] Unlike complex **1**, the electronic spectrum of complex **2** shows a broad d–d band at 608 nm with a shoulder at ~847 nm in a CH_3OH–CH_3CN (1 : 1) solution, indicative of a different molecular geometry. A tetrahedrally distorted square-planar CuN_4 chromophore is suggested,[11] consistent with the crystal

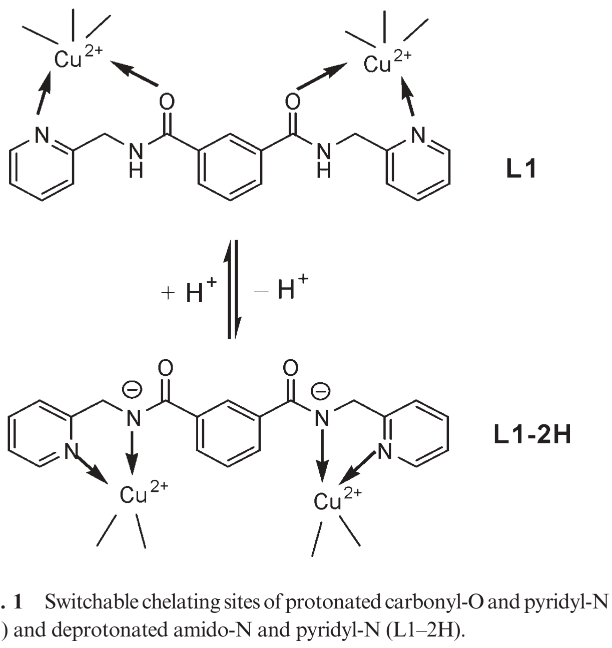

Fig. 1 Switchable chelating sites of protonated carbonyl-O and pyridyl-N (L1) and deprotonated amido-N and pyridyl-N (L1–2H).

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structure of **2**.§ The electronic spectra measured in the solid state (diffusion reflectance spectrum) and in CH_3OH–CH_3CN (1 : 1) are very similar, implying that the stereochemistry of the copper(II) center does not change in solution. The absorption patterns of complexes **1** and **2** are so much different that the presence of these two complexes can easily be detected in UV-Vis spectra (Fig. 2, curves a and b). Complex **2** is converted back to **1** upon the addition of 4 equivalents of $HClO_4$ and can also be shifted back quantitatively to **2** by adding 4 equivalents of $[(CH_3)_4N]OH$, exhibiting a reversible process. The structural transformation can be visualized by the color change of the solution (blue ↔ green). Similarly, substituting RCOOH (R = CH_3 and C_6H_5) for $HClO_4$, a new reversible process occurred with a new band appearing (λ_{max} 674 nm for CH_3COOH, curve c in Fig. 2, λ_{max} 689 nm for C_6H_5COOH, curve d in Fig. 2), suggesting that carboxylate anions coordinate to the copper(II) ions of complex **1**. Consequently, complex **1** reacts with RCOONa to give the same d–d absorption band as when complex **2** reacts with RCOOH. Since there is essentially no reaction between RCOOH and complex **1**, at a molar ratio of 1 : 1, this confirms the interaction of $RCOO^-$ with Cu^{2+}. Therefore, RCOOH provides not only a proton but also a coordinated carboxylate anion.

The crystal structure of the cation of complex **1** indicates a one-strand polymeric structure. The asymmetric unit, shown in Fig. 3 (1), consists of a Cu(II) ion coordinated to two portions of two discrete L1 ligands through one O-atom of the carbonyl group and one N-atom of the pyridine, and a perchlorate anion. The copper(II) ions exhibit a nearly square pyramidal coordination with $\tau = 0.05$.[12] The structure of the neutral complex **2** is shown in Fig. 3 (2), confirming the formation of a double-helical structure. Each copper(II) center is bound by two pyridine and two amido-N atoms, forming a distorted tetrahedral coordination geometry. The coordination to two metal centers leads to interannular twisting and the formation of a double-strand array. The bond lengths are in the normal ranges. The two copper(II) centers are separated by 4.8985(8) Å, and the ligand twists around the copper–copper axis. Due to the strong donor capability of the deprotonated amido-N donors, it would be expected to have short Cu–N_{amido} bond lengths. Indeed, the average Cu–N_{amido} bond length (1.937 ± 0.005 Å) is considerably shorter than that of the Cu–$N_{pyridine}$ bond (2.007 ± 0.005 Å). In complex **1**, the weak axial Cu–$OClO_3$ bond with a length of 2.297(6) Å can readily be replaced by other neutral or anionic ligands, for example, CH_3COO^- or $C_6H_5COO^-$, *etc.* Taking advantage of such a conformational change, a fluorophore with a carboxylate group, the coumarine 343 anion, was introduced into this system because of its quenching properties for 5-coordinated copper(II) complexes.[6,13] The binding/releasing of the fluorophore to/from the copper(II) ion may lead to the quenching/revival of the fluorescent emission, thus functioning as a switch.

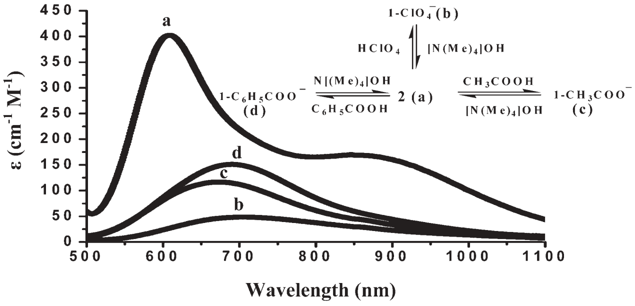

Fig. 2 UV-vis spectra of complex **2** (curve a), complex **1**–ClO_4^- (curve b), **1**–CH_3COO^- (curve c), and **1**–$C_6H_5COO^-$ (curve d).

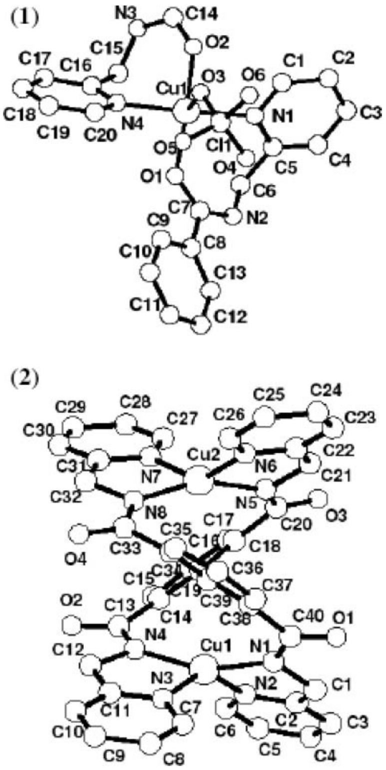

Fig. 3 Molecular structures of a portion of the cation of **1** (1) and the left-handed dicopper helicate **2** (2). Selected bond distances (Å) for **1**: Cu1–N1 2.000(7), Cu1–N4 2.021(7), Cu1–O1 1.962(5), Cu1–O2 1.973(5), Cu1–O3 2.297(6); bond angles (°) for **1**: O1–Cu1–O2 174.8(2), O1–Cu1–N1 97.6(3), O2–Cu1–N1 84.8(3), O1–Cu1–N4 86.9(2), O2–Cu1–N4 90.1(2), N1–Cu1–N4 171.7(3), O1–Cu1–O3 89.2(2), N1–Cu1–O3 92.3(3), N4–Cu1–O3 94.2(3). Selected bond distances (Å) for **2**: Cu1–N1 1.938(4), Cu1–N2 2.007(4), Cu1–N3 2.002(4), Cu1–N4 1.939(4), Cu2–N5 1.932(4), Cu2–N6 2.005(4), Cu2–N7 2.012(4), Cu2–N8 1.940(4); bond angles (°) for **2**: N1–Cu1–N4 157.8(2), N2–Cu1–N4 106.5(2), N1–Cu1–N2 83.2(2), N3–Cu1–N4 83.9(2), N1–Cu1–N3 102.2(2), N2–Cu1–N3 138.6(2), N5–Cu2–N8 157.8(2), N5–Cu2–N6 83.5(2), N6–Cu2–N8 104.7(2), N5–Cu2–N7 103.0(2), N7–Cu2–N8 83.6(2), N6–Cu2–N7 141.5(2).

In fluorescence quenching experiments (see ESI for details†), a polymeric complex **1** solution in MeCN–MeOH (1 : 1) was added to a coumarine 343, $R_{343}COOH$, MeCN–MeOH (1 : 1) solution. The emission band corresponding to the undissociated $R_{343}COOH$ centered at λ_{max} 491 nm was quenched only slightly when the molar ratio was 1 : 1. As the molar ratio of complex **1** to coumarine reached 100 : 1, the emission band shifted to λ_{max} 480 nm, indicative of Cu^{II}–$R_{343}COO^-$ adduct formation.[6] The $R_{343}COO^-$ anion, produced by the dissociation of $R_{343}COOH$, bonded to complex **1** forming a Cu^{II}–$R_{343}COO^-$ adduct and promoted the dissociation of $R_{343}COOH$ as the amount of Cu^{II} increased, in spite of the very low K_a value ($\sim 10^{-7}$)[13] of $R_{343}COOH$. Consequently, this confirms that the carboxylate group of coumarine 343 anion can interact with complex **1**, similar to CH_3COO^- or $C_6H_5COO^-$.

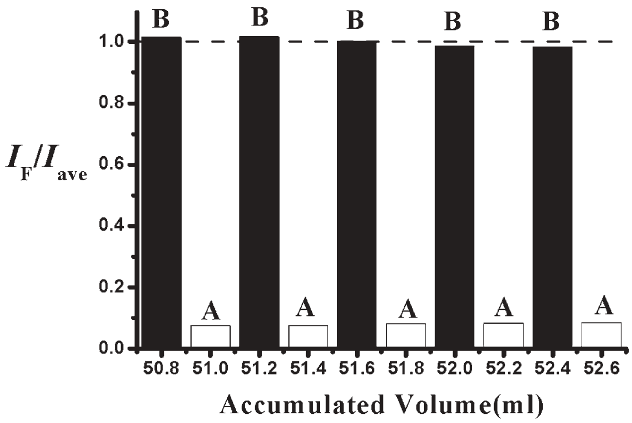

Fig. 4 Normalized fluorescent intensity, I_F/I_{ave}, of a bulk solution (50 ml) of complex **2** (2×10^{-5} M) with the addition of 1/50 equivalents coumarine 343 anion solution in 5 cycles of proton abstraction/supply expriments. A (λ_{max} 480 nm): addition of $HClO_4$ (8×10^{-5} M, 0.2 ml per cycle); B (λ_{max} 471 nm): addition of $[(CH_3)_4N]OH$ (8×10^{-5} M, 0.2 ml per cycle).

Since the stoichiometric reaction of $[Cu_2(L1–2H)_2]$ with $R_{343}COOH$ takes place as shown in eqn (3), the quenching effect of $R_{343}COOH$ will be greatly reduced due to the emission from the counter anion, $R_{343}COO^-$. Therefore, an effective way to enhance the difference of the signals (I_F/I_{ave}) is to introduce a small quantity (1/50 equivalents) of $R_{343}COO^-$ as the fluorophore and 4 equivalents of $HClO_4$ as the proton and the counter anion, ClO_4^-, sources.

$$n\left[\mathrm{Cu_2}(\mathbf{L1{-}2H})_2\right] \xrightarrow{+4nR_{343}\mathrm{COOH}} \left\{\left[\mathrm{Cu_2}(\mathbf{L1})_2(R_{343}\mathrm{COO})_2\right](R_{343}\mathrm{COO})_2\right\}_n \tag{3}$$

As shown in eqn (4), when the coumarine anion was delivered to the helicate solution in a molar ratio of 1 : 50, an emission with λ_{max} 471 nm (due to free coumarine 343 anion)[13] revealed the "fluorescent on" condition. When 4 equivalents of $HClO_4$ was subsquently added, the 471 nm emission was quenched to a large extent, while an emission at λ_{max} 480 nm (due to Cu^{II}-$R_{343}COO^-$ adduct)[6] appeared, representing the "fluorescent off" condition. When 4 equivalents of $[(CH_3)_4N]OH$ were added again for deprotonation, an emission of λ_{max} 471 nm was revived, indicative of releasing $R_{343}COO^-$, namely, the reversed reaction of eqn (4). Such an ON ↔ OFF situation can be repeated a number of times by a series of protonation–deprotonation processes. The fluorescent outcome of the quenching/revival is shown in Fig. 4.

$$\underset{\textit{fluorescent on}}{n\left[\mathrm{Cu_2}(\mathbf{L1{-}2H})_2\right] + \frac{1}{50}n\,R_{343}\mathrm{COO^-}} \underset{4n\left[(\mathrm{CH_3})_4\mathrm{N}\right]\mathrm{OH}}{\overset{4n\,\mathrm{HClO_4}}{\rightleftharpoons}} \underset{\textit{fluorescent off}}{2\left\{\left[\mathrm{Cu{-}}R_{343}\mathrm{COO}\right]\text{adduct}\right\}_n} \tag{4}$$

$$\left\{\left[\mathrm{Cu{-}}R_{343}\mathrm{COO}\right]\text{adduct}\right\}_n = \left\{\left[\mathrm{Cu}(\mathbf{L1})(\mathrm{ClO_4})_{99/100}(R_{343}\mathrm{COO})_{1/100}\right](\mathrm{ClO_4})\right\}_n$$

In summary, we investigated the controllable behavior of a simple pyridyl-carboxamide ligand L1 that forms two stable complexes upon complexation with copper(II) ion *via* a deprotonation–protonation process. While maintaining the same oxidation state, the appearance of a reversible spatial rearrangement demonstrates the advantage of employing such a ligand as a proton-dependent switch in the control of molecular architectures. In addtion, introducing a small quantity (1/50 equivalents) of fluorophore with a carboxylate functional group, such as the coumarine 343 anion, enhances the signal of the photo-switch. Related studies regarding fluorescent switches with other metals, such as nickel, iron, and cobalt, are currently in progress.

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Notes and references

‡ Crystal data for **1** squeezed $2Et_2O$: $C_{40}H_{36}Cl_4Cu_2N_8O_{20}$, $M = 1217.65$, monoclinic, blue crystals, space group $P2_1/c$, $a = 10.902(1)$, $b = 17.764(2)$, $c = 15.503(2)$ Å, $\alpha = 90°$, $\beta = 110.58°$, $\gamma = 90°$, $V = 2810.7(5)$ Å^3, $Z = 2$, $Dc = 1.439$ g cm^{-3}, $F(000) = 1236$, λ(Mo-Kα) = 0.71073 Å, 11329 reflections measured (Bruker Smart CCD diffractometer) in the θ range 2.30 to 25.27°, 4794 unique ($R_{int} = 0.1255$), 335 parameters refined on F^2 using 4794 reflections to final indices: R_f [$I > 2\sigma(I)$] = 0.0814, $R_w = 0.2138$. CCDC 620454. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b613583h.

§ Crystal data for $\mathbf{2}\cdot 2H_2O$: $C_{40}H_{36}Cu_2N_8O_6$, $M = 851.85$, monoclinic, green crystals, space group $P2_1/n$, $a = 11.6029(2)$, $b = 23.2657(4)$, $c = 16.6550(3)$ Å, $\alpha = 90°$, $\beta = 108.035(1)°$, $\gamma = 90°$, $V = 4275.1(1)$ Å^3, $Z = 4$, $Dc = 1.324$ g cm^{-3}, $F(000) = 1752$, λ(Mo-Kα) = 0.71073 Å, 25181 reflections measured (Bruker Smart CCD diffractometer) in the θ range 2.04 to 25.34°, 7539 unique ($R_{int} = 0.0537$), 505 parameters refined on F^2 using 7539 reflections to final indices: R_f [$I > 2\sigma(I)$] = 0.0597, $R_w = 0.1757$. CCDC 618879. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b613583h.

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