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Monitoring the Redox-Driven Assembly/Disassembly of a Dicopper(I) Helicate with an Auxiliary Fluorescent Probe

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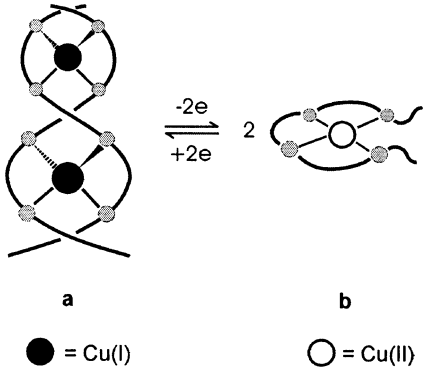
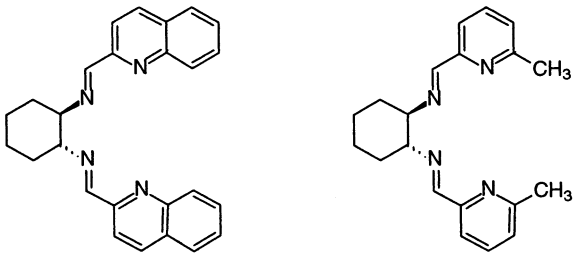
The assembly/disassembly of a dicopper(I) helicate with a bis-bidentate imine-quinoline ligand is driven by the Cu^{II}/Cu^{I} redox change and is signaled by a fluorescent probe bearing a $-COO^-$ group (coumarine 343). The probe coordinates the Cu^{II} center of the monomeric complex, which quenches its emission (fluorescence off), and is released upon reduction and formation of the Cu^{I} helicate (fluorescence on).

The formation of a polynuclear helicate complex requires a good agreement between the stereoelectronic requirements of the metal and the special features of the ligand (rigidity, spacer between the coordinating groups, etc.).[1] For instance, d^{10} cations, which prefer tetrahedral coordination, will favor the assembly of two molecules of a bis-bidentate ligand to give a double-helix arrangement (see structure **a** in Scheme 1).

Changing the oxidation state, when feasible, alters the geometrical preferences of the metal, which might no longer be compatible with the helical assembly. This is the case for the copper center, whose Cu^{I} state, d^{10}, prefers tetrahedral coordination and forms a dimeric helicate complex with rigid bis-bidentate ligands (indicated as L∩L, where L represents a bidentate subunit): $[Cu_2^{I}(L\cap L)_2]^{2+}$. On the other hand, Cu^{II}, a d^9 cation, shows a distinct propensity for tetragonal coordination, a geometrical arrangement that does not match the formation of a double helix. Thus, the Cu^{I}-to-Cu^{II} redox change induces the disassembly of the dicopper(I) helicate into two monomeric moieties, $[Cu^{II}(L\cap L)]^{2+}$, sketched as **b** in Scheme 1. The process is fully reversible, so that switching of the metal oxidation state from +2 to +1 and vice versa causes the assembly of the two tetragonal complexes into a double helix, in one direction, and the disassembly of the dimeric system into the monomeric complexes, in the opposite direction.[2]

Scheme 1. Redox-Driven Disassembly of a Dimeric Helicate via the Cu^{I}/Cu^{II} Redox Change





1 **2**

A well-defined case is that of the copper complexes of the quadridentate ligand **1**, which consists of two imine-quinoline halves, linked by a 1,2-cyclohexane spacer.[3] The π-acceptor features of the coordinating nitrogen atoms stabilize the Cu^{I} state, while the relative rigidity of the

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skeleton disfavors ligand folding to give monomeric complexes. This promotes the formation of the stable dicopper(I) helicate $[Cu^{I}_2(\mathbf{1})_2]^{2+}$. However, the stabilization energy experienced by the Cu^{II} transition metal ion in a square ligating environment helps to overcome the steric obstacles related to the folding of the quadridentate ligand, and upon Cu^{I}-to-Cu^{II} oxidation, the tetragonally coordinated monomeric complex $[Cu^{II}(\mathbf{1})]^{2+}$ forms. Noticeably, the $[Cu^{I}_2(\mathbf{1})_2]^{2+}$ and $[Cu^{II}(\mathbf{1})]^{2+}$ species are stable both in solution and in the solid state. In particular, they have been isolated as crystalline salts, and their molecular structures have been determined through X-ray diffraction studies.[4] Moreover, the dimeric (Cu^{I}) and monomeric (Cu^{II}) natures of the species present in solution have been confirmed through ESI mass spectroscopy studies.[4]

The occurrence and progress of the redox-driven assembly/disassembly process in solution can be monitored spectroscopically. The classical procedure is based on the measure of the absorption spectra in the visible region of the Cu^{I} and Cu^{II} complexes. Herein, we devise a new method based on the measurement of emission spectra and involving an auxiliary fluorescent probe. Studies with bis-bidentate systems **1** and **2**, which differ in the nature of the heterocyclic fragment (either quinoline, **1**, or 2-methylpyridine, **2**), are considered to assess the potential of the new procedure.

Experimental Section

The preparation of ligands **1** and **2** and of the corresponding Cu^{I} and Cu^{II} complexes has been described elsewhere.[3,4] All other chemicals, including coumarine 343, were purchased from Aldrich-Fluka and used without further purification.

Fluorescence studies were carried out by using a Perkin-Elmer LS-50B luminescence spectrometer. Fluorescence quenching experiments on coumarine 343 were performed in methanol by adding a 10^{-4} M solution of $[Cu^{I}_2(\mathbf{1})_2]^{2+}$ or $[Cu^{II}(\mathbf{1})]^{2+}$ to a 2×10^{-6} M solution of the fluorophore, containing 1 equiv of $[Bu_4N]OH$ to keep the carboxylic group of coumarine 343 deprotonated. The indicator was excited at 420 nm, and emission spectra were collected between 450 and 550 nm. The solution of the $[Cu^{II}(\mathbf{1})]^{2+}$ complex deeply quenched the fluorescence of coumarine 343; the spectrofluorimetric titration curve was fitted with the nonlinear least-squares program HYPERQUAD[5] to evaluate the association constant ($\log K = 5.53 \pm 0.02$). The obtained value is consistent with the coordination of the carboxylate group of coumarine 343 in methanol to the copper(II) metal center. In the case of the $[Cu^{I}_2(\mathbf{1})_2]^{2+}$ complex, the spectrofluorimetric titration profile followed Stern−Volmer behavior; the mere decreasing of the fluorescence can be attributed to the absorption properties of the metal complex itself. The titration diagrams indicate that, in a solution containing coumarine 343 and a large excess of the complex, the oxidation state

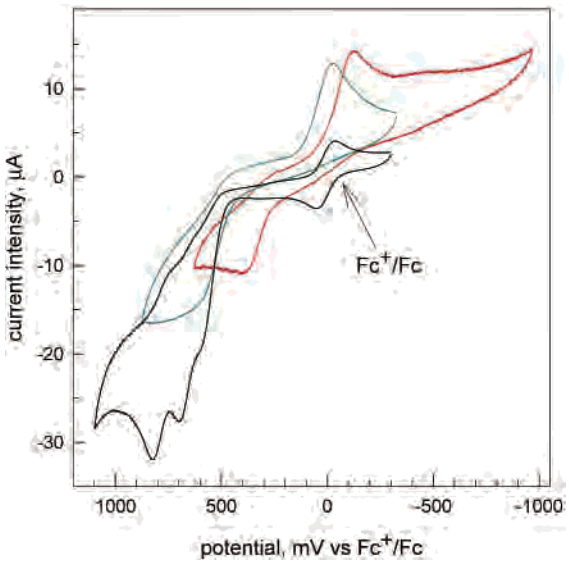

Figure 1. Cyclic voltammetry profiles for $[Cu^{I}_2(\mathbf{1})_2]^{2+}/[Cu^{II}(\mathbf{1})]^{2+}$ (green line) and $[Cu^{I}_2(\mathbf{2})_2]^{2+}/[Cu^{II}(\mathbf{2})]^{2+}$ (red line), in MeOH 0.1 M $[Bu_4N]ClO_4$; potential scan rate = 100 mV s^{-1}. The black line refers to a solution of coumarine 343, to which a small amount of ferrocene had been added, as an internal standard.

of the metal center is signaled by the emission of the coumarine 343. Similar behavior was observed for $[Cu^{I}_2(\mathbf{2})_2]^{2+}$ and $[Cu^{II}(\mathbf{2})]^{2+}$ complexes.

Electrochemical studies (both cyclic voltammetry, CV, and controlled potential coulometry, CPC) were carried out with a Princeton Applied Research model 273 potentiostat−galvanostat. CV investigations on MeOH solutions, made 0.1 M in $[Bu_4N]ClO_4$, were carried out in a conventional three-electrode cell, using a platinum microsphere as the working electrode and a silver wire as the pseudo-reference electrode, which was calibrated vs the Fc^{+}/Fc couple used as an internal standard.[6] CPC experiments were carried out on MeOH solutions, using a platinum gauze as the working electrode. The counterelectrode compartment was separated from the working compartment by a U-shaped bridge filled with the same electrolyte solutions. The reference electrode was a platinum wire dipped in the working cell (its potential was calibrated through CV measurements prior to CPC). CV experiments were carried out on 10^{-3} M solutions of the complexes. The assembly/disassembly processes were studied in bulk conditions by performing a CPC experiment on a 2×10^{-6} M solution of coumarine 343 in the presence of a 10-fold excess of one of the two complexes (2×10^{-5} M). Typically, the reduction of the Cu^{II} complex required almost 20 min and was accompanied by the progressive restoration of the emission intensity. The emission was quenched again by reversing the potential of the working electrode for another 20 min.

Results and Discussion

Cyclic voltammetry studies on the $[Cu^{I}_2(\mathbf{1})_2]^{2+}/[Cu^{II}(\mathbf{1})]^{2+}$ system in MeOH solution, made 0.1 M in $[Bu_4N]ClO_4$, gave the two-peak profile shown in Figure 1 (green line). The large

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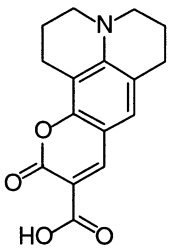
separation of the two peaks is consistent with an EC + EC square scheme, in which the Cu^{II}/Cu^{I} reduction step (E) is followed by the very fast assembly process (C), and the Cu^{I}/Cu^{II} oxidation (E) step is followed by the very fast disassembly process (C). The mechanistic aspects of such a process have been discussed previously.[3,4]

In bulk conditions, the occurrence of the redox-driven interconversion equilibrium $[Cu_2^{I}(\mathbf{1})_2]^{2+} \rightleftarrows 2[Cu^{II}(\mathbf{1})]^{2+} + 2e^-$ can be followed both visually and spectrophotometrically, as the $[Cu_2^{I}(\mathbf{1})_2]^{2+}$ complex is red-violet, due to a rather intense absorption band centered at $\lambda_{max} = 530$ nm (MLCT transition, $\epsilon = 1015\ m^{-1}\ cm^{-1}$), whereas the $[Cu^{II}(\mathbf{1})]^{2+}$ complex is green (metal-centered transition, $\lambda_{max} = 665$ nm, $\epsilon = 145\ m^{-1}\ cm^{-1}$). The dimer−monomer interconversion can be carried out through exhaustive electrolysis experiments, by setting the working electrode at the appropriate potential: (a) reduction potential, 120 mV lower than the reduction peak of the CV profile; (b) oxidation potential, 120 mV higher than the oxidation peak of the CV diagram. The process is fast and reversible and can be carried out consecutively in either direction.

It should be noted that visual and instrumental detection of the assembly/disassembly equilibrium is concentration-dependent. In particular, the interconversion, although clearly sensed at a concentration 10^{-3} M or more as a red-to-green color change, is perceived at 10^{-5} M as a variation from pale pink to colorless. We considered that the visual (and instrumental) signal could be amplified by making use of a property other than color and absorbance: fluorescence. Actually, fluorescence is a convenient property for monitoring phenomena at the molecular level, as it (i) provides a powerful signal, (ii) can be measured with a wide variety of instrumentation, and (iii) can be switched on/off through well-defined mechanisms (electron transfer, eT, and energy transfer, ET).[7] Thus, we decided to make use of a fluorescent probe to monitor the $[Cu^{I}_2(\mathbf{1})_2]^{2+}/[Cu^{II}(\mathbf{1})]^{2+}$ redox-driven interconversion. As an essential prerequisite, such a probe should interfere to a rather different extent with the $[Cu^{I}_2(\mathbf{1})_2]^{2+}$ and $[Cu^{II}(\mathbf{1})]^{2+}$ forms.



3

In this connection, we looked at the fluorescent fragment **3**, coumarine 343, which, when excited at $\lambda = 420$ nm, emits a yellow light with $\lambda_{max} = 480$ nm. **3** contains a −COOH group, which, when deprotonated, can act as a ligand for a coordinatively unsaturated metal center. Then, an MeOH solution 2×10^{-6} M in **3**, in its $-COO^-$ form after the addition of 1 equiv of $[Bu_4N]OH$, was titrated with a MeOH solution of the dimeric $[Cu_2^{I}(\mathbf{1})_2]^{2+}$ complex. The yellow fluorescent emission of **3** was only slightly affected, and the fluorescence intensity, I_F, decreased very moderately, even after the addition of several equivalents of the helicate complex (see open triangles in Figure 2).

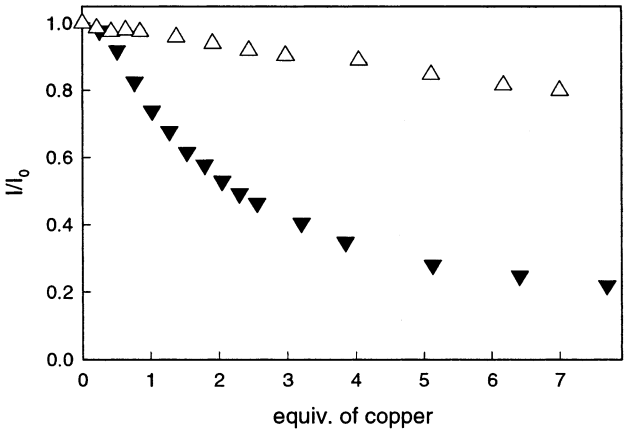


Figure 2. Titration of a MeOH solution of the anion of coumarine, **3**, with the dimeric system $[Cu_2^{I}(\mathbf{1})_2]^{2+}$ (open triangles) and with the monomeric complex $[Cu^{II}(\mathbf{1})]^{2+}$ (filled triangles).

This behavior can be explained by considering that each Cu^{I} center in the $[Cu_2^{I}(\mathbf{1})_2]^{2+}$ complex is coordinatively saturated and has no way to interact with the $-COO^-$ group of **3** and to interfere with the fluorophore. On the other hand, upon titration with a solution of the $[Cu^{II}(\mathbf{1})]^{2+}$ complex, I_F was observed to decrease until substantial quenching had occurred (filled triangles in Figure 2). We suggest that fluorescence quenching is associated to the metal−ligand interaction of the carboxylate group of coumarine with the Cu^{II} center of the $[Cu^{II}(\mathbf{1})]^{2+}$ complex to give a five-coordinate species. In particular, nonlinear least-squares fitting of the I_F vs number of equivalents profile (filled triangles in Figure 2) indicated the formation of a 1:1 adduct and a log K value of 5.53 ± 0.02 for the equilibrium $[Cu^{II}(\mathbf{1})]^{2+} + RCOO^- \rightleftarrows [Cu^{II}(\mathbf{1})(RCOO)]^{+}$ (where $RCOO^-$ represents the coumarine anion). The value of the association constant is similar to those measured for the formation of the 1:1 adduct with benzoate ($\log K = 5.5 \pm 0.1$) and with acetate ($\log K = 5.8 \pm 0.1$) determined spectrophotometrically under the same conditions. Fluorescence quenching in the $[Cu^{II}(\mathbf{1})(RCOO)]^{+}$ complex should be ascribed to the occurrence of an intramolecular process, of either eT or ET nature, involving the transition metal center and the excited fluorophore.[8]

Then, a solution 2×10^{-5} M in $[Cu^{II}(\mathbf{1})]^{2+}$ and 2×10^{-6} M in the coumarine anion was electrolyzed at a constant potential, by using a platinum gauze as the working electrode. Prior to the electrolysis, the solution was pale yellow (the color of coumarine) and nonfluorescent. First, the potential of the electrode was set at a value 120 mV more negative than the potential of the cathodic peak measured in a

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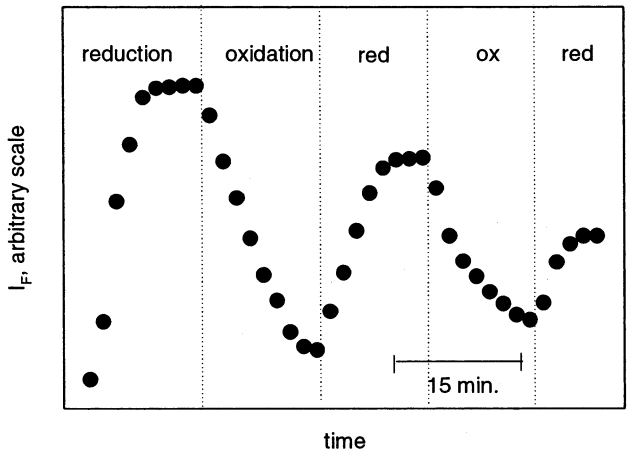

Figure 3. Fluorescent intensity, I_F, of a MeOH solution 2×10^{-5} M in $[Cu^{II}(\mathbf{1})]^{2+}$ and 2×10^{-6} M in the anion of **3** in the course of consecutive electrolysis experiments at constant potential. Maximum and minimum values of I_F correspond to a situation in which 1 mol of electrons per mole of copper has been consumed. Upon reduction, the indicator is released to the solution, and fluorescence is revived; upon oxidation, the indicator is taken up by the $[Cu^{II}(\mathbf{1})]^{2+}$ complex, and fluorescence is quenched.

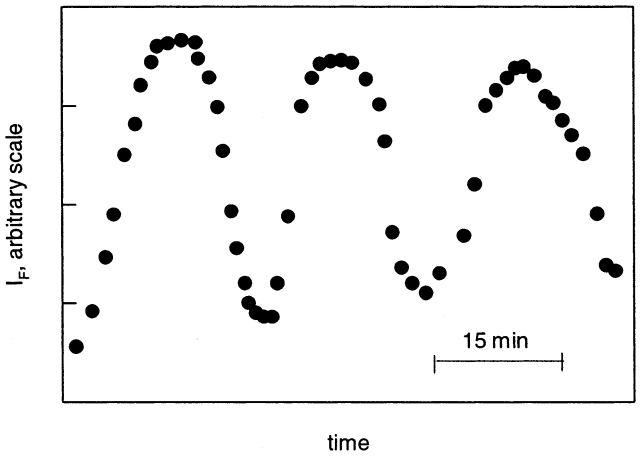

Figure 4. Consecutive reduction and oxidation cycles in a controlled potential electrolysis experiment on a MeOH solution 2×10^{-5} M in $[Cu^{II}(\mathbf{2})]^{2+}$ and 2×10^{-6} M in the anion of **3**. The vertical axis reports the fluorescence intensity, I_F, of **3** in the course of the electrolysis.

preliminary cyclic voltammetry experiment, carried out at a scan rate of 100 mV s^{-1}. Upon reduction, the solution began to fluoresce, and an intense band with $\lambda_{max} = 480$ nm developed in the emission spectrum. I_F values measured in the course of the exhaustive reduction are shown as filled circles in the diagram in Figure 3. When the quantity of current reached a constant value (corresponding to the passage of 1.0 ± 0.1 mol of electrons per mole of $[Cu^{II}(\mathbf{1})]^{2+}$), the potential of the working electrode was set at a value 120 mV more positive than the anodic peak measured in the CV experiment to promote Cu^{I}-to-Cu^{II} oxidation. Upon oxidation, a progressive decrease of I_F was observed, which ceased after the passage of 1 equiv of electrons. On alternating the potential of the working electrode between the two values, a saw-tooth profile of the fluorescence intensity was obtained, as shown in Figure 3. Such behavior must be associated with the release (fluorescence on)/uptake (fluorescence off) of the coumarine anion, $RCOO^-$, as long as the copper complexes assemble/disassemble according to the redox equilibrium

$$2[Cu^{II}(\mathbf{1})(RCOO)]^+ + 2e^- \rightleftarrows [Cu_2^{I}(\mathbf{1})_2]^{2+} + 2RCOO^- \quad (1)$$

The progressive signal attenuation observed in the course of the consecutive reduction and oxidation cycles can be ascribed to the decomposition at the electrode of the fluorescent indicator. In particular, it should be noted that coumarine 343 is not especially stable in an electrochemical sense, undergoing irreversible oxidation processes at the platinum electrode. In this connection, the CV profile of coumarine 343 in 0.1 M $[Bu_4N]ClO_4$ MeOH solution is shown in Figure 1 (black line). It is seen that the first (irreversible) oxidation peak develops at a potential that is almost coincident with the oxidation peak of the $[Cu_2^{I}(\mathbf{1})_2]^{2+}$ helicate complex. The addition of 1 equiv of Bu_4NOH to the solution of **3**, to generate the corresponding anion, did not induce any significant modification of the CV profile.

To circumvent the problem of the competitive oxidation of the fluorophore, two different routes can be followed in principle: (i) using a fluorogenic fragment more resistant to oxidation or (ii) using a dicopper(I) helicate complex whose oxidation/disassembly process takes place at a less positive potential. The first route can scarcely be followed because visible-light-emitting fluorophores have a rather fragile structure and undergo oxidative decomposition at potentials even less positive than coumarine. In terms of route ii, we considered that, in the family of Schiff's base ligands derived from *trans*-1,2-cyclohexanediamine, a system exists for which the Cu^{I}/Cu^{II} oxidation process takes place at a potential distinctly less positive than for $[Cu_2^{I}(\mathbf{1})_2]^{2+}$: the dicopper(I) helicate complex with the bis-bidentate ligand **2**. In this connection, the CV profile for the $[Cu_2^{I}(\mathbf{2})_2]^{2+}/[Cu^{II}(\mathbf{2})]^{2+}$ system is shown in Figure 1 (red line). It can be observed that the oxidation peak of $[Cu_2^{I}(\mathbf{2})_2]^{2+}$ is located at a potential more than 200 mV less positive than that of $[Cu_2^{I}(\mathbf{1})_2]^{2+}$. Moreover, the oxidation peak of $[Cu_2^{I}(\mathbf{2})_2]^{2+}$ anticipates well the first oxidation peak of coumarine 343.

Thus, we carried out a controlled potential electrolysis experiment on an MeOH solution that was 2×10^{-5} M in $[Cu^{II}(\mathbf{2})]^{2+}$, 2×10^{-6} M in coumarine anion, and 0.1 M in $[Bu_4N]ClO_4$. In particular, by setting the potential of the working electrode at the appropriate values (−120 mV than the reduction peak, +120 mV than the oxidation peak of the CV response), consecutive cycles of reduction and oxidation were induced, to which alternating revival/quenching of the coumarine fluorescence corresponded according to a saw-tooth profile (see Figure 4). Noticeably, the attenuation of the fluorescence signal was much less pronounced than in the case of the $[Cu_2^{I}(\mathbf{1})_2]^{2+}/[Cu^{II}(\mathbf{1})]^{2+}$ system. This might be a beneficial effect of operating the oxidation cycle at a potential low enough to avoid substantial decomposition of the auxiliary fluorescent probe. It should

be noted that moderate signal attenuation is still present, which indicates the occurrence of some oxidative decomposition. Such an effect becomes significant in view of the rather high dilution (micromolar scale) of the fluorophore.

Conclusions

A general interest exists in developing molecular systems that generate signals as a first step toward information processing at the molecular level. In particular, the envisaged system should be able to turn on/off the signal at will, behaving as a switch. Typically, switching derives from a definite change (large amplitude motion or variation in shape) that the envisaged system undergoes; representative examples include rotaxanes (sliding of the wheel between two unequivalent stations on the axle),[9,10] catenanes (half-turn rotation of one ring with respect to the other),[11,12] and scorpionates (dangling of a pendant arm into/out of an attached ring).[13,14] On the other hand, fluorescence is a convenient property, which, coupled to spatial rearrangement, can be switched on/off.[15]

In the present work, we devised a procedure for coupling a controllable molecular motion (the assembly/disassembly of a dimetallic helicate) to the quenching/revival of a fluorescent signal via an external input: variation of the electrode potential. The method did not involve any covalent linking of a fluorescent fragment to the movable system, an approach that might require serious synthetic efforts, but simply utilizes a fluorescent probe present at very low concentration (micromolar). In particular, the binding/release of the probe to/from the metal center in a given oxidation state induces the quenching/revival of the fluorescent emission. Very interestingly, any metal-containing molecular or supramolecular system undergoing a controllable motion between two different topologies can be converted to a fluorescence switch through the addition of a light-emitting probe displaying moderate binding tendencies toward the metal center. The essential prerequisite is that only one of the two states be coordinatively unsaturated, so that it can interact with and quench the fluorophore. Such an approach has been recently employed to monitor the pH-driven translocation of a Cu^{II} ion within a two-compartment ligand.[16]

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