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Redox Switching of Anthracene Fluorescence through the Cu^{II}/Cu^{I} Couple

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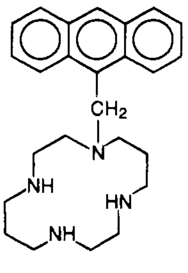
Optical signals can be generated and treated by means of a two-component supramolecular device.[1] A typical device should combine (i) a luminescent fragment and (ii) a control unit, capable of modifying the light-emitting properties of the adjacent subunit. The control unit can be a receptor, and its interaction with a metal ion can enhance/quench luminescence, which forms the basis for the design of luminescent sensors.[2] Recently, a system in which the fluorescent $[Ru^{II}(bpy)_3]^{2+}$ core has been covalently linked to the redox active quinone fragment has been synthesized and characterized.[3] Quinone promotes an electron transfer process from the excited state of the fluorophore and quenches fluorescence. Chemical or electrochemical reduction of quinone to hydroquinone prevents the electron transfer and revives fluorescence, in a reversible way. This system is the prototype of a molecular photoswitch, which can be operated from outside by varying the redox potential.



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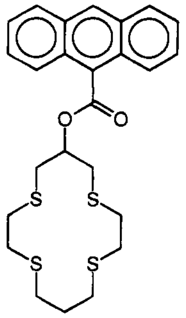

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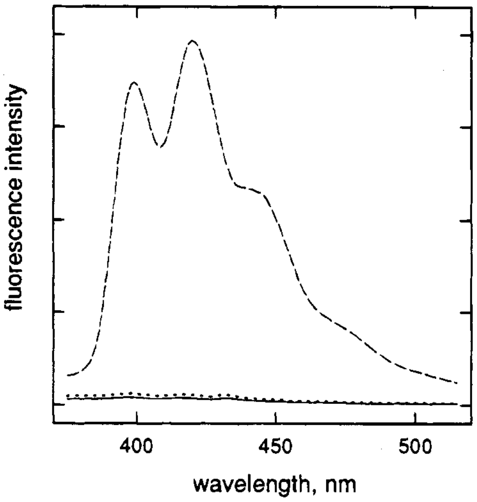

Figure 1. Fluorescence spectra in acetonitrile solution, at room temperature: (i) the uncomplexed system **1** (—); (ii) $[Zn^{II}(\mathbf{1})]^{2+}$ (– –); (iii) $[Cu^{II}(\mathbf{1})]^{2+}$ (--).

We were interested in designing molecular photoswitches operating through a transition metal center. Transition metals display a rich and versatile redox activity, and the electrode potential of a given couple can be modulated by modifying its coordinative environment: this may open the way to a conspicuous number of very versatile switches. We chose anthracene as a light emitting fragment, in view of its strong emission and chemical stability. Then, a *cyclam* ring was appended to the anthracene framework, through a $-CH_2-$ group, to give **1**.[4] The tendency of cyclam to promote the redox activity of encircled metal centers is well documented.[5] **1** itself does not fluoresce in a MeCN solution at room temperature. Fluorescence quenching can be ascribed to an electron transfer process from the proximate tertiary amine nitrogen atom of the tetraaza ring to the excited state of the anthracene fragment, *An. Noticeably, the $[Zn^{II}(\mathbf{1})](ClO_4)_2$ derivative displays the typical anthracene emission spectrum (see Figure 1). Coordination by Zn^{II} (d^{10} ion) lowers the energy of the tertiary amine group and prevents electron transfer (and consequent quenching) on a thermodynamic basis. On the other hand, the $[Cu^{II}(\mathbf{1})](ClO_4)_2$ derivative does not fluoresce in a MeCN solution at room temperature. It is possible that the radiationless deactivation of the *An fragment takes place through an energy transfer process (electron exchange type)[6] involving the half-filled $d_{x^2-y^2}$ orbital of Cu^{II} (d^9).

The proposed mechanisms have been confirmed by spectrofluorimetric investigations on the frozen solutions. In fact, freezing at 77 K awakens fluorescence of the uncomplexed system **1** (expected behavior for an electron transfer process),[7] but does not induce any emission for a solution of $[Cu^{II}(\mathbf{1})]^{2+}$ (energy transfer process). The above findings would suggest that a redox couple based on a d^{10}/d^9 change could act as a fluorescence switch for an adjacent anthracene fragment. The most practicable d^{10}/d^9 change seemed Cu^I/Cu^{II}. However, cyclam is not the appropriate receptor to favor such a redox change, as $[Cu^I(cyclam)]^+$ is formed at a very negative potential and lasts in solution only for the time scale of the cyclic voltammetry experiment.[8] On the other hand, a redox switch should operate through two consecutive oxidation states of comparable stability (a *bistable* unit).

Thus, we moved to the polythiaether analogue of cyclam: *thiacyclam* (1,4,8,11-tetrathiacyclotetradecane). Tendency of thiaether macrocycles to stabilize Cu^I is well documented.[9] In particular, both $[Cu^I(thiacyclam)]^+$ and $[Cu^{II}(thiacyclam)]^{2+}$ complexes have been isolated and their structures determined.[10] It appeared synthetically convenient to append the thiacyclam ring to the anthracene fragment through an estereal bridge, to

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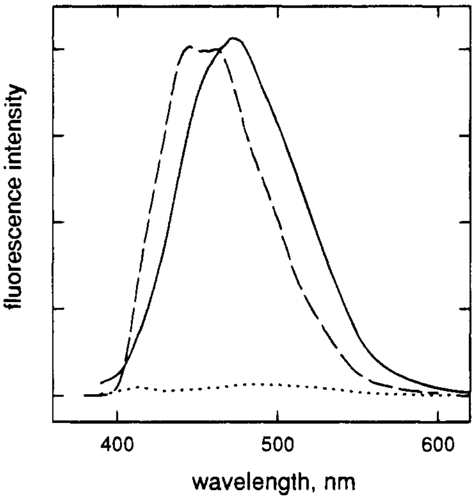

Figure 2. Fluorescence spectra in acetonitrile solution, at room temperature: (i) ethyl ester of 9-anthracenoic acid (—); (ii) the uncomplexed system **2** (– –). On addition of $\mathrm{Cu^I}$ to the solution of **2**, the $[\mathrm{Cu^I}(\mathbf{2})]^+$ species forms, but the emission is not modified (— —); on addition of an excess of $[\mathrm{NO}]\mathrm{BF_4}$, $[\mathrm{Cu^I}(\mathbf{2})]^+$ is oxidised to $[\mathrm{Cu^{II}}(\mathbf{2})]^{2+}$ and fluorescence is quenched (--).

give **2**.[11] Noteworthy, **2**, in a MeCN solution, displays a fluorescence spectrum less intense, much less structured and shifted toward higher wavelengths than that of anthracene (see Figure 2). The spectrum is similar to that of the ethyl ester of 9-anthracenoic acid and should be ascribed to a charge transfer excited state ($*\mathrm{An_{CT}}$).[12] On addition of 1 equiv of $[\mathrm{Cu^I(MeCN)_4}](\mathrm{ClO_4})$ to the solution of **2**, the monovalent cation was incorporated by the tetrathia ring, but the emission spectrum was not altered. Subsequently, an excess of the mild oxidising agent $[\mathrm{NO}]\mathrm{BF_4}$ was added: the solution turned bright blue, due to the formation of the $\mathrm{Cu^{II}}$ derivative, and fluorescence was completely quenched. The reversible interconversion of the $\mathrm{Cu^I}$ and $\mathrm{Cu^{II}}$ derivatives was demonstrated by the following experiment: the isolated $[\mathrm{Cu^{II}}(\mathbf{2})](\mathrm{ClO_4})_2$ complex was dissolved in MeCN, and the corresponding solution was observed not to fluoresce. Then, a controlled-potential electrolysis experiment was carried out on the same solution, setting the potential of the platinum gauze working electrode at 200 mV vs SCE: the solution decolored, due to the formation of the $[\mathrm{Cu^{II}}(\mathbf{2})]^+$ species, and fluorescence was revived. Thus, the potential of the platinum electrode was set to 800 mV vs SCE, which made the color turn blue again and quenched fluorescence.[14] Fluorescence could be switched on/off at will, by varying the potential of the working electrode.

The above results indicate that the $\mathrm{Cu^{II}/Cu^I}$ couple, inside an $\mathrm{S_4}$ coordinative environment, behaves as an efficient photoswitch. It remains now to elucidate the nature of the switching mechanism. Freezing at 77 K of a MeCN solution of $[\mathrm{Cu^{II}}(\mathbf{2})](\mathrm{ClO_4})_2$ made fluorescence revive, indicating that quenching at room temperature had to be assigned to an electron transfer process (from the $*\mathrm{An_{CT}}$ state to the $\mathrm{Cu^{II}}$ center), as described by the following equation:

$$*\mathrm{An_{CT}} + [\mathrm{Cu^{II}(S_4)}]^{2+} = \mathrm{An}^+ + [\mathrm{Cu^{I}(S_4)}]^+ \qquad (1)$$

Process (1) is very favored from a thermodynamic point of view, as indicated by the remarkably positive value of the variation of potential $\Delta E_{\mathrm{ET}}(*\mathrm{An_{CT}} \rightarrow \mathrm{Cu^{II}})$, which has been calculated as follows:

$$\Delta E_{\mathrm{ET}}(*\mathrm{An_{CT}} \rightarrow \mathrm{Cu^{II}}) = E(*\mathrm{An_{CT}}) + E\,°(\mathrm{Cu^{II}/Cu^{I}}) - E\,°(\mathrm{An^+/An}) = 2.0\ \mathrm{V} \qquad (2)$$

where $E(*\mathrm{An_{CT}})$ has been obtained from the energy of the emission band (460 nm → 2.7 V; see Figure 2) and $E\,°(\mathrm{Cu^{II}/Cu^{I}})$ and $E\,°(\mathrm{An^+/An})$ values have been obtained from voltammetric investigations in MeCN solution (0.1 and 0.8 V vs $\mathrm{Fc^+/Fc}$, respectively). Then, one could ask why an electron transfer process does not take place also in the $[\mathrm{Cu^I}(\mathbf{2})]^+$ system, as described by the following equation:

$$*\mathrm{An_{CT}} + [\mathrm{Cu^{I}(S_4)}]^{2+} = \mathrm{An}^- + [\mathrm{Cu^{II}(S_4)}]^{2+} \qquad (3)$$

The associated potential variation $\Delta E_{\mathrm{ET}}(*\mathrm{An_{CT}} \leftarrow \mathrm{Cu^{I}})$, calculated from eq 4, ($E\,°(\mathrm{An/An^-}) = -2.4$ V), is only slightly

$$\Delta E_{\mathrm{ET}}(*\mathrm{An_{CT}} \leftarrow \mathrm{Cu^{I}}) = E(*\mathrm{An_{CT}}) - E\,°(\mathrm{Cu^{II}/Cu^{I}}) + E\,°(\mathrm{An/An^-}) = 0.2\ \mathrm{V} \qquad (4)$$

positive, but much smaller than that associated with the ET process (1). Equations 3 and 4 give rather approximate ΔE_{ET} values. However, their difference is well beyond uncertainties and accounts for the switching effect exerted by the $\mathrm{Cu^I/Cu^{II}}$ couple on the luminescent fragment of system **2**. In particular, even if slightly favored from a thermodynamic point of view, the ET process (3) may be too slow to affect the radiative decay of the $*\mathrm{An_{CT}}$ excited state.

In conclusion, we took inspiration from the photophysical properties of $[\mathrm{Zn^{II}}(\mathbf{1})]^{2+}$ and $[\mathrm{Cu^{II}}(\mathbf{1})]^{2+}$ derivatives and we wanted to design a photoswitch operating *via* an "energy transfer" mechanism, through the a $\mathrm{d^{10}/d^9}$ redox change (e.g. $\mathrm{Cu^I/Cu^{II}}$). The bistable system $[\mathrm{Cu^{I,II}}(\mathbf{2})]^{+/2+}$ was prepared, which indeed behaved as an efficient fluorescence switch. However, switching was not matter of *electronic configuration*, but of *redox potential*. In the OFF situation, the $*\mathrm{An_{CT}}$ excited state is able to transfer an electron to the $\mathrm{Cu^{II}}$ center, in view (i) of the relatively high value of the $\mathrm{Cu^{II}/Cu^I}$ redox couple potential (a property provided by the $\mathrm{S_4}$ environment) and (ii) of the tendency on anthracene to be oxidized. On the other hand, (i) the $\mathrm{Cu^I}$ state is poorly reducing and, in particular, (ii) anthracene is especially resistent to the reduction, which does not induce any electron transfer process, maintains fluorescence and generates the ON situation. Finally, it should be noted that the ester bridge connecting the fluorescent moiety and the redox-active subunit in the supramolecule **2** plays an active and fundamental role. In fact, its interaction with the anthracene fragment lowers the energy of the excited state of the fluorophore (which has a charge transfer character) and drastically reduces the excitation potential, compared to unperturbed anthracene ($E(*\mathrm{An}) = 3.1$ V). Thus, the not too energetic $*\mathrm{An_{CT}}$ excited state displays a *discriminating* effect, allowing the ET process (1) and not allowing the ET process (3).

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Supplementary Material Available: Text giving details of the synthesis and characterization of **1** and **2** (1 page). Ordering information is given on any current masthead page.

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(11) **2** was obtained by reacting 9-anthracenoic acid with equimolar amounts of 1,1′-carbonyldiimidazole and 6-hydroxy-1,4,8,11-tetrathiatetradecane[13] in dry THF.

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(14) $[\mathrm{Cu^{II}}(\mathbf{2})](\mathrm{ClO_4})_2$ undergoes an irreversible redox change at 0.1 V vs $\mathrm{Fc^+/Fc}$ (=0.5 V vs SCE) in MeCN solution, 0.1 M in $\mathrm{Bu_4NClO_4}$, as shown by voltammetric studies. The $[\mathrm{Cu^{II}}(1,4,8,11\text{-tetrathiacyclotetradecane})](\mathrm{ClO_4})_2$ complex undergoes a reversible redox change ($\mathrm{Cu^{II}/Cu^{I}}$) at 0.10 V vs $\mathrm{Fc^+/Fc}$, under the same conditions.