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# Supramolecular Functions Related to the Redox Activity of Transition Metals

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The combination of the properties of different subunits in a multicomponent system may give rise to a function which is defined supramolecular. The presence of transition metals in one or more subunits may induce inter-component processes related to their redox and electron transfer (eT) properties, which trigger the supramolecular function (SF). The following examples are considered: (1) a receptor for transition metals is covalently linked to a fluorescent fragment; following recognition, a metal-to-fluorophore eT process quenches the fluorescence. SF: fluorosensing. (2) an azacyclam macrocycle, hosting the Ni<sup>II</sup>/Ni<sup>III</sup> redox couple, is covalently linked to a photoactive fragment: the Ni<sup>III</sup> state quenches the neighboring fluorophore through an eT mechanism, the Ni<sup>II</sup> state does not. SF: redox switching of a fluorescent signal. (3) a Cu<sup>II</sup> ion is coordinated by two 2,2'-bipyridine molecules, each bearing a cyclam subunit containing a nickel centre; when nickel is in the divalent state, an inorganic anion X<sup>-</sup> (N<sub>3</sub><sup>-</sup>, NCO<sup>-</sup>, NCS<sup>-</sup>) is bound to Cu<sup>II</sup>; on oxidation, X<sup>-</sup> moves to the Ni<sup>III</sup> centre. SF: electrochemically triggered translocation of X<sup>-</sup> from copper to nickel and *vice versa*.

*Keywords:* Fluorescent sensors; Electron transfer; Redox switches; Anion translocation; Tetra-aza macrocycles

## 1. THE DEFINITION OF SUPRAMOLECULAR FUNCTION

Molecules and ions can assemble to give supramolecular architectures of varying complexity, taking profit from non-covalent interactions: hydrogen bonding,  $\pi$ -stacking, the coordinative bond. The resulting systems are called *supramolecules* [1]. Thus, whereas classical molecular organic chemistry typically relies on the covalent bond, supramolecular chemistry focuses its attention on non-covalent interactions [2].

Each molecular component of a supramolecule brings its own properties and it may happen that properties from different components combine to generate a new property or a function. Indeed, the construction of function-making multi-component systems (devices [3], switches [4–7], machines [8,9]) represents one of the most appealing and frequented areas of supramolecular chemistry. Interest towards

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these functional aspects has led some Authors to extend the definition of a supramolecular system: [10] it is not stringent that the components of a supramolecule are held together by non-covalent interactions, they can be even covalently linked, through either a direct covalent bond or a spacer (*e.g.*, a  $-\text{CH}_2\text{CH}_2-$  group): the critical point is that an inter-component process takes place within the system and/or a new function – a supramolecular function – is generated. Thus a multi-component system, either covalently or non-covalently linked, is defined as a supramolecule on the basis of the function it is able to display. We will try to illustrate this point with an example from our recent research work.

One of the envisioned components is the tetra-aza macrocycle dioxocyclam, **1**, which possesses two secondary amine nitrogen atoms and two secondary amide nitrogen atoms. In neutral and even slightly acidic solution, **1** is able to incorporate a divalent transition metal (*i.e.*,  $\text{Cu}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ ), with simultaneous deprotonation of the two amide groups: neutral  $[\text{M}^{\text{II}}(\text{dioxocyclamato}(2-))]$  complexes are formed, in which the excess electrons occupy  $\pi$  molecular orbitals delocalised over the NCO fragments [11]. Formation of the  $[\text{Cu}^{\text{II}}(\text{dioxocyclamato}(2-))]$  complex is visually perceived at a concentration  $\geq 10^{-3}\text{M}$  by the appearance of a pink-violet colour, due to a d-d band centred at 510 nm (molar absorbance,  $\epsilon = 98\text{M}^{-1}\text{cm}^{-1}$ ).  $\text{Ni}^{\text{II}}$  forms a low-spin yellow complex ( $\lambda = 452\text{nm}$ ,  $\epsilon = 92\text{M}^{-1}\text{cm}^{-1}$ ). Spin pairing is promoted by the strong in-plane interactions exerted by the 14-membered macrocycle.

Formation of both  $\text{Cu}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$  complexes can be followed through spectrophotometric titration experiments. For comparative purposes (*vide infra*) the experiments are carried out in an MeCN/water solution (4:1 v/v). In particular, the solution in the spectrophotometric cuvette contains dioxocyclam, **1** equiv. of  $\text{M}^{\text{II}}$ , plus excess acid, and is titrated with standard

NaOH. Metal complex formation is announced by colour appearance and is quantitatively expressed by the increase of the absorption of the pertinent d-d band (see Fig. 2). The absorbance *vs.* pH sigmoidal profile of  $\text{Cu}^{\text{II}}$  anticipates by 2 pH units that observed with  $\text{Ni}^{\text{II}}$ , which reflects the greater solution stability of the copper(II) complex. No other divalent 3d metal ion except  $\text{Cu}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$  form dioxocyclamato

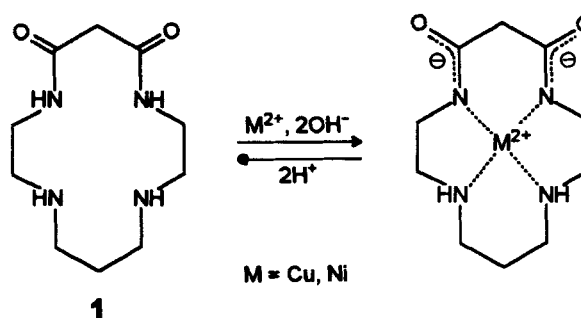


FIGURE 1 The coordinating behaviour of dioxocyclam, **1**. Metal complexation proceeds with the simultaneous deprotonation of the two amide groups. Only divalent metals late in the first transition series (*i.e.*,  $\text{Cu}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ ) establish coordinative interactions strong enough to outbalance the very endothermic amide deprotonation process.

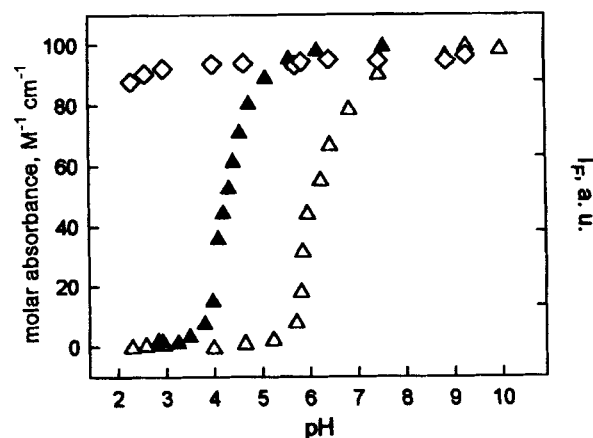


FIGURE 2 pH dependent complexation of  $\text{Cu}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$  by dioxocyclam, **1**, in an MeCN/water mixture (4:1 v/v). Metal complexation is indicated by the development of an absorption band centred at 510 nm in the case of  $\text{Cu}^{\text{II}}$  (absorbance: full triangles) and at 452 nm for  $\text{Ni}^{\text{II}}$  (open triangles). The intensity of the emission band of anthracene,  $I_{\text{F}}$  (diamonds) does not vary over the investigated pH range.

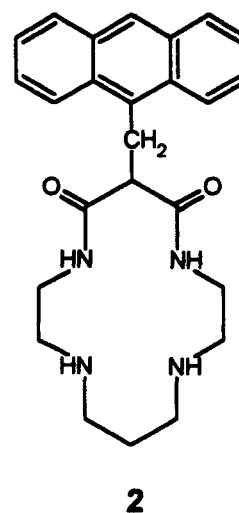
(2-) complexes in aqueous acetonitrile solution. This is due to the fact that the deprotonation of the amide group is a very endothermic process (in fact, amide itself does not display any acidic tendency in aqueous solution,  $pK_A > 14$ ) and only metal ions forming particularly strong M–N interactions (*i.e.*, those late in the 3d series) are capable of outbalancing this unfavourable effect, thus promoting complexation. Therefore, dioxocyclam exhibits discriminating tendencies towards 3d metals: when added to a solution containing  $Mn^{II}$ ,  $Fe^{II}$ ,  $Co^{II}$ ,  $Ni^{II}$  and  $Cu^{II}$ , it incorporates only the last two ions, even under strongly basic conditions. The last metal of the 3d series,  $Zn^{II}$ , which has a  $d^{10}$  electronic configuration and cannot profit at all from ligand field effects, cannot promote amide deprotonation and is not included into the dioxocyclam ring.

$[M^{II}(\text{dioxocyclamato}(2-))]$  complexes possess two peculiar properties: (i) they quickly demetallate on addition of acid, a unique feature among transition metal tetra-aza-macrocyclic complexes. In particular, the protonation of the hardly accessible nitrogen donor atoms in the complexes with saturated and unsaturated tetra-aza-macrocycles is kinetically very disfavoured, which prevents metal extrusion (the kinetic macrocyclic effect) [15]. The easy demetallation of  $[M^{II}(\text{dioxocyclamato}(2-))]$  complexes in acidic solution is due to the fact that protons have not to seek the nitrogen atoms which point their lone pairs into the ring, but they have simply to attack the oxygen atoms of the deprotonated amide groups, which point outwards and, due to  $\pi$ -delocalisation, are partially negatively charged. Following oxygen protonation, an enol-amide tautomeric rearrangement takes place, which minimizes the nitrogen atom coordinating tendencies and induces metal extrusion [12]. Thus, complexation by dioxocyclam is reversible and the fast metal inclusion/extrusion process can be driven by varying the pH. (ii)  $[M^{II}(\text{dioxo-cyclamato}(2-))]$  complexes undergo one-electron oxidation to the corresponding trivalent complexes at a moderately

positive potential ( $Cu^{III}/Cu^{II}$ : 0.89 V *vs.* NHE;  $Ni^{III}/Ni^{II}$ : 0.75 V *vs.* NHE) [13]. Aqueous stable  $[Cu^{III}(\text{dioxocyclamato}(2-))]^+$ , brown, low-spin, and  $[Ni^{III}(\text{dioxocyclamato}(2-))]^+$ , green, low-spin, can be obtained by oxidation of the divalent complexes with peroxydisulphate [14]. The ease of the  $M^{II}$ -to- $M^{III}$  oxidation process is a consequence of the intense in-plane coordinative interactions (which raise the energy of the anti-bonding level, essentially metallic in character, from which the electron is abstracted), and of the moderate increase of the net electrical charge (from nil to +1, considering that the ligand is doubly negatively charged).

The other molecular component we focus the attention on is anthracene, one of the most classical fluorescent molecules. It absorbs light in the UV region (vibrationally structured absorption band, centred at 356 nm,  $\log \epsilon = 3.84$ ), in an EtOH solution, due to a  $\pi-\pi^*$  transition and it emits light in the UV-visible borderline region (vibrationally structured emission band centred at 400 nm, quantum yield  $\Phi = 0.22$ , lifetime of the  $\pi-\pi^*$  excited state  $\tau = 4.5$  ns, in EtOH).

If we dissolve equimolecular amounts of dioxocyclam and anthracene in the same solution (MeCN/water, 4:1 v/v), each component displays its individual properties and does not



interfere with the other: dioxocyclam incorporates selectively  $\text{Cu}^{\text{II}}$  (or  $\text{Ni}^{\text{II}}$ ), present in equimolecular amount in solution, and anthracene fluoresces, over the entire 2–12 pH range. This rather obvious reference experiment is illustrated by the diagrams in Figure 2.

Let us now consider system 2, in which anthracene and dioxocyclam have been covalently connected by a  $-\text{CH}_2-$  spacer [16]. In aqueous acetonitrile, the dioxocyclam component maintains its tendency to incorporate  $\text{Cu}^{\text{II}}$  in the 4.5–5.5 pH interval, as indicated by the sigmoidal absorbance *vs.* pH profile shown in Figure 3.

However, the fluorescence intensity,  $I_{\text{F}}$ , of the anthracene subunit of 2 is not maintained over all the investigated pH range, but is quenched according to a sigmoidal profile centred at the same pH, but symmetrically inverted with respect to the absorbance *vs.* pH profile (see Fig. 3). This indicates that fluorescence quenching of the anthracene fragment has to be correlated to the complexation of  $\text{Cu}^{\text{II}}$  by the dioxocyclam subunit. In particular, quenching

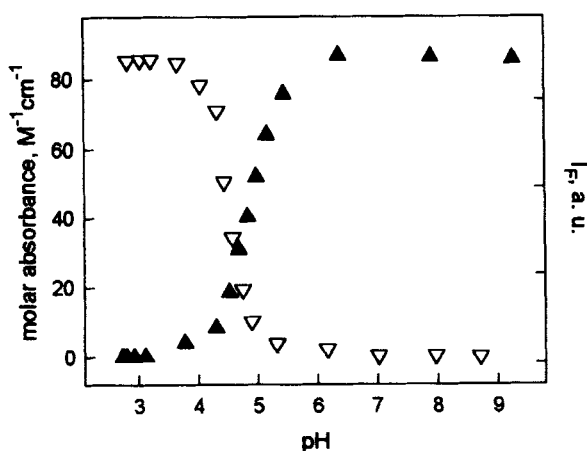
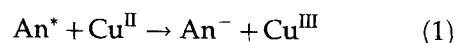


FIGURE 3 pH controlled recognition of  $\text{Cu}^{\text{II}}$  by the two-component system, 2, in an MeCN/water mixture (4:1 v/v). Metal complexation by the dioxocyclam subunit of 2 is indicated by the development of an absorption band centred at 510 nm (absorbance: full triangles). The bound metal quenches the nearby photoexcited anthracene fragment through an electron transfer process ( $I_{\text{F}}$ , open triangles). Thus, the occurrence of  $\text{Cu}^{\text{II}}$  recognition is signalled by fluorescence quenching.

must be ascribed to the occurrence of an intramolecular electron transfer (eT) process from the metal centre to the photo-excited anthracene fragment (An), as described by Eq. (1):



The  $\Delta G_{\text{eT}}^{\circ}$  value associated to process (1) is distinctly negative ( $-0.5 \text{ eV}$ ); it can be calculated through Eq. (2), which results from the combination of the relevant photophysical and electrochemical quantities involved in the thermodynamic cycle illustrated in Figure 4.

$$\Delta G_{\text{eT}}^{\circ} = -[E^{0-0} - eE^{\circ}(\text{Cu}^{\text{III}}/\text{Cu}^{\text{II}}) + eE^{\circ}(\text{An}/\text{An}^-)] = -0.5 \text{ eV} \quad (2)$$

There is no doubt that the facility of the oxidation of the dioxocyclamato(2-) encircled  $\text{Cu}^{\text{II}}$  centre, as expressed by the moderately positive  $E^{\circ}(\text{Cu}^{\text{III}}/\text{Cu}^{\text{II}})$  value, favourably contributes to the occurrence of the eT process (1).

Also in presence of 1 equiv. of  $\text{Ni}^{\text{II}}$ , a sigmoidal  $I_{\text{F}}$  *vs.* pH profile is observed, centred at the same pH of the inverted corresponding absorbance *vs.* pH profile. In fact, the  $\Delta G_{\text{eT}}^{\circ}$  value associated to the  $\text{Ni}^{\text{II}}$ -to- $\text{An}^*$  eT process is definitely negative in the present case too ( $-0.35 \text{ eV}$ ).

Thus, an intercomponent process is active with system 2 and generates a useful function: sensing of transition metal ions. In particular, the two-component system 2 can be considered as a fluorescent molecular sensor of  $\text{Cu}^{\text{II}}$  and

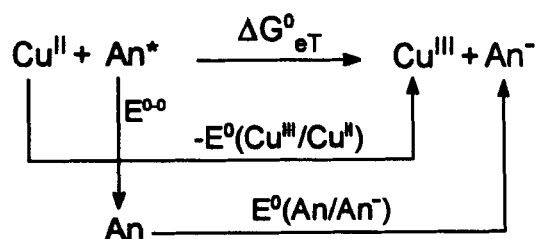


FIGURE 4 Thermodynamic cycle associated to the intramolecular electron transfer process from the  $\text{Cu}^{\text{II}}$  centre to the photoexcited anthracene fragment,  $\text{An}^*$ , in the two-component system 2.

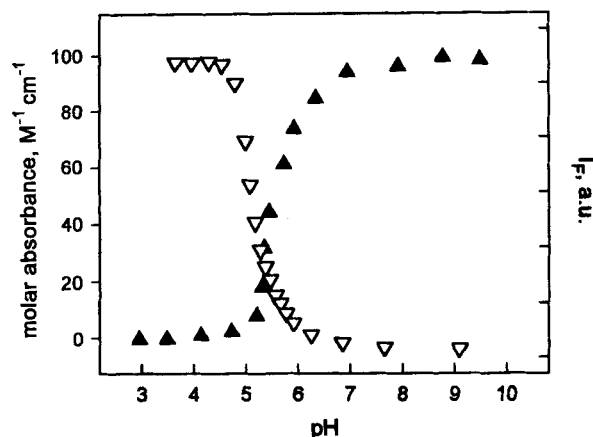


FIGURE 5 pH controlled recognition of Ni<sup>II</sup> by the two-component system, **2**, in an MeCN/water mixture (4:1 v/v). Ni<sup>II</sup> complexation by the dioxocyclam subunit of **2** is indicated by the development of an absorption band centred at 452 nm (absorbance: full triangles). When coordinated by the macrocyclic subunit, the metal quenches the nearby photoexcited anthracene fragment through an electron transfer process ( $I_F$ , open triangles). Thus, Ni<sup>II</sup> recognition is communicated to the outside by fluorescence quenching.

Ni<sup>II</sup>: it has a receptor subunit (dioxocyclam) capable of recognising the metal and a signalling subunit (the anthracene fragment) which communicates to the outside the occurrence of the recognition process. Fluorescence is a convenient property for signalling purposes, as it can be visually and instrumentally detected at rather low concentration levels (*e.g.*,  $\geq 10^{-7}$  M, when using the anthracene fragment as a reporter).

Thus, we consider **2** as a supramolecule, as its combined fragments (covalently linked in the present case) display a function (transition metal fluorosensing) that the two separate components, when coexisting in solution, are not able to perform. Following a more visual approach, the supramolecular behaviour clearly results from the comparison of the plots displayed in Figures 3 and 5.

Simple linking of components may not suffice to generate the function. An inter-component process must operate (the eT mechanism, in the example described above) and, in this sense, the role of the spacer is essential. The electron can move from the Cu<sup>II</sup> centre along the rigid and  $\pi$ -delocalised portion of the macrocycle containing the deprotonated amide groups and through the  $-\text{CH}_2-$  bridge to reach the photo-excited

anthracene subunit. Moreover, free rotation around the  $-\text{CH}_2-$  linker may bring the An fragment and the  $[\text{M}^{\text{II}}(\text{dioxocyclamato}(2-))]$  subunit to occasional Van der Waals contact, allowing a fast intramolecular eT process to take place. However, one could predict that the derivative in which the fluorophore and the receptor are linked by a much longer aliphatic chain, *e.g.*,  $-(\text{CH}_2)_{16}-$ , does not display any fluorosensing function, since (i) the long aliphatic chain is hardly permeable to electrons and (ii) the probability that the An fragment and the  $[\text{M}^{\text{II}}(\text{dioxocyclamato}(2-))]$  subunit come into contact is extremely low. Thus, in absence of the inter-component process, the covalently linked An- $(\text{CH}_2)_{16}$ -dioxocyclam system (not synthesised, yet!) should not be considered a supramolecule.

## 2. REDOX SWITCHING OF FLUORESCENCE

In the example described in the previous Section, the supramolecular function of switching OFF/ON the emission of an anthracene fragment was provided by an ionic input, either

the  $\text{Cu}^{\text{II}}$  or the  $\text{Ni}^{\text{II}}$  cation. In particular, switching was associated to the pH-controlled inclusion/extrusion of the transition metal into/from the receptor ring of system **2**. However, fluorescence switching by a transition metal can be performed also by holding the metal centre permanently close to the light-emitting fragment, *i.e.*, firmly encircled by a macrocycle linked to the fluorophore. In this case, however, one has to modify the oxidation state of the metal, *e.g.*, from  $\text{M}^{\text{n}+}$  to  $\text{M}^{(\text{n}+1)+}$ . In fact, it may happen that one oxidation state undergoes an eT process to/from the nearby photoexcited sub-unit and the other oxidation state does not. Under these favourable conditions, fluorescence can be consecutively switched OFF/ON at will, by alternating the  $\text{M}^{\text{n}+}/\text{M}^{(\text{n}+1)+}$  couple, *via* either chemical or electrochemical oxidation/reduction cycles. Such a switching situation is pictorially sketched in Figure 6.

It may occur also that both the oxidation states of the metal centre become involved in an eT process with the proximate photo-excited fragment,  $\text{Fl}^*$ . This generates the disagreeable situation of a system perpetually in the OFF state,

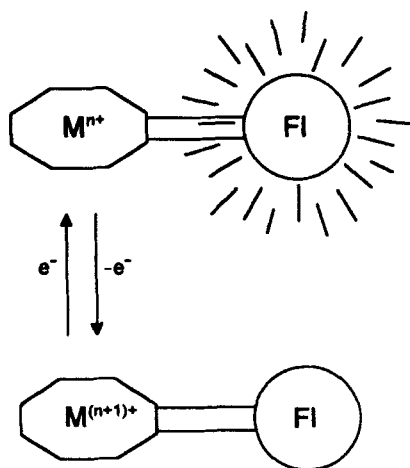
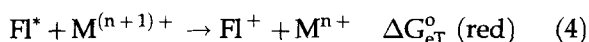
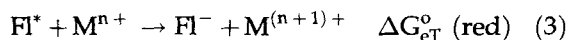


FIGURE 6 ON/OFF switching of the fluorescence in a three-component system: [redox subunit]-[spacer]-[fluorophore]. In the reported example, the oxidised metal centre  $\text{M}^{(\text{n}+1)+}$  quenches the proximate fluorophore *via* an electron transfer process, while the reduced metal  $\text{M}^{\text{n}+}$  does not. Fluorescence can be consecutively switched OFF/ON at will, by alternating the  $\text{M}^{\text{n}+}/\text{M}^{(\text{n}+1)+}$  couple.

whose emission cannot be awakened on addition of whatever redox agent.

In principle, the behaviour of a two-component system of the type illustrated in Figure 7 can be predicted by considering the free energy change values,  $\Delta G_{\text{eT}}^{\circ}$ , associated to each of the two possible photoinduced electron transfer processes, (3) and (4).



Corresponding  $\Delta G_{\text{eT}}^{\circ}$  values can be obtained through thermodynamic cycles of the type reported in Figure 4, by combining the pertinent photophysical and electrochemical quantities.

In spite of the strict thermodynamic conditions that govern processes (3) and (4), the behaviour of a freshly designed molecular switch of fluorescence is not always predictable. Things are complicated by the fact that another mechanism of metal-fluorophore interaction can compete: the electronic Energy Transfer (ET) process. Factors determining the dominance of

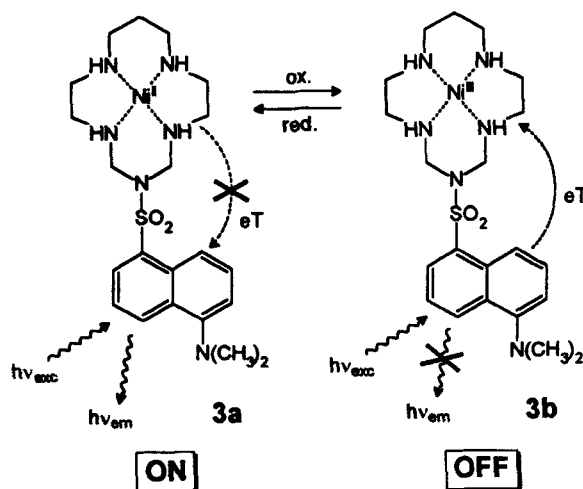


FIGURE 7 Redox switching of fluorescence.  $\text{Ni}^{\text{III}}$  quenches the fluorescence of the nearby dansylamide fragment,  $\text{Ni}^{\text{II}}$  does not. Dansylamide emission can be reversibly switched ON/OFF at will, through consecutive chemical or electrochemical oxidation and reduction processes.

one mechanism over the other in two-component molecular switches of fluorescence have been recently discussed [17].

We will consider in the following two examples of redox switches of fluorescence operating through the eT mechanism: an ON/OFF case ( $\Delta G_{\text{eT}}^{\circ}(\text{red}) > 0$ ;  $\Delta G_{\text{eT}}^{\circ}(\text{ox}) < 0$ ) and an unpleasant, all quenched, OFF/OFF case ( $\Delta G_{\text{eT}}^{\circ}(\text{red}) < 0$ ;  $\Delta G_{\text{eT}}^{\circ}(\text{ox}) < 0$ ).

In system 3, a nickel tetra-aza-macrocyclic complex has been connected through a sulphonamide bridge to the dansyl (Dns) photoactive fragment [18]. The 14-membered macrocycle contains five nitrogen atoms, but only the secondary ones are coordinated to the metal. The tertiary nitrogen atom has an amide nature and plays a mere architectural role. The 14-membered macrocycle displays the same coordinating tendencies as the iso-structural cyclam, thus belonging to the family of azacyclams [19].

$[\text{Ni}^{\text{II}}(\text{azacyclam})]^{2+}$  complexes are obtained through a one-pot reaction, which involves the open-chain tetramine 2.3.2-tet, two molecules of

formaldehyde, and an  $\text{R-NH}_2$  molecule formally behaving as a diprotic acid (a primary amine, a primary amide, either carboxyamide or sulphonamide). The  $\text{Ni}^{\text{II}}$  ion acts as a template, preorientating the tetramine before Schiff base reaction of formaldehyde molecules at the terminal primary nitrogen atoms and the subsequent stepwise nucleophilic attack of the deprotonated  $\text{R-NH}_2$  fragment at the  $-\text{N}=\text{CH}_2$  bonds. The reaction involving sulphonamides, sketched in Figure 8, is especially useful, as it allows to synthesise a nickel(II) complex having appended at the azacyclam framework any desirable R group, provided that the corresponding sulphonamide derivative  $\text{RSO}_2\text{NH}_2$  is available [20]. In this sense, the synthetic procedure outlined in Figure 8 represents a very convenient way to generate a two-component system, in which one component displays controllable redox activity. In fact, as it has been mentioned in the previous Section, encircling of  $\text{Ni}^{\text{II}}$  by a quadridentate aza-macrocycle makes the otherwise unstable  $\text{Ni}^{\text{III}}$  state easily accessible. This tendency is particularly evident in the

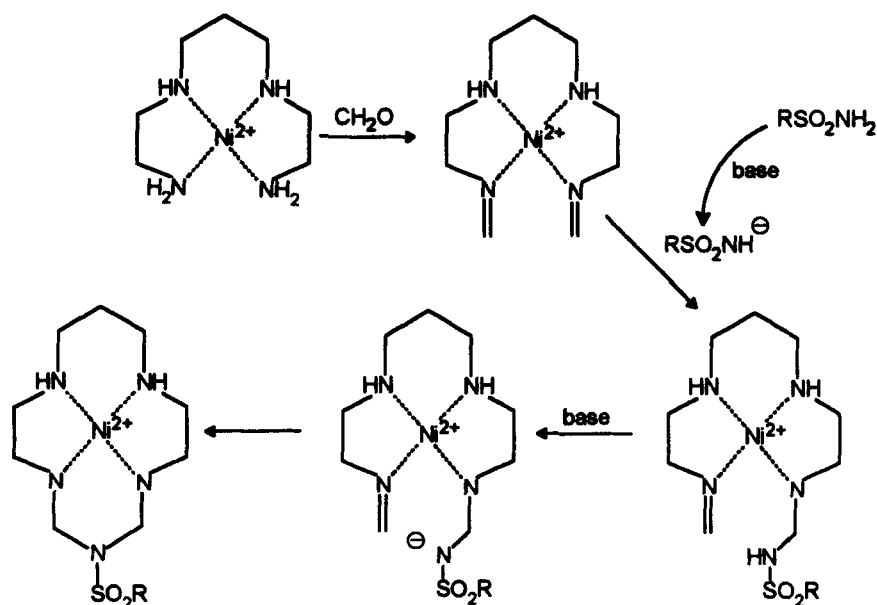


FIGURE 8 The multistep mechanism of the one-pot synthesis of  $[\text{Ni}^{\text{II}}(\text{azacyclam})]^{2+}$  derivatives having a desired appended R functionality.



case of 14-membered quadridentate macrocycles (cyclam-like ligands, including azacyclams) and results from the ligand capability to impose a square coordination and to establish especially strong in-plane interactions. In this connection, it should be noted that the  $E_{1/2}$  value associated to the reversible  $[\text{Ni}^{\text{III,II}}(\text{cyclam})]^{3+,2+}$  couple in 1 M HCl is 0.73 V *vs.* NHE [21], to be compared, for instance, to the more familiar  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox couple in acidic solution (0.77 V *vs.* NHE). Thus, solution stable  $\text{Ni}^{\text{III}}$  complexes of cyclam-like macrocycles can be generated in solution using mild oxidising agents. On the other hand, treatment with mild reducing agents restores the  $\text{Ni}^{\text{II}}$  derivative and the oxidation-reduction cycle can be repeated several times without decomposition of the complex. In this sense, the  $[\text{Ni}^{\text{III,II}}(\text{cyclam})]^{3+,2+}$  couple represents a perfect bistable system.

The dansyl fragment gives rise to a charge transfer excited state which involves the dimethylamine donor group. In fact, its excitation spectrum is similar to that of plain naphthalene, but the emission spectrum is quite different, the poorly structured emission band being red-shifted to 510 nm (to be compared to 335 nm of the vibrationally structured emission band of naphthalene).

The emission properties of the dansyl fragment are maintained in the reduced form of the two-component system **3a**. Both the excitation and the emission spectra of **3a** in MeCN are shown in Figure 9. Thus, the  $\text{Ni}^{\text{II}}$  centre does not interact with the excited state  $\text{Dns}^*$  and does not alter its emission properties. The distance between the metal centre and the closest carbon of the aromatic fragment (the one bound to the sulphur atom) is 5.87 Å, as measured from the crystal structure [18]. It may be surprising that a transition metal does not quench so close a fluorophore through either an ET or an eT mechanism. The occurrence of an ET process of the Dexter type requires that the fluorophore and the metal come to Van der Waals contact,

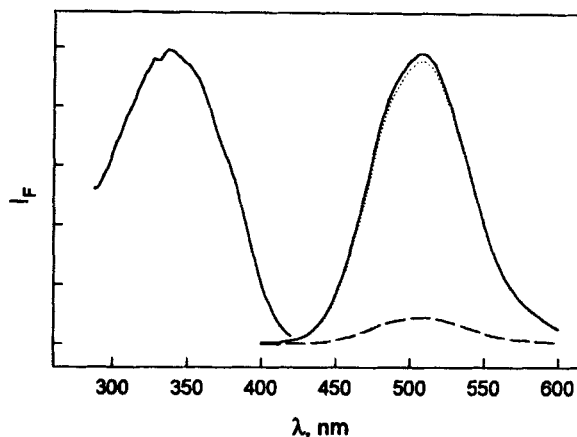


FIGURE 9 Optical properties of the dansylamide subunit within the multicomponent system **3**. Solid line,  $\lambda < 420$  nm: excitation spectrum of the reduced derivative **3a** in MeCN; solid line,  $\lambda > 400$  nm: emission spectrum of a solution of **3a**; dashed line: emission spectrum of the same solution after exhaustive electrolysis at 0.33 V *vs.*  $\text{Fc}^+/\text{Fc}$  (**3a** has been oxidised to **3b**); dotted line: emission spectrum of the solution above, which has now been electrolysed at  $-0.03$  V (**3b** has been reduced to **3a** again).

then undergoing a circular double electron exchange. Such an opportunity is prevented by the rigid sulphonamide spacer which hinders the occasional folding of the molecule and keeps  $\text{Ni}^{\text{II}}$  and  $\text{Dns}^*$  well away from each other. On the other hand, the  $\pi$ -orbitals extended over the sulphonamide bridge should allow the occurrence of an eT process. However, this mechanism is prevented on a thermodynamic basis, as the  $\Delta G_{\text{eT}}^{\circ}$  value associated to the  $\text{Ni}^{\text{II}}$ -to- $\text{Dns}^*$  eT process is distinctly positive:  $\Delta G_{\text{eT}}^{\circ}(\text{Ni}^{\text{II}} \rightarrow \text{Dns}^*) = -E^{0-0} + eE^{\circ}(\text{Ni}^{\text{III}}/\text{Ni}^{\text{II}}) - eE^{\circ}(\text{Dns}^+/\text{Dns}) = -2.4 + 0.008 - (\geq -3.0) = \geq 0.68$  eV. Thus, failure of the  $\text{Ni}^{\text{II}}$ -to- $\text{Dns}^*$  eT process to occur is mainly due to the extremely poor ability of the  $\text{Dns}$  fragment to accept an electron.

One-electron oxidation of **3a** to **3b** with  $\text{S}_2\text{O}_8^{2-}$  in EtOH/ $\text{H}_2\text{O}$  95/5 solution induces complete quenching of the dansyl fluorescence. The quenching process can be ascribed to a  $\text{Dns}^*$ -to- $\text{Ni}^{\text{III}}$  eT process. In fact, the pertinent free energy change is clearly negative:  $\Delta G_{\text{eT}}^{\circ}(\text{Dns}^* \rightarrow \text{Ni}^{\text{III}}) = -E^{0-0} - eE^{\circ}(\text{Ni}^{\text{III}}/\text{Ni}^{\text{II}}) + eE^{\circ}(\text{Dns}^+/\text{Dns}) =$

$-2.4 - 0.08 + 0.55 = -1.93$  eV. Moreover, the genuine eT nature of the quenching process is demonstrated by the fact that on freezing the solution at the liquid nitrogen temperature, fluorescence is fully restored. The redistribution of the electrical charges which follows an eT process induces a drastic rearrangement of the solvent molecules. On solvent immobilisation, the eT process is prevented and the photoexcited fluorophore can undergo its usual radiative decay. Recording of the fluorescence spectra of fluorophore-quencher systems dissolved in a frozen medium is a simple but efficient way to discriminate between the eT and the ET mechanism. In fact, an ET process does not induce any charge redistribution and rearrangement of solvating molecules and operates efficiently both in a fluid solution (at room temperature) and in an immobilised medium (at 77 K). Thus, freezing a solution containing a fluorophore quenched at room temperature *via* an ET mechanism does not induce any fluorescence revival.

When  $\text{NO}_2^-$  is added to the solution, **3b** is reduced to **3a** and the fluorescence is fully restored. Consecutive switching OFF/ON of the fluorescence can be conveniently carried out in the course of a controlled potential electrolysis experiment in MeCN, by alternating the potential of the platinum gauze acting as a working electrode at 0.33 V *vs.*  $\text{Fc}^+/\text{Fc}$  (**3a**-to-**3b** oxidation) and at -0.03 V (**3b**-to-**3a** reduction). The emission profiles taken during the first electrochemical redox cycle are shown in Figure 9.

System **3** is interesting in that it profits in a full way from the electron transfer tendencies of a transition metal: (i) a thermal eT process is used to move from one state to the other of the bistable system; (ii) a photoinduced eT process is responsible for the selective quenching of the Dns\* fragment.

The supramolecular nature of the fluorescence switching function described before is confirmed by the following reference experiment. A solution  $10^{-5}$  M in both dansylamide and

$[\text{Ni}^{\text{II}}(\text{methanesulphonamideazacyclam})]$  is prepared. When an equivalent amount of peroxydisulphate is added, the  $\text{Ni}^{\text{II}}$  macrocyclic complex is oxidised to  $\text{Ni}^{\text{III}}$  (and the colour of the solution turns from pale yellow to green), but the emission of the dansylamide molecule is not altered. Needless to say, the two components have to be positioned at a convenient and permanently short distance (*e.g.*, in a supramolecular system) to combine their properties and to generate the desired function.

$\text{Cu}^{\text{III}}/\text{Cu}^{\text{II}}$  is another redox couple one could try to use for switching purposes. It has been mentioned in Section 1 that, when encircled by a dioxocyclamato(2-) ring,  $\text{Cu}^{\text{II}}$  can be oxidised to the trivalent state, to give the aqueous stable  $[\text{Cu}^{\text{III}}(\text{dioxocyclamato(2-)})]^+$  species, brown in colour and diamagnetic. Thus, the two-component system **2**, when hosting the  $\text{Cu}^{\text{III}}/\text{Cu}^{\text{II}}$  couple, deserves to be tested for the function of fluorescence switching. We have already seen that in the  $\text{Cu}^{\text{II}}$  derivative the fluorescence of the anthracene fragment is quenched through a  $\text{Cu}^{\text{II}}$ -to- $\text{An}^*$  eT process. On chemical oxidation to the  $\text{Cu}^{\text{III}}$  derivative in an aqueous MeCN solution with  $\text{S}_2\text{O}_8^{2-}$ , emission is not restored. Quenching, in this case, has to be ascribed to a thermodynamically favoured  $\text{An}^*$ -to- $\text{Cu}^{\text{III}}$  eT process:  $\Delta G_{\text{eT}}^{\circ}(\text{An}^* \rightarrow \text{Cu}^{\text{III}}) = -E^{0-0} - eE^{\circ}(\text{Cu}^{\text{III}}/\text{Cu}^{\text{II}}) + eE^{\circ}(\text{An}^+/\text{An}) = -3.1 - 0.44 + 0.84 = -2.7$  eV. The eT nature of the quenching mechanism in both  $\text{Cu}^{\text{II}}$  and  $\text{Cu}^{\text{III}}$  derivatives is confirmed by the fact that vitrification of their butyronitrile solutions induces full restoration of the anthracene emission band. Thus, we are in presence of an OFF/OFF system, completely useless for signalling purposes, whose behaviour at room temperature is illustrated in Figure 10. The system does not display a supramolecular function, but, in spite of that, it should be still considered a supramolecular system, as an intercomponent process is present. It is disappointing that this process operates both in the oxidised and in the reduced form.

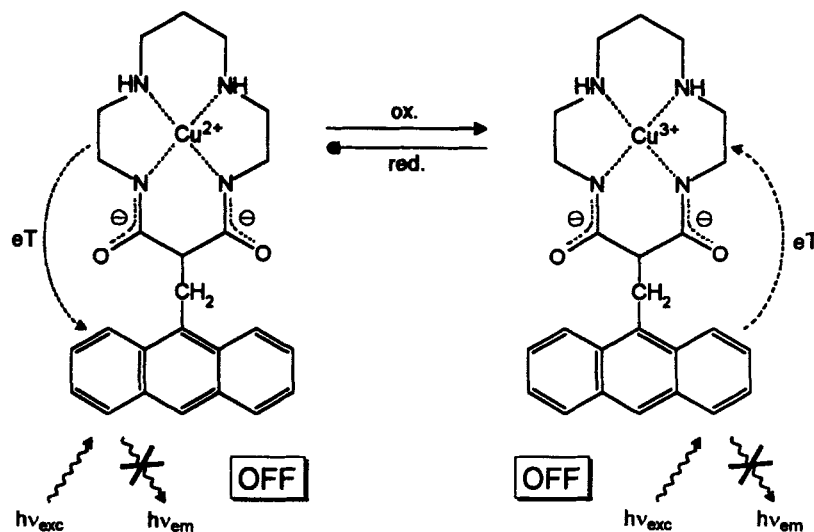


FIGURE 10 An example of an OFF/OFF redox switch of fluorescence. In both the reduced and oxidised form, the anthracene fluorescence is quenched *via* an electron transfer process involving the metal centre.

### 3. INTRAMOLECULAR ANION HOPPING BETWEEN METAL CENTRES

Changing the oxidation state of a transition metal centre may drastically modify its stereochemical preferences, its coordination number and its affinity towards donor atoms. This general property can be used to induce the controlled motion of metal ions within a defined molecular space (cation translocation). An attractive case is that of the  $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$  redox couple.  $\text{Fe}^{\text{II}}$  has a strong affinity towards the bpy ligand (2,2'-bipyridine) and forms a very stable and robust  $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$ , octahedral, low-spin complex; on the other hand,  $\text{Fe}^{\text{III}}$  exhibits a strong preference for the hydroxamate ligand ( $\text{ham}^-$ ): the  $[\text{Fe}^{\text{III}}(\text{ham})_3]$  is an octahedral, low-spin species with an extreme solution stability ( $\log \beta_3$  for the acetohydroxamate ligand is 28.3) [22]. Shanzer has recently designed a tripodal multidentate ligand which contains an upper tris-hydroxamate chamber and a lower tris-2,2'-bipyridine compartment [23]. The aqueous  $\text{Fe}^{\text{III}}$  ion goes to occupy the upper cavity (light-brown

solution); on addition of ascorbic acid the iron centre is reduced and  $\text{Fe}^{\text{II}}$  descends to occupy the lower cavity (the solution turns purple-red). On addition of peroxydisulphate,  $\text{Fe}^{\text{III}}$  forms again and jumps up into the tris-hydroxamate cavity (the original light-brown colour of the solution is regenerated).

The iron complex of the hydroxamate-bipyridine tripodal system is a multi-component assembly which allows the controlled movement of a metal centre between two defined positions. It can be considered a machine at a molecular level as it converts energy into a mechanical work, *i.e.*, the motion of a chemical body along a fixed distance, in a repeatable way.

Not only cations, but also anions can be translocated at will in a defined molecular space, still taking profit from redox changes involving transition metal centres. The most simple system should contain two prepositioned metals  $M_1$  and  $M_2$  (see Fig. 11).  $M_2$  is redox active through the  $n + / (n + 1) +$  redox couple: one of the oxidation states, *e.g.*,  $M_2^{(n+1)+}$ , has a strong affinity towards the anion  $X^-$ ; the other,  $M_2^{n+}$ , has a very poor or no affinity. On the other hand,  $M_1$  is not redox

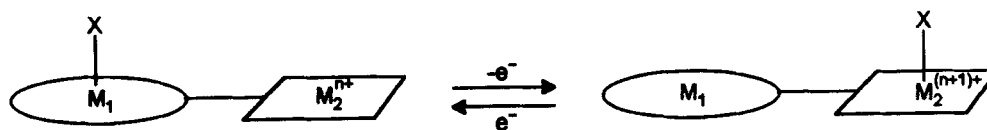


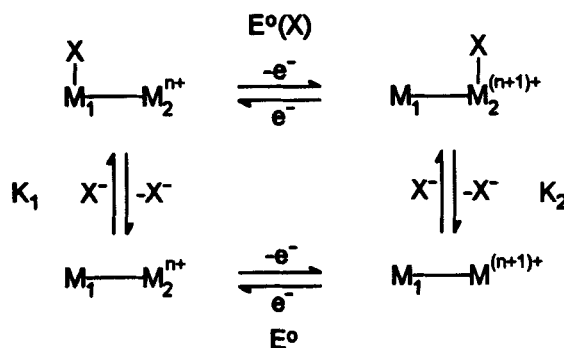
FIGURE 11 Redox driven intramolecular anion translocation between metal centres. When  $M_2$  is in its reduced form,  $M_2^{n+}$ , the  $X^-$  anion is located on the  $M_1$  centre. Following  $M_2^{n+}$ -to- $M_2^{(n+1)+}$  oxidation,  $X^-$  moves on the  $M_2$  centre. On reduction,  $X^-$  jumps back to  $M_1$ .

active and possesses an intermediate affinity towards  $X^-$ .

When  $M_2$  is in its reduced form,  $M_2^{n+}$ , the  $X^-$  anion stays on the  $M_1$  centre. On  $M_2^{n+}$ -to- $M_2^{(n+1)+}$  oxidation,  $X^-$  moves on the  $M_2$  centre. On reduction,  $X^-$  jumps back to  $M_1$ . Thus, the anion can be moved alternatively from  $M_1$  to  $M_2$  and *vice versa*, simply changing the oxidation state of the redox active centre  $M_2$ .

From a thermodynamic point of view, the behaviour of the  $[M_1 \sim M_2]/X^-$  system is described by the cycle shown in Figure 12.

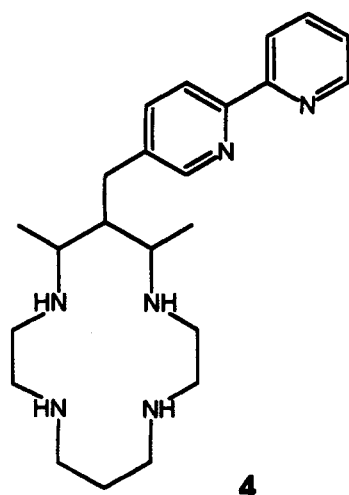
Occurrence of the translocation process, equilibrium (1) in Figure 12, requires that  $\log K_2 > \log K_1$  and, as a consequence, that  $E^\circ(X) < E^\circ$ . In other words, in order to have redox controlled anion translocation, the oxidation of  $M_2^{n+}$  to  $M_2^{(n+1)+}$  within the  $[M_1 \sim M_2]$  system, must be distinctly favoured in presence of  $X^-$ .



$$E^\circ - E^\circ(X) = RT/F(\ln K_2 - \ln K_1)$$

FIGURE 12 Thermodynamic bases of the anion translocation process illustrated in Figure 11. Occurrence of  $X^-$  translocation from  $M_1$  to  $M_2$  requires that  $\log K_2 > \log K_1$  and, as a consequence, that  $E^\circ(X) < E^\circ$ .

We have recently designed a multi-component system which fulfills the above mentioned requirements for redox driven anion translocation [24]. It derives from molecule 4, a cyclam ring with an appended 2,2'-bipyridine fragment. The tetra-aza macrocycle can host the  $Ni^{II}/Ni^{III}$  redox couple. Linking at the 4 position prevents the bpy subunit from binding the metal centre encircled by the macrocycle according to a scorpionate mode [25]. Thus, the bpy fragment points outwards and is available for coordination of any other metal ion. In particular, it chelates a  $Cu^{II}$  ion according to a 2:1 stoichiometry. This produces a trimetallic  $[Ni \sim Cu \sim Ni]$  species, 5, a three-component system held together by coordinative interactions (in this sense, 5 can be defined as a supramolecular



coordination compound [26], or as a complex of a complex) [27].

In general, an isolated  $[\text{Cu}^{\text{II}}(\text{bpy})_2]^{2+}$  species tends to give a five-coordinate complex, by coordinating in the fifth position either a solvent molecule or an  $\text{X}^-$  anion. The same happens in the reduced form of the trimetallic system, **5a**,  $[\text{Ni}^{\text{II}} \sim \text{Cu}^{\text{II}} \sim \text{Ni}^{\text{II}}]$ . In particular, the  $\text{Cu}^{\text{II}}$  centre, in aqueous solution, displays a special affinity towards the triatomic anions  $\text{N}_3^-$ ,  $\text{NCO}^-$ ,  $\text{NCS}^-$ . The corresponding  $\log K_1$  values, reported in Table I, are much greater than those observed for the monometallic  $[\text{Cu}^{\text{II}}(\text{bpy})_2]^{2+}$  complex. The unusually high affinity towards anions has to be mainly ascribed to the highly positive overall electrical charge of the trimetallic system ( $6+$ ).

Each proximate  $\text{Ni}^{\text{II}}$  centre,  $d^8$ , low-spin, has a square stereochemistry and does not compete with the central  $\text{Cu}^{\text{II}}$  cation for the  $\text{X}^-$  anion.

TABLE I Parameters pertinent to the anion translocation process in multicomponent system **5**, as illustrated in the general scheme reported in Figure 12

Anion, $\text{X}^-$	$\log K_1^a$	$\Delta E = E^\circ - E^\circ(\text{X}), \text{mV}^b$
$\text{N}_3^-$	$3.0 \pm 0.1$	155
$\text{NCO}^-$	$2.4 \pm 0.1$	120
$\text{NCS}^-$	$2.5 \pm 0.1$	120

<sup>a</sup>Constants for the equilibrium:  $[\text{Ni}^{\text{II}} \sim \text{Cu}^{\text{II}} \sim \text{Ni}^{\text{II}}] + \text{X}^- = [\text{Ni}^{\text{II}} \sim \text{Cu}^{\text{II}}(\text{X}) \sim \text{Ni}^{\text{II}}]$ , in aqueous solution.

<sup>b</sup> $E^\circ$  is the potential for the  $\text{Ni}^{\text{III}}/\text{Ni}^{\text{II}}$  redox change within the  $[\text{Ni} \sim \text{Cu} \sim \text{Ni}]$  system in 0.1 M  $\text{NaClO}_4$ ,  $E^\circ(\text{X})$  is the potential in presence of 1 equiv. of  $\text{X}^-$ .

On the contrary, the  $\text{Ni}^{\text{III}}$  state,  $d^7$ , low-spin, has a strong preference towards a *trans*-octahedral stereochemistry and tends to uptake  $\text{X}^-$  anions to reach coordination number 6. Thus, if 1 equiv. of  $\text{X}^-$  is added to an aqueous solution of the trimetallic system in its reduced form, **5a**,  $[\text{Ni}^{\text{II}} \sim \text{Cu}^{\text{II}} \sim \text{Ni}^{\text{II}}]$ , the anion goes on the copper centre. The

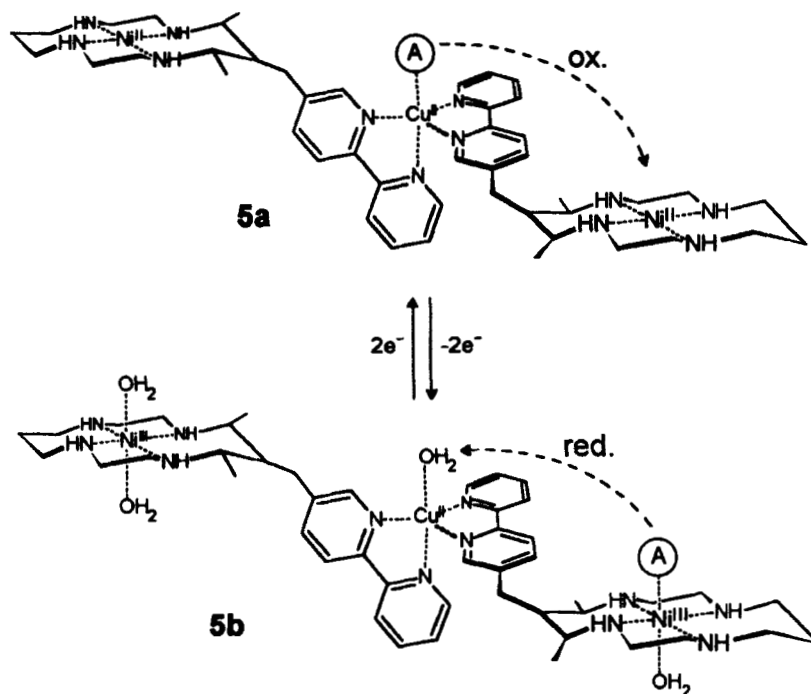


FIGURE 13 Electrochemically triggered anion translocation in a multicentric supramolecular coordination compound. On  $\text{Ni}^{\text{II}}$ -to- $\text{Ni}^{\text{III}}$  oxidation, the  $\text{X}^-$  anion moves from  $\text{Cu}^{\text{II}}$  to one of the two available proximate trivalent centres. Following the  $\text{Ni}^{\text{III}}$ -to- $\text{Ni}^{\text{II}}$  reduction,  $\text{X}^-$  moves back from the periphery to the centre.

oxidation of 5a in presence of 1 equiv. of  $X^-$  takes place at a potential distinctly lower than in its absence: the corresponding  $\Delta E^\circ$  values for the considered triatomic anions are reported in Table I.

Thus, system 5 behaves according to the model outlined in Figure 11 and described by the equations of Figure 12: on  $Ni^{II}$ -to- $Ni^{III}$  oxidation, the  $X^-$  anion moves from  $Cu^{II}$  to one of the two available proximate trivalent centres. In particular, due to the fact that each  $Ni^{III}$  ion has a *trans*-octahedral stereochemistry, the  $X^-$  anion can choose among four equivalent axial positions: from an electrochemical point of view, this corresponds to an advantage of 35.6 mV ( $= (RT/F)\ln 4$  at 25°C). On  $Ni^{III}$ -to- $Ni^{II}$  reduction,  $X^-$  goes back from the periphery to the centre of system 5. The quickly reversible redox driven anion translocation from a metal centre to the other is pictorially illustrated in Figure 13.

Also in the present case, a molecular machine is at work. A tiny rod-like body is moved back and forth along an 9.4 Å distance. The machine is fueled by electrical energy, provided by the working electrode in the electrochemical cell.

#### 4. CONCLUSIONS

3d metal ions are ubiquitous in natural systems and in most cases their role is related to their electron transfer properties and to their capability of existing in two adjacent oxidation states of different stereochemical features. As an example, the  $Fe^{III}/Fe^{II}$  redox change triggers a spectacular and sophisticated molecular motion associated to dioxygen uptake in haemoglobin [28]. The dioxygen-free  $Fe^{II}$ , high-spin is five-coordinate: the metal centre lies 0.6 Å above the heme plane and the nitrogen atom of an histidine fragment occupies the fifth, apical position. A dioxygen molecule binds the metal from below the porphyrin plane: iron is oxidised

to the trivalent state, low-spin, and pulled down to 0.2 Å over the plane, to achieve six-coordination. The 0.4 Å displacement of the metal towards the heme plane induces a motion of the proximal histidine residue, which in turn generates subtle changes in the position of other residues in the protein chain: these conformational changes are responsible for cooperativity effects, *i.e.*, the  $O_2$  binding to a  $Fe^{II}$  centre enhances the affinity for dioxygen of the remaining deoxygenated sites. A dramatic change of stereochemical preferences is observed with the  $Cu^{II}/Cu^I$  couple. The change is especially drastic as one moves from a transition cation,  $Cu^{II}$ ,  $d^9$ , to a non-transition cation,  $Cu^I$ ,  $d^{10}$ . Nature profits from these features with the copper-zinc superoxide dismutase metalloenzyme, in order to quickly eliminate the harmful  $O_2^-$  radical through disproportionation to  $O_2$  and  $H_2O_2$  [29]. Moving back to the chemistry of unnatural substances, the  $Cu^{II}/Cu^I$  redox change has been extensively used by Sauvage to induce and control molecular motions of supramolecular systems containing polypyridine chelating subunits. In particular, profiting from the preference of  $Cu^I$  for coordination number 4 and of  $Cu^{II}$  for higher coordination numbers, it has been possible to promote, *via* redox processes, the swinging motions of the rings of a 2-catenane [30,31] and the sliding of the ring along the axis of a rotaxane [32,33].

During the last two billions of years or so, the evolution has taken the greatest advantage from the redox properties of transition metals (at least the most widely available ones) in order to develop useful and sophisticated mechanisms and functions. Quite recently, chemists have begun to utilise transition metals (no matter their cost and availability) to develop systems of increasing complexity, which may appear to someone as curiosities or elegant exercises, but which undoubtedly form the background of the incipient molecule-based technology.

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