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Giancarlo De Santis[a]; Luigi Fabbrizzi[a]; Maurizio Licchelli[a]; Carlo Mangano[a]; Piersandro Pallavicini[a]; Antonio Poggi[a]; Donatella Sacchi[a]; Angelo Taglietti[a]
[a] Dipartimento di Chimica Generale, Universita di Pavia, Pavia, Italy

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Supramolecular assemblies containing metallocyclam subunits

GIANCARLO DE SANTIS, LUIGI FABBRIZZI*, MAURIZIO LICCHELLI, CARLO MANGANO, PIERSANDRO PALLAVICINI, ANTONIO POGGI, DONATELLA SACCHI and ANGELO TAGLIETTI

Dipartimento di Chimica Generale, Universita di Pavia, 27100 Pavia, Italy

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The synthetic approach to supramolecular systems containing one or more metallocyclam subunits is reviewed. In particular, the template synthesis of azacyclam complexes has been used to design supramolecular coordination compounds displaying multi-electron redox activity. Moreover, it is shown that whenever the supramolecular design requires a component able to provide a fast and reversible redox change, a metallocyclam subunit should be used. Finally, the design of supramolecular systems in which a light-emitting fragment (anthracene) has been linked to a metallocyclam subunit has been considered. In particular, anthracene fluorescence can be switched on/off through the Cu^{I}/Cu^{II} redox couple inside a tetra-thia-macrocyclic environment, *via* an electron transfer mechanism.

INTRODUCTION

Supramolecular chemistry originated and developed from macrocyclic chemistry. This is pictorially illustrated by the logo of the *Italian Group of Supramolecular Chemistry* (see Figure 1).

At least two metaphors stay behind the logo. First, as one of the ultimate goals of supramolecular chemistry is the design of molecular devices, the logo features the most simple mechanical device: the gear. In particular, in each of the two toothed wheels constituting the gear, the formula of a famous macrocycle has been drawn: *18-crown-6* in the lower wheel, *cyclam* in the upper one. Cyclam, which is a very good ligand for transition metal ions, belongs to the realm of coordination chemistry and of inorganic chemistry. 18-crown-6 is a selective ligand for *s* block metal ions, but, in view of its many applications in the field of organic synthesis and catalysis, is considered an object of organic chemistry. Thus, a second metaphor comes: inorganic chemistry (symbolised by the upper wheel of the gear) and organic chemistry (the lower wheel), after decades of academic and, in some cases, cultural separation, cooperate tightly to the development of the interdisciplinary supramolecular science. However, some old fashioned inorganic chemist still argues that organic people have maintained their well known domineering and overbearing character and have caught the larger wheel. Beyond the metaphor, the two above mentioned macrocycles have played important and independent roles in the development of supramolecular chemistry, during the last 20–30 years. Thus, it may be useful to locate each cyclic molecule in its historical context.

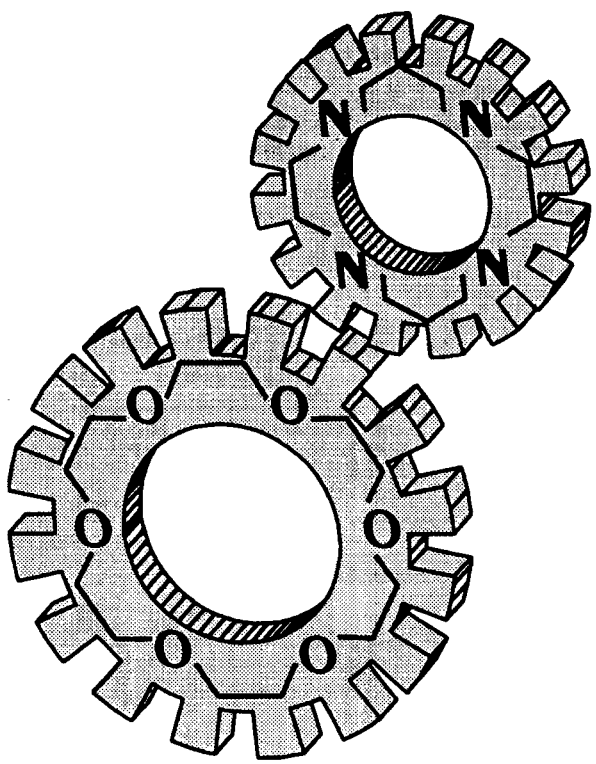


Figure 1 The logo of the *Italian Group of Supramolecular Chemistry*. Methaphors beyond the logo are illustrated in the text.

*To whom correspondence should be addressed.

Figure 2 illustrates the development of macrocyclic polyamines. Ammonia was probably the first molecule deliberately used as a ligand, about one century ago, by Alfred Werner at the University of Zurich. In the following decades, polyamines of varying denticity, able to firmly interact with transition metals, were synthesized and the reasons of the especially high solution stability of the corresponding complexes were clearly assessed by Gerold Schwarzenbach in the 1950s (the *thermodynamic chelate effect*).[1] Whereas cyclization of polyamines was achieved since 1936 (Van Alphen's synthesis of cyclam, **1**),[2] interest towards aza-macrocycles arose during the 1960's, with the introduction of *metal template* syntheses by Busch[3] and Curtis.[4] It was immediately recognized that, compared to their open-chain analogues, metal complexes of cyclic polyamines of the type of cyclam present new and interesting properties: a solution extra-stability (*the thermodynamic macrocyclic effect*)[5] and an extreme inertness towards demetallation (*the kinetic macrocyclic effect*)[6]. In the late 1970's, amine macrocycles moved toward tridensionality with Sargeson's cobalt(III) template preparation of six-coordinating cages: sepulchrand[7] and sarcophagine, **2**.[8]

The formally analogous evolution of oxygen-containing multidentate ligands, and the parallel development of alkali metal coordination chemistry, is illustrated in Figure 3. The unidentate ancestor, water, is only nominally mentioned. The affinity of ethereal oxygen towards alkali and alkaline earth metal ions is so scarce as to nullify the favourable contribution of the chelate effect and a coordination chemistry of open-chain polyethers never developed. In 1967, Pedersen[9] showed that on ligand cyclization, to give *crown polyethers*, **3**, by virtue of the favourable contribution of the thermodynamic macrocyclic effect, fairly stable alkali and alkaline earth metal complexes form in solution and can be

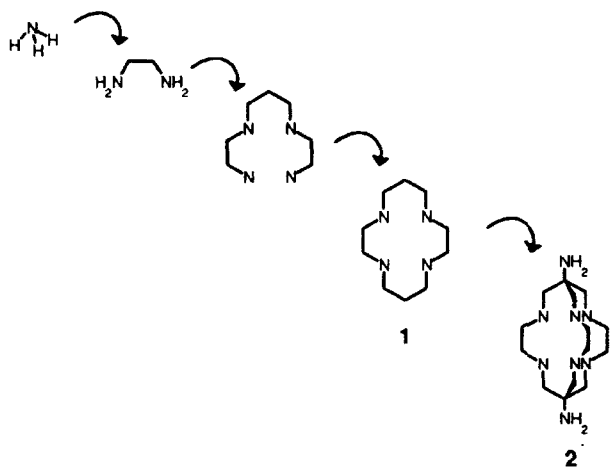


Figure 2 The evolution of amine macrocycles. From the coordination chemistry of ammonia (Werner, 1893) to Sargeson's cages (1977).

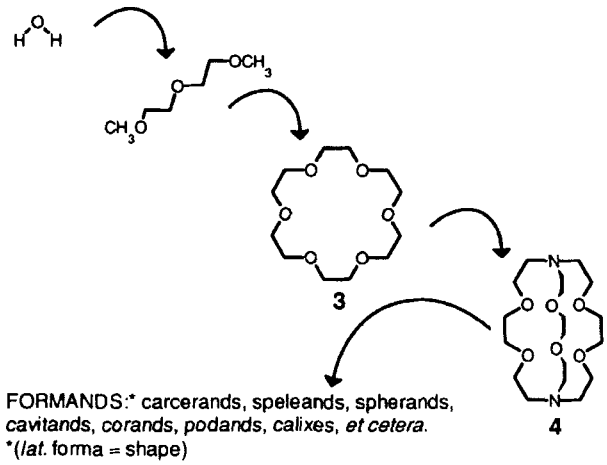


Figure 3 The never-ending evolution of macrocycles containing oxygen donor atoms.

isolated in the solid state. Moreover, the dependence of the solution stability upon the matching between crown-ether ring size and metal ion radius opened the way to the design of tailor-made and selective ligands. The jump from two-dimensional to three-dimensional ligating systems, i.e. from rings to cages, took only two years. In particular, in 1969 Lehn[10] reported the synthesis and the alkali metal complex formation of *cryptands*, **4**, and introduced the intriguing and successful fashion of calling complicated molecules with appealing and imaginative names inspired from the everyday life: (i) look at a thing your molecule resembles (or you would like it resembles) and (ii) add the *-and* termination to its name. The work by Pedersen and Lehn stimulated the design of sophisticated systems of varying shape and size, able to interact not only with metal ions, but also with polyatomic cations, anions and neutral species. Systems of the above type have accumulated at an incredibly high rate during the past two decades and belong to the broad realm of supramolecular chemistry. Some of these systems are grouped in Figure 3 under the general name of *formands*. Lehn's style name (lat. *forma* = shape) stresses that the synthetic efforts were mostly directed to give the new molecule a desired shape (which is the basis of the molecular recognition).[11]

Comparison of the evolutive pathways outlined in Figures 2 and 3 shows that (i) polyamine systems have developed at a much slower pace than polyether counterparts, and (ii) they did not go beyond cages. The strikingly different behavior can be trivially accounted for considering that molecules of Figure 3 were in the skilful hands of the organic chemists, who have a preeminent interest in synthesis and fully master the preparative methodology, which has made an astonishing progress during the last years. Inorganic chemists, responsible for the development of the systems displayed

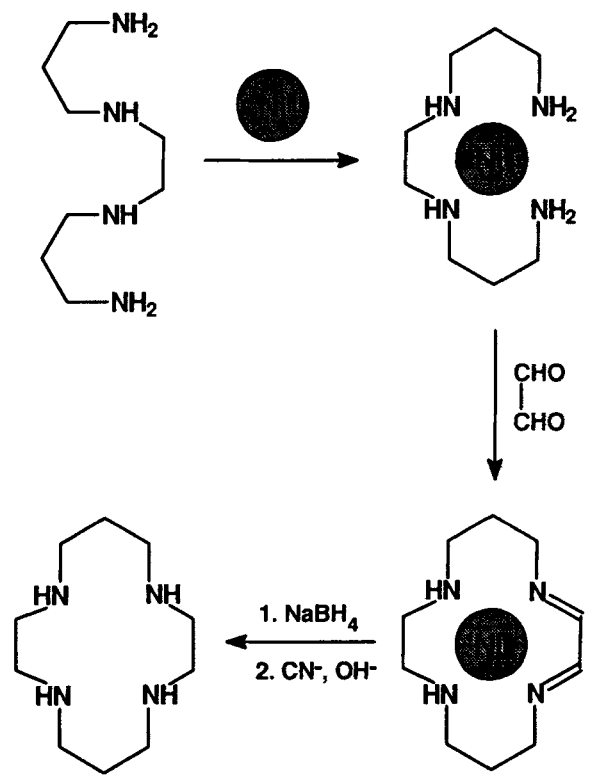
in Figure 2, do not have, in general, such skills, are rather reluctant to undertake a multistep preparation with milligram yields and tend to devote their attention to the metal centre rather than to the ligand organic backbone. On the other hand, transition metals are so versatile that even simple structural modifications on primitive polyaza frameworks such as that of cyclam may induce interesting and useful changes of their electronic properties (spin state, colour, magnetism) and reactivity (redox chemistry, electron transfer processes, binding and activation of anions and small molecules).

Template routes to functionalised *cyclam* analogues: *azacyclams*

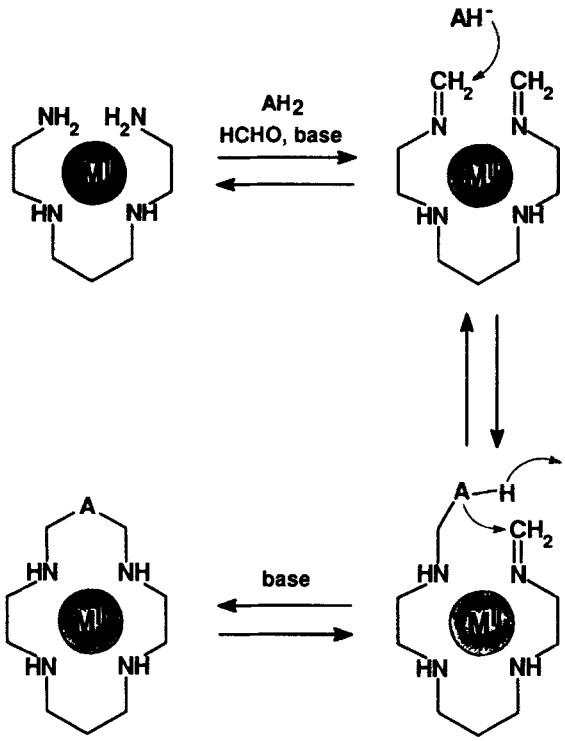
The most popular polyamine macrocycle is undoubtely the 14-membered quadridentate ligand: *cyclam*. The appropriate ring size and symmetrical topology of the four secondary amine nitrogen atoms make cyclam the ideal ligand to chelate *3d* metal ions in a planar fashion. As a consequence, cyclam complexes display the most pronounced thermodynamic and kinetic macrocyclic effects. For instance, the demetallation process: $[Ni^{II}(cyclam)]^{2+} + 4H^+ \rightarrow Ni^{2+} + cyclamH_4^{4+}$ is completely displaced to the right (logK = 4.0),[2] but it is so slow that the $[Ni^{II}(cyclam)]^{2+}$ complex persists almost indefinitely in strongly acidic solutions (e.g. $t_{1/2} \approx 30$ years in 1 M $HClO_4$).[13] Moreover, coordination by cyclam promotes the redox activity of the encircled metal centre and favours the access to unusual and otherwise unstable oxidation states.[14] For instance, oxidation of $[Ni^{II}(cyclam)]^{2+}$ to the $[Ni^{III}(cyclam)X_2]^+$ species (X = an inorganic anion, e.g. Cl^-) takes place at a moderately positive potential (0.71 V vs NHE, in 1 M HCl; compare for instance to the $Fe^{3+} + e^- = Fe^{2+}$ couple, 0.77 V vs NHE, in 1 M HCl), according to a fast and reversible redox change.[15] Redox versatility coupled to the coordinative unsaturation (two axial positions, above and below the N_4 plane, are open to a further coordination) generates interesting functions. In particular, $[Ni^{II}(cyclam)]^{2+}$ catalyses the electrochemical reduction of CO_2 to CO in an acetonitrile solution, through a step which involves axial CO_2 coordination to the Ni^I complex.[16] Noticeably, any structural change of the cyclam framework (N-substitution, ring expansion or contraction, introduction of a further nitrogen atom in the donor set) drastically reduces or cancels the catalytic efficiency.[17] Such a redox versatility is extended to other transition metal centres: the otherwise unstable Cu^{III},[18] Ag^{II} and Ag^{III} oxidation states [19] can be obtained in solution through coordination by cyclam or cyclam-like tetra-aza macrocycles. Thus, when the supramolecular design requires a component providing fast and reversible one-electron redox activity, the use a metallocyclam fragment as a subunit is recommended.

Cyclam can be conveniently obtained through the nickel(II) template condensation of the open-chain tetramine 3.2.3-tet and glyoxal, followed by hydrogenation of the C=N bonds and demetallation with excess cyanide in 1M NaOH[20] (see Scheme 1). Then, cyclam (L) can be selectively protected on all but one >NH groups and reacted with any desired RX fragment to give the two-component L-X system (or functionalised macrocycle).[21] According to an alternative approach, unprotected cyclam is made to react with RX. However, a large excess of the tetramine is required (≥5:1), in order to minimize the formation of polysubstituted products.[22] Both synthetic methodologies suffer quite serious drawbacks: the troublesome ligand protection/deprotection procedures in the first case, the tedious purification of the L-X product from the excess reagent L in the second one. Therefore, it would be desirable to have a template reaction giving in one step the metal complex of the functionalised cyclam or cyclam-like ligand. Such a reaction exists and is illustrated in Scheme 2.

In particular, a divalent 3d metal centre (Ni^{II} or Cu^{II}) preorientates the open-chain tetramine 2.3.2-tet, whose terminal primary amine groups give Schiff-base condensation with two molecules of formaldehyde. Then, an H_2A molecule, containing two acidic hydrogen atoms, transfers a proton to the excess base present in solution (e.g. triethylamine) and the HA^- ion gives a nucleophilic attack to one of the two C=N bonds. Finally, after a



Scheme 1

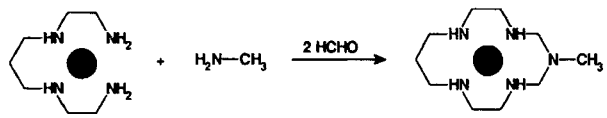


Scheme 2

further proton release, the linked -A⁻ charged group, favoured by the chelate effect, attacks the other C=N bond, closing the ring. In principle, any diprotic acid H_2A can act as a locking fragment for the ring closure around the metal centre.

The first reaction of the type illustrated in Scheme 2 involved the condensation of an $[M^{II}(en)_2]^{2+}$ complex (M = Cu, Ni; en = 1,2-ethane-diamine) with two molecules of the carbon acid $CH_3CH_2NO_2$, in presence of formaldehyde and triethylamine.[23] Such a reaction has to be considered as the two-dimensional version of the Co^{III} template synthesis of the diNOsar hexa-aza cage, which involves the reaction of $[Co^{II}(en)_3]^{3+}$ with two molecules of the triprotic acid CH_3NO_2, which acts as a capping fragment in presence of formaldehyde and excess base.[24] Then, primary amines, RNH_2, were found to act as efficient padlocks in reactions of the type outlined in Scheme 2,[25] in analogy with ammonia, which had been used by Sargeson as a cap in the synthesis of the Co^{III} sepulchrate complex.

On reaction of the locking fragment CH_3NH_2 with the $[Ni^{II}(2.3.2\text{-tet})]^{2+}$ complex (see Scheme 3), the low-spin Ni^{II} penta-aza-macrocyclic complex **5** was obtained.[26] X-ray investigations showed that only the four secondary amine nitrogen atoms are bound to the metal centre, according to a square stereochemical arrangement, which is quite similar to that of cyclam in the corresponding $[Ni^{II}(cyclam)]^{2+}$ species. The tertiary amine nitrogen atom in **5** is not involved in the coordination and plays just an



5

Scheme 3

architectural role. Moreover, it exhibits a rather flattened nature, which indicates a hybridisation intermediate between sp^3 and sp^2 and justifies the surprisingly poor basicity (being protonated only in presence of a strong acid of concentration higher than 0.1 M). Similarity of **5** to $[Ni^{II}(cyclam)]^{2+}$ is not restricted to the structural parameters, but it is extended also to the solution properties. In particular, **5** displays the typical macrocyclic inertness towards demetallation and it can be easily oxidised to the Ni^{III} species. This has led to the suggestion to give the penta-aza macrocycle present in the complex **5**, and the 14-membered macrocycles of similar kind, the name of *azacyclam*.

We have recently observed that the $-NH_2$ fragment of amides (both carboxamides, $R(CO)NH_2$, and sulphonamides, $R(SO_2)NH_2$, of either aliphatic or aromatic nature) is a convenient and versatile locking agent for the synthesis of Ni^{II} and Cu^{II} azacyclam complexes.[27] Using amide padlocks is especially interesting as it allows the appending of any R functionality to a cyclam-like macrocycle and opens the route to the one-pot template synthesis of supramolecular systems containing a metallo-azacyclam subunit.[28,29]

Figure 4 reports the Ni^{II} and Cu^{II} azacyclam complexes which have been obtained through reaction of a $[M^{II}(2.3.2\text{-tet})]^{2+}$ complex with the appropriate amide, in aqueous ethanol and in the presence of formaldehyde and triethylamine. The reaction is usually carried out under mild conditions (20–50°C) and in general the azacyclam complex separates from the reaction mixture on standing at room temperature, as a crystalline or microcrystalline precipitate, with a satisfactory yield.

Crystal structures have been reported for some Cu^{II} and Ni^{II} azacyclam complexes and in any case the penta-aza macrocycle places its four secondary nitrogen atoms at a corners of a regular square, according to the coordination mode of cyclam. Studies on the solution behaviour have confirmed the analogy of $[M^{II}(azacyclam)]^{2+}$ complexes with cyclam analogues. Such an analogy is particularly rich in the case of nickel(II) complexes. First, $[Ni^{II}(azacyclam)]^{2+}$ complexes show the typical resistance towards demetallation. For instance, the methanesulphonamide derivative lasts intact in a 5 M $HClO_4$ solution for 1 week, as indicated by the persistence of the absorption band centred at 458 nm. Moreover, water soluble complexes exist as an equilibrium mixture of the high-spin diaquo-octahedral species (of a pale blue colour) and of the low-spin square

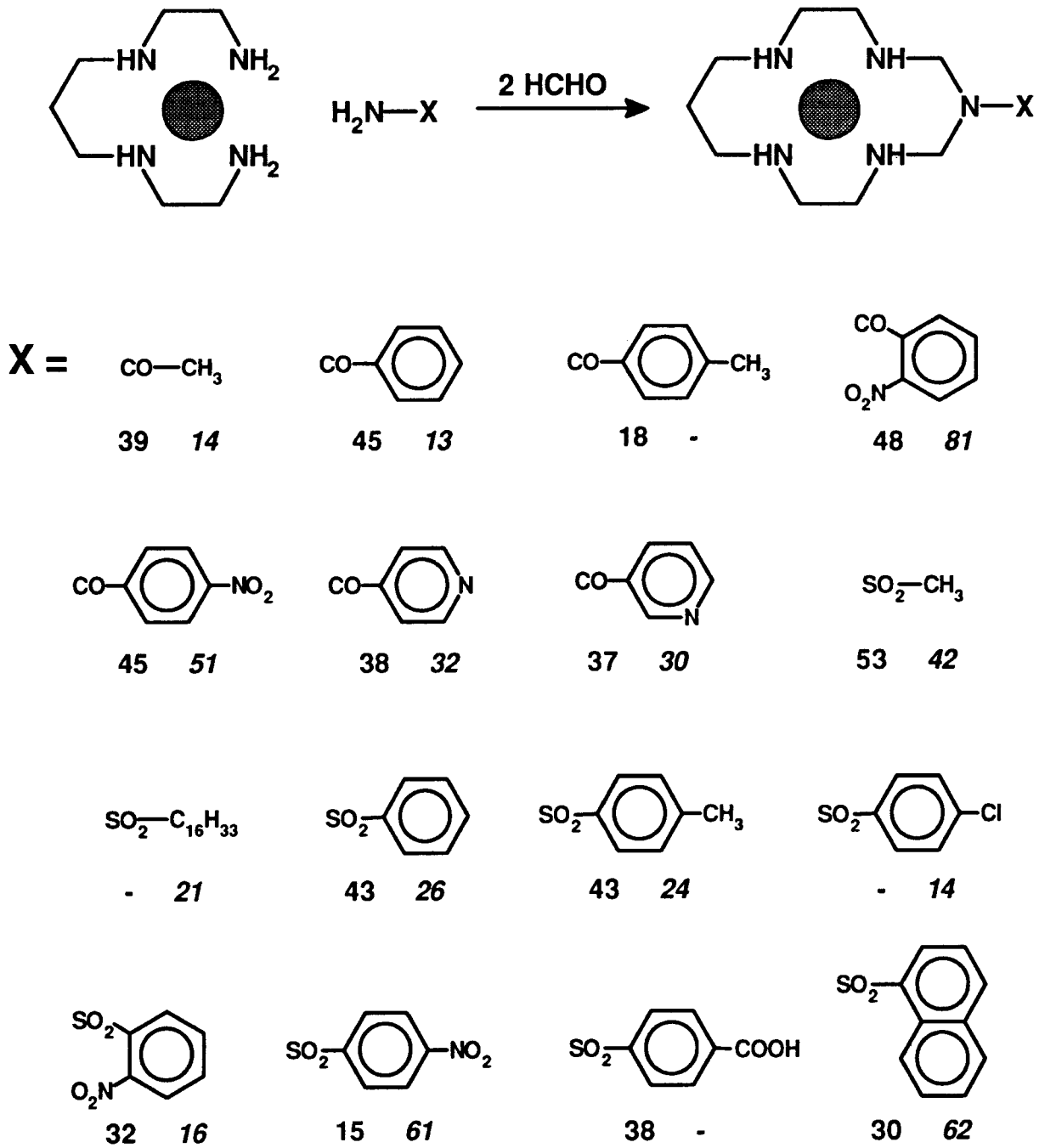


Figure 4 Template synthesis of *azacyclam* metal complexes. Figures below the X- radical are yields (%). Normal character: Cu^{II}; italic character: Ni^{II}.

complex (of a bright yellow colour), a feature which was first observed for the $[Ni^{II}(cyclam)]^{2+}$ complexes. For instance, at a 0.1 M ionic strength, $[Ni^{II}(cyclam)]^{2+}$ exists as 72% of the low-spin form and 28% of the high-spin form.[30] The azacyclam complex obtained from the methanesulphonamide padlock gives a 42% (yellow)—58%(blue) mixture. A balanced mixture of the high-spin and low-spin forms is observed for all the 14 investigated $[Ni^{II}(azacyclam)]^{2+}$ complexes in acetonitrile solution.

$[Ni^{II}(cyclam)]^{2+}$ undergoes a reversible one-electron oxidation process in an acetonitrile solution at 0.59 V (vs the Fc^{+}/Fc internal reference). This value is the less positive among nickel(II) complexes with polyamine macrocycles of varying ring size and denticity.[31] In a qualitative sense, the very easy access to the Ni^{III} state

reflects the strong metal-ligand in-plane interactions exerted by the 14-membered quadridentate macrocycle that raise the energy of the 3*d* orbital from which the electron is abstracted during the oxidation process. Azacyclam complexes undergo analogous reversible one-electron oxidation to give solution stable Ni^{III} complexes.[17] However, the process takes place at a potential that is distinctly more positive than for $[Ni^{II}(cyclam)]^{2+}$. In a general sense, the $E_{1/2}$ (Ni^{III}/Ni^{II}) value increases along the series (only the locking fragment originating from the azacyclam ring is indicated):

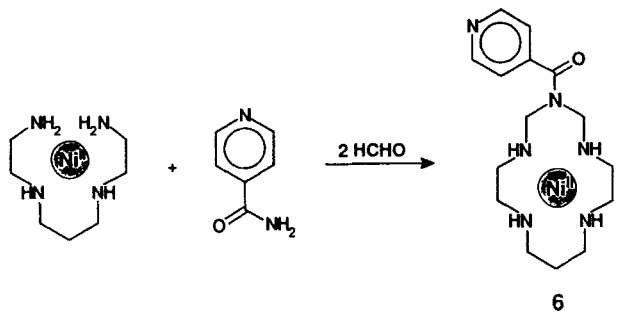
$$\text{cyclam} \approx NCH_3 < N(CO)_{(aliphatic)} < N(CO)_{(aromatic)} < N(SO_2)_{(al.)} < N(SO_2)_{(ar.)}$$

Such a behaviour can be related to the existence of π interactions between the metal centre and the amide fragment. In particular, the Ni^{II} ion is able to transfer through a π mechanism electron charge to a π^* molecular orbital of the amide group, which accounts for the especially short Ni^{II}-N(amide) distance. On oxidation, the electron charge on the metal centre decreases and the extent of the π donation decreases. Destabilisation of the Ni^{III} state is more pronounced, and the $E_{1/2}$ (Ni^{III}/Ni^{II}) value is more positive, in the sulfonamido complexes, where the metal-to-nitrogen π donation is more important. Moreover, for a given amide fragment, either carboxamide or sulfonamide, the destabilisation of the Ni^{III} state is higher for the aromatic rather than the aliphatic derivative, which reflects the electron withdrawing tendencies.

Using azacyclam complexes to build-up supramolecular coordination compounds

Coordinating side-chains have been appended to cyclam and analogous macrocycles in order to improve their binding tendencies towards the encircled metal centre.[32] The existence of an aggressive tail, ready to bite a firmly chelated metal, accounted for the trivial name of *scorpiand*.[33] In particular, scorpiands have an appended arm pointing its donor group *inward* to the ring, to further coordinate the metal centre. We were interested in synthesizing cyclam-like macrocycles with a pendant arm pointing *outward* and available for the coordination of further metal centres. Such systems can be conveniently prepared through template reactions of the type described in the preceding Section. In particular, reaction of $[Ni^{II}(2.3.2\text{-tet})]^{2+}$ with 4-pyridine-carboxamide (see Scheme 4), gives in good yield the azacyclam complex **6**, in which the appended pyridine subunit is sterically inhibited to the apical binding of the Ni^{II} centre and is ready to coordinate another metal.[34]

Reaction of 2 equivalents of **6** with $[Pt^{II}Cl_4]^{2-}$ gave the complex species **7**, *cis*-$[Pt^{II}Cl_2(\mathbf{6})_2]$. **7** fulfils the requirement for being considered a supramolecular system, as it is made by distinct components (the two Ni^{II} azacyclam

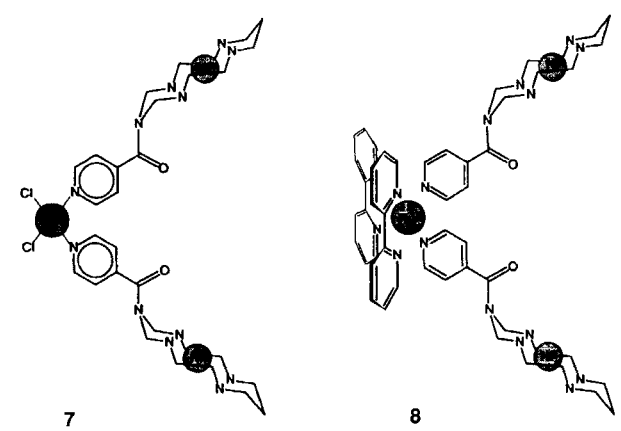


Scheme 4

complexes plus the *cis*-$[Pt^{II}Cl_2(py)_2]$ core), which are held together by non-covalent interactions. Since the interactions are of the metal-ligand type, **7** should be defined as a *supramolecular coordination compound*. Interestingly, **7** behaves as a two-electron redox agent. In fact, voltammetric investigation showed that **7** undergoes two consecutive one-electron oxidation processes at a platinum working electrode, which are separated only by the statistical term, 36 mV. Each process corresponds to the Ni^{II}/Ni^{III} change in each azacyclam subunit. The large distance prevents any electrostatic repulsive effect between the two redox sites.

In system **7**, the central element Pt^{II} does not exhibit any redox activity and plays only an architectural role. More interesting should be the case of a central element displaying its own redox activity. Such a metal should also be able to interact firmly with pyridine and give stable and inert complexes. This is the case of Ru^{II}. In particular, reaction of *cis*-$[(bpy)_2Ru^{II}Cl_2]$ with two equivalents of **6** gives the supramolecular coordination compound **8**.

8 behaves in solution as a three-electron redox agent, as shown by electrochemical investigations. In particular, in an acetonitrile solution made 0.1 M in Bu_4NClO_4, a one-electron oxidation process is observed at a not too positive potential (0.45 V vs Fc^+/Fc). Such a process is to be ascribed to the Ru^{II}/Ru^{III} change. On scanning the potential towards higher values, a two-electron process is



observed, which has to be assigned to the oxidation of the two independent nickel centres (Ni^{II}/Ni^{III} couple), taking place at the same potential, or, more precisely, at two distinct potentials, separated by the statistical term (36 mV).

If Bu_4NClO_4 is replaced by Bu_4NCl as a supporting electrolyte, a completely different electrochemical response is observed: the two-electron process is observed first, taking place at a moderately positive potential; then, at a distinctly more positive potential, the one-electron oxidation process takes place. Thus, changing the 'inert' electrolyte produces drastic variations of the redox potential and, in particular, inverts the sequence of the electron release: [1+2] in Bu_4NClO_4, [2+1] in Bu_4NCl. Figure 5 shows that replacing ClO_4^- by Cl^- produces a dramatic decrease of the potential associated to the Ni^{II}-to-Ni^{III} oxidation processes (by about 700 mV), but causes a very moderate decrease of the Ru^{II}/Ru^{III} couple potential. Such a behaviour has to be related to the donor tendencies of the anions of the background electrolyte and to the stereochemical changes taking place in the course of the envisaged redox changes. In particular, it has been pointed out in the previous section that Ni^{II} azacyclam complexes exist in polar solvents as an equilibrium mixture of the blue, high-spin, *trans*-octahedral species, $[Ni^{II}LS_2]^{2+}$ (L = azacyclam, S = a solvent molecule) and of the yellow low-spin, square form $[Ni^{II}L]^{2+}$. On oxidation, the low-spin *trans*-octahedral species $[Ni^{III}LS_2]^{3+}$ is formed. In the perchlorate solution, the poorly donating ClO_4^- anion cannot compete for apical coordination with solvent molecules and the oxidation process is correctly described by the half-reaction: $\{[Ni^{II}LS_2]^{2+} + [Ni^{II}L]^{2+}\} \rightarrow [Ni^{III}LS_2]^{3+} + e^-$. In the chloride-containing solution, it is possible that the Cl^- anion does not replace solvent molecules in the trans-octahedral divalent form, but occupy the axial positions of the trivalent complex. Thus, the oxidation half-reaction should be written: $\{[Ni^{II}LS_2]^{2+} + [Ni^{II}L]^{2+}\} + 2Cl^- \rightarrow [Ni^{III}LCl_2]^+ + e^- + 2S$. Axial coordination by Cl^- strongly stabilizes the Ni^{III} state, which is reflected in the especially low potential. Such a stabilization effect is not experienced by the coordinatively saturated ruthenium centre. The moderate decrease of the Ru^{II}/Ru^{III} potential observed on changing Bu_4NClO_4 with Bu_4NCl is probably to be ascribed to the formation of loosely bound ion pairs in the acetonitrile solution. Formation of an ion pair stabilizes the more charged complex cation (Ru^{III}) and the smaller chloride will establish stronger electrostatic interactions than perchlorate.

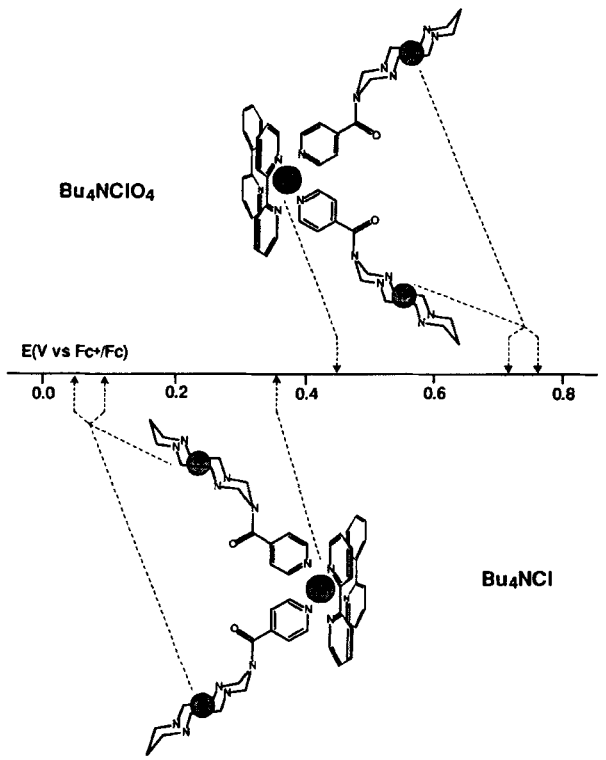


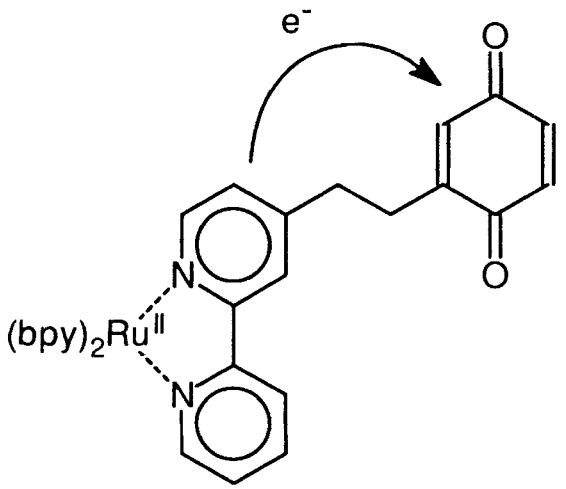
Figure 5 Potential diagram for the supramolecular coordination compound **8**. $E_{\frac{1}{2}}$ values have been measured through cyclic voltammetry investigations in MeCN solution, made 0.1 M in Bu_4NX. Changing X inverts the sequence of electron release: from [1+2] in Bu_4NClO_4 to [2+1] in Bu_4NCl.

Thus, coupling of open shell and closed shell redox active subunits produce supramolecular systems whose redox activity and mode of the electron release can be controlled from outside, simply changing the background salt.

Metallocyclam subunits as switching devices in supramolecular fluorescent systems

The propensity of metallocyclam subunits to display redox activity is well documented and, in particular, some examples referring to the Ni^{II}/Ni^{III} change have been illustrated in the previous section. From the point of view of the supramolecular design, it derives that, whenever an envisaged system requires a redox active component, a metallocyclam fragment should be used. In this connection, we will consider the design of a redox switchable fluorescent system, i.e. a supramolecular assembly in which the emission of a fluorescent fragment can be modified by varying the oxidation state of an adjacent redox active fragment. An example of such a switching device has been recently reported,[35] in which the light-emitting $[Ru^{II}(bpy)_3]$ fragment has been covalently linked to a quinone subunit, **9**.

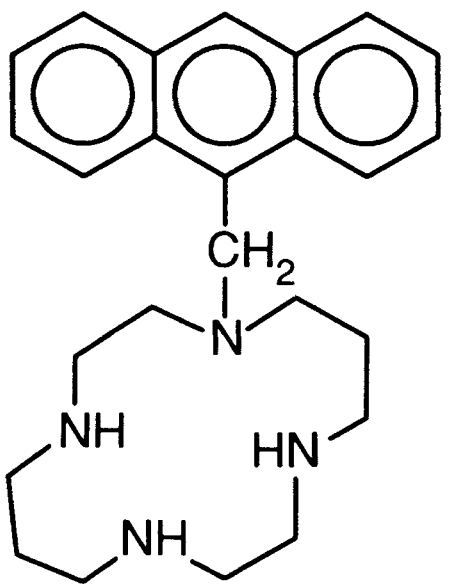
The electron-withdrawing quinone moiety quenches $[Ru^{II}(bpy)_3]$ fluorescence, through an electron transfer process. Chemical or cathodic reduction of quinone to the hydroquinone form prevents any electron transfer process and revives fluorescence. Thus, the fluorescence of the appended inorganic fragment can be switched on/off through consecutive addition of a reducing and of an oxidising agent.



9

In our design, we chose anthracene as a light-emitting fragment and we wanted to control its luminescence by varying the oxidation state of an adjacent metal centre. In this connection, we first appended a cyclam ring to the anthracene framework (**10**).

The uncomplexed system **10** does not fluoresce at all, in an acetonitrile solution, at room temperature. Fluorescence quenching has to be ascribed to an electron transfer process from the easily oxidisable tertiary amine nitrogen atom of the appended cyclam subunit to the excited anthracene fragment,*An (see Figure 6-a). Photoinduced electron transfer in anthracene derivatives containing an appended tertiary amine group is well documented.[36]



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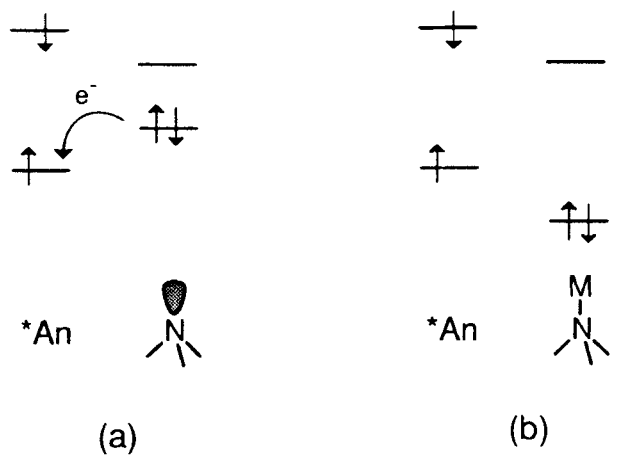


Figure 6 Photoinduced electron transfer process in a system in which a tertiary amine nitrogen atom has been linked through a $-CH_2-$ bridge to anthracene (e.g. molecule **10**). An electron is transferred from the oxidisable tertiary amine group to the excited state of anthracene, which causes fluorescence quenching (a). Stabilization of the tertiary amine group through coordination by a metal centre (e.g. Zn^{II} in **10**) prevents the electron transfer process on a thermodynamic basis and revives fluorescence (b).

On the contrary, the zinc(II) complex of **10** exhibits the typical intense emission spectrum of anthracene (see Figure 7).

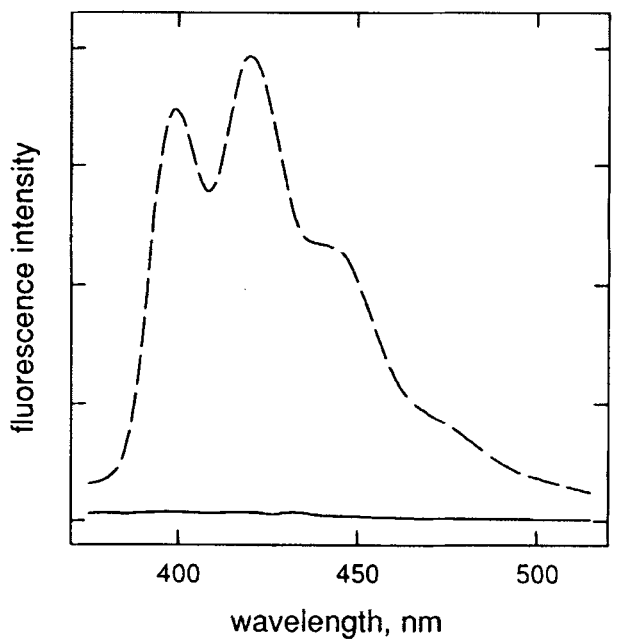


Figure 7 Fluorescence spectra of **10** and of its metal complexes. The uncomplexed system **10** does not fluoresce (solid line), due to an *electron transfer* process from the tertiary amine nitrogen atom to the excited state of anthracene (mechanism (a) of Figure 6). Coordination by Zn^{II} prevents the electron transfer and awakens fluorescence (dashed line; mechanism (b) of Figure 6). Coordination by Ni^{II} or Cu^{II} quenches again fluorescence, through an *energy transfer* process (the mechanism is pictorially illustrated in Figure 8).

Such a behaviour can be accounted for considering that, on coordination of the Zn^{II} centre, the oxidation potential of the tertiary amine nitrogen atom is drastically reduced, which thermodynamically disfavours the electron transfer process and prevents fluorescence quenching (see Figure 6-b). On the other hand, acetonitrile solutions of $[Ni^{II}(\mathbf{10})]^{2+}$ and $[Cu^{II}(\mathbf{10})]^{2+}$ complexes, at room temperature, are not fluorescent. Luminescence quenching, in the present case, has to be ascribed to a different mechanism with respect to the uncomplexed system **10**. In fact, also in this case, formation of strong coordinative bonds between the tertiary amine nitrogen atom of the cyclam fragment and Ni^{II} (or Cu^{II}) prevents the electron transfer process on a thermodynamic basis. However, Ni^{II} (electronic configuration: d^8) and Cu^{II} (d^9) ions possess empy or half-filled *d* levels of relatively low energy. This makes possible an energy transfer process of the electron exchange type,[37] which deactivates the anthracene excited state in a radiationless mode, as illustrated in Fig. 8.

The existence of a different mechanism for fluorescence quenching in system **10** and in the $[Ni^{II}(\mathbf{10})]^{2+}$ and $[Cu^{II}(\mathbf{10})]^{2+}$ complexes has been demonstrated by the measurement of emission spectra of solutions frozen at 77 K. In particular, freezing at liquid nitrogen temperature makes the emission spectrum of **10** revive. Such a behaviour is that expected for an electron transfer mechanism. On the other hand, the frozen solution of $[Cu^{II}(\mathbf{10})]^{2+}$ does not show any fluorescence (fluorescence intensity at 415 nm is $\leq 10^{-3}$ of that of **10**, under the same conditions). Freezing immobilizes solvent molecules, prevents their interaction with electrically charged species, thus disfavouring the electron transfer process and inhibiting fluorescence quenching.[38] The fact that fluorescence is not revived in the frozen solid solution of $[Cu^{II}(\mathbf{10})]^{2+}$ indicates that the energy transfer mechanism is operative in the present situation. In any case, the above evidence would suggest that a metal centre capable of displaying a d^9–d^{10} redox change should switch the fluorescence of an adjacent anthracene fragment: the d^9 state should quench fluorescence, the d^{10} state should revive it. The most obvious and convenient d^9–d^{10} couple is undoubtly Cu^{II}/Cu^{I}.

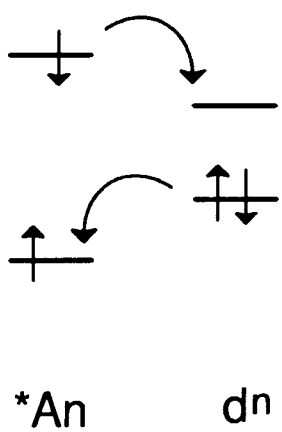
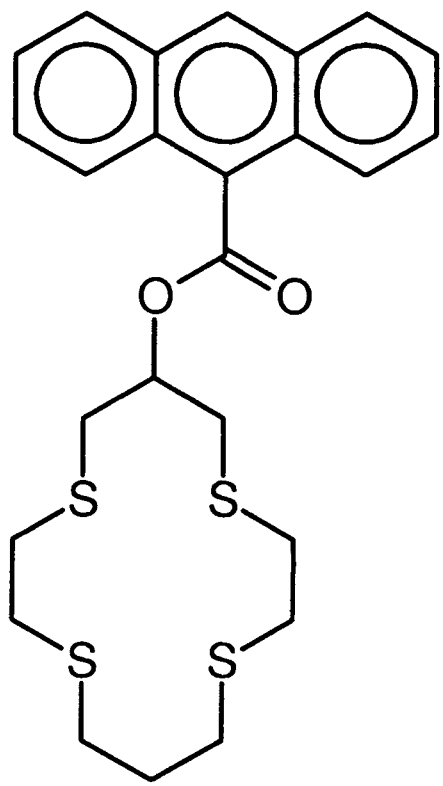


Figure 8 The mechanism of the energy transfer process (electron exchange type) that deactivates the excited state of anthracene in a radiationless mode, via an adjacent metal centre having empty or *half-filled d orbitals of appropriate energy* (e.g. Ni^{II}, d^8 electronic configuration; Cu^{II}, d^9, in system **10**).

However, the cyclam subunit does not offer a favourable environment to realize such a redox change in the proper way. In fact, a redox system, in order to operate as a switch, should present two consecutive oxidation states of comparable stability (a *bi-stable* system). This is not the case for cyclam, which establishes strong in-plane metal-ligand interactions and stabilizes the Cu^{II} transition cation very much. As a consequence, the Cu^{I} state can be achieved only at a very cathodic potential (-1.46 V vs Fc^+/Fc, in a MeCN solution made 0.1 M in Bu_4NClO_4) and lasts in solution only in the time scale of the cyclic voltammetry experiment.[39] These circumstances prompted us to use as a metal receptor a ligand able to form a more stable Cu^{I} complex. We wanted to keep a cyclic structure in order maintain the macrocyclic inertness and to avoid demetallation. In particular, we used a thiacyclam subunit, i.e. a cyclam-like ligand in which the four secondary amine nitrogen atoms have been replaced by thioethereal sulfur atoms. Poly-thia macrocycles have been shown to make the Cu^{I} state



11

stable and easily accessible.[40] Inside coordinative environments of this type, the Cu^{II}/Cu^{I} redox change takes place at positive potentials (vs Fc^{+}/Fc, in a MeCN solution). Thus, we linked the thiacyclam subunit to the anthracene fragment by means of an estereal bridge (**11**)[41]. Noticeably, a MeCN solution of **11** displays fluorescence at room temperature, but the emission spectrum is not that of anthracene (see Figure 9). In particular, the band is much less structured, it is displaced towards higher wavelengths and its intensity is about one order of magnitude smaller. Quite interestingly, the emission spectrum of **11** is rather similar to that of the ethyl esther of the 1-anthracenecarboxylic acid (see Figure 9). Fluorescence spectra of esters of anthracenecarboxylic acids have been assigned to a charge transfer (CT) excited state.[42] Then, we progressively added $[Cu^{I}(MeCN)_4]ClO_4$ to the MeCN solution of **11**, up to 1 equivalent: the Cu^{I} centre was incorporated by the tetra-thia ring, but the fluorescence spectrum was not affected at all. Then an excess of the oxidising agent $NOBF_4$ was added: the solution took the bright blue colour of the Cu^{II} complex and the fluorescence was almost completely quenched.

Moreover, the $[Cu^{II}(\mathbf{11})](ClO_4)_2$ was isolated and its MeCN solution did not show any fluorescence. Voltammetry studies disclosed a poorly reversible wave at 0.10 V vs Fc^{+}/Fc (i.e. 0.50 vs SCE), to be assigned to the Cu^{II}/Cu^{I} redox change. Thus, controlled potential electrolysis experiments were carried out on a MeCN solution of $[Cu^{II}(\mathbf{11})](ClO_4)_2$, made 0.1 M in Bu_4NClO_4, using a platinum gauze as a working electrode. The potential was first set at 200 mV vs SCE: the solution decolorated due to the formation of the $[Cu^{I}(\mathbf{11})]^{+}$ form and fluorescence was completely revived. Then, the potential of the working electrode was set at 800 mV vs SCE: the blue colour formed and fluorescence was quenched again (see Figure 10).

The experiments described above have demonstrated that the Cu^{II}/Cu^{I} couple, inside a tetra-thia-macrocyclic environment, works very well as a switch of the fluorescence of an adjacent anthracenoic ester subunit. However, it remained to assess whether the switching mechanism was based also in this case on an energy transfer process, as observed with the anthracene-metallocyclam conjugate system. Thus, a spectrofluorimetric investigation was carried out on a MeCN solution of $[Cu^{II}(\mathbf{11})](ClO_4)_2$, frozen at 77K. Quite surprisingly, the frozen solution displayed an emission spectrum, whose intensity was comparable to that of **11**, under the same conditions. This indicated unambiguously that the quenching mechanism had to be assigned to an *electron transfer* process from the CT excited state to Cu^{II}. Such a process can be described by the following equation:

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

and should be extremely favoured from a thermodynamic point of view, as indicated by the variation of the potential associated to eq. (1), $\Delta E_{ET}(*An_{CT} \rightarrow Cu^{II}) = 2.0$

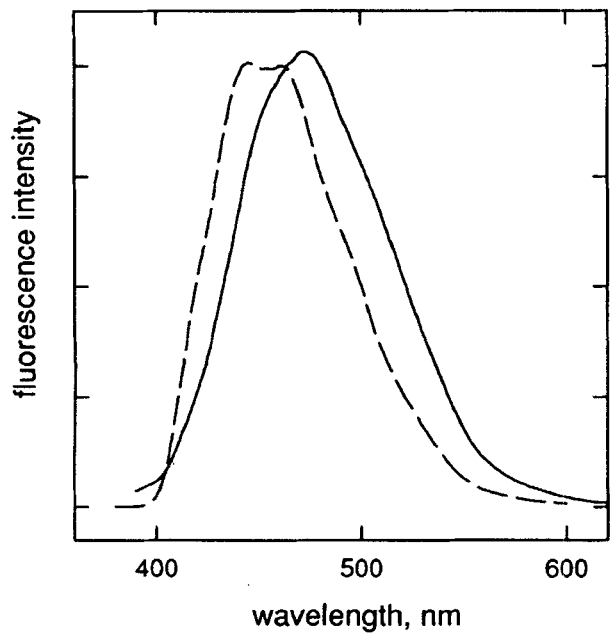


Figure 9 Fluorescence spectra of **11** (solid line) and of the ethyl ester of 1-anthracenoic acid (dotted line) in MeCN solution at room temperature. Spectra are typical of a charge transfer excited state.

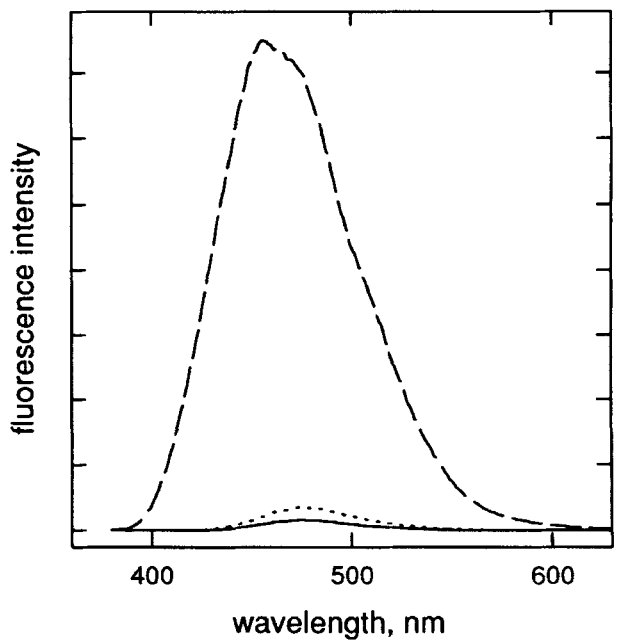


Figure 10 Fluorescence spectra of: an MeCN solution of $[Cu^{II}(\mathbf{11})](ClO_4)_2$ (_____); of the solution electrolysed with the working electrode set at 200 mV vs SCE (-----), the Cu^{I} complex is formed and fluorescence revives; of the solution electrolysed with the working electrode set at 200 mV vs SCE (.....), the Cu^{II} complex is formed again and fluorescence is quenched.

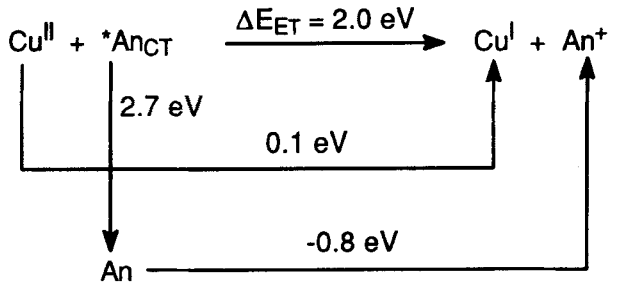


Figure 11 Thermodynamic cycle to evaluate the potential change ΔE_{ET} associated to the electron transfer process (1). ΔE_{ET} value is very positive and the process is extremely favoured (which accounts for fluorescence quenching).

eV, which was calculated through the thermodynamic cycle illustrated in Figure 11. In particular, $E(*An_{CT})$ has been obtained from the energy of the maximum of the emission band of **11**, whereas $E°(An^+/An)$ and $E°(Cu^{II}/Cu^{I})$ values have been obtained as $E_{\frac{1}{2}}$ values from voltammetric investigations in MeCN solution. Quantities reported in the cycle in Figure 11 indicates that the occurrence of the electron transfer process results both from the rather easy access to the Cu^{I} state in the tetra-thia coordinative environment and from the tendency of the anthracene fragment to be oxidised. Then, one could ask why a similar mechanism is not active also in the $[Cu^{I}(\mathbf{11})]^+$ system, which displays fluorescence even at room temperature. In this case, the electron transfer process (from the Cu^{I} centre to the CT excited state) is described by equation (2):

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

and the associated $\Delta E_{ET}(Cu^{I} \rightarrow *An_{CT})$ value is calculated through the cycle reported in Figure 12.

The $\Delta E_{ET}(Cu^{I} \rightarrow *An_{CT})$ value, even if still positive (0.2 eV), is much smaller that that associated to the photoinduced electron transfer process (1). ΔE_{ET} values calculated through the thermodynamic cycles of Figures 11 and 12 should be considered as rather approximate. However their large difference is well beyond uncertainties and accounts for the different effect exerted by Cu^{II} and Cu^{I} on the adjacent luminescent fragment.

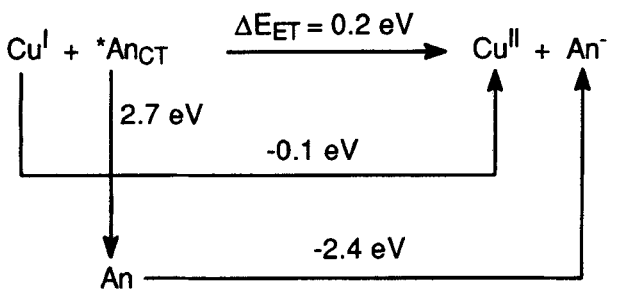


Figure 12 Thermodynamic cycle to evaluate the potential change ΔE_{ET} associated to the electron transfer process (2). ΔE_{ET} value is only moderately positive and the process is slightly favoured and very slow (which accounts for anthracene fluorescence persistence).

In conclusion, looking at the anthracene-metallocyclam conjugate system **10**, we had the feeling that anthracene fluorescence could be switched on/off *via* an energy transfer mechanism involving an adjacent metal centre and we considered the Cu^{II}/Cu^{I} (d^9/d^{10}) redox change. Indeed, the Cu^{II}/Cu^{I} couple in the system **11** worked well, switching the fluorescence of the CT excited state, but through a different mechanism: electron transfer.

Thus, switching was not a matter of electronic configuration, but of redox potential. The excited state of the fluorophore transfers an electron to Cu^{II}, due the relatively high value of the Cu^{II}/Cu^{I} redox couple potential and also to the tendency of anthracene to be oxidised. On the other hand, the Cu^{I} centre does not transfer an electron to the excited fluorophore in view its high stability and of the resistence of anthracene to the reduction. It should be noted also that the ester bridge in **11** plays an essential role. Its interaction with the anthracene fragment lowers the energy of the excited state (which has a charge transfer nature) and substantially reduces the excitation potential, compared to that of unperturbed anthracene (3.1 eV). Thus, the CT excited state of the anthracenoic ester fragment can discriminate between the two electron transfer mechanisms (1) and (2) and generates a switching situation. Such a situation could not be induced by the too energy rich excited state of plain anthracene.

On the basis of the above findings, one could forecast that further redox couples besides Cu^{II}/Cu^{I} could switch on/off the fluorescence of system **11**, independent of the electronic configuration of the involved metal centres M^{n+} and $M^{(n+1)+}$. The only requirement is a rather high value of the potential of the $M^{(n+1)+}/M^{n+}$ couple. In particular, it should be comparable to that of the couple used as an internal reference (Fc^+/Fc) in an acetonitrile solution.

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