

Transition Metals as Switches

LUIGI FABBRIZZI,* MAURIZIO LICCHELLI, AND PIERSANDRO PALLAVICINI

Dipartimento di Chimica Generale, Università di Pavia, via Taramelli 12, I-27100 Pavia, Italy

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Introduction

There exists in today's applied research a seemingly unstoppable tendency to bring technology and its objects to a progressively smaller size, down to the nanoscopic level. On the other side, chemists are trying to develop, on their own, a technology based on single molecules.¹ In this context, several molecular systems capable of performing elementary acts have been designed, which are reminiscent of the devices typically provided by macroscopic technology. Thus, molecular systems of varying complexity which behave as machines,² motors,³ brakes,⁴ gears,⁵ ratchets,⁶ batteries,⁷ plugs, and sockets⁸ have been synthesized in recent years. Some other molecules are addressed to more advanced functions and behave as logic gates.^{9–12} In any case, all these systems invariably perform their activity when dissolved in solution (typically at the 10^{-3} – 10^{-5} M concentration level), and the displayed function can be controlled through an external input, such as change of pH, variation of the redox potential, or illumination. In most cases, the molecular device obeys a very simple rule: the external stimulus makes it work (output on) or not (output off). This binary behavior derives essentially from the fact that the envisaged molecular system contains a component (the control subunit) that exists in two states of comparable stability, A and B, which can be interconverted reversibly by the external input. Each state interacts to a different extent, through an intercomponent process

(bonding interaction, electron or energy transfer, etc.), with another portion of the system (the active subunit). It is the different extent of the interaction between the control subunit and the active subunit that generates the function, which can be turned on/off through the external parameter. Thus, the control subunit behaves as a switch, and indeed the term "switch", either as a noun or as a verb, is one of the most used words in the language of single-molecule technology.

In the present article, we would like to demonstrate that transition metals are among the best candidates for the role of molecular switches, on account of the following peculiar properties: (i) They can form couples of consecutive oxidation states, A and B, easily interconverted through a fast and reversible one-electron redox change. The relative stability of the two states (which is expressed exactly by the standard electrode potential associated with the half-reaction) can be modulated by properly varying the coordinative environment around the metal center. (ii) The one-electron change in most cases modifies drastically the properties of the metal center (stereochemical preferences, magnetism, electron-transfer tendencies, binding affinity toward a donor atom).

In the macroscopic world, the switch par excellence is the light switch, i.e., a device that opens/closes an electric circuit in which a bulb is inserted. The external input responsible for turning light on/off is, for instance, the pressure of a finger. Perhaps inspired by the most common switch of everyday life, we first devoted our interest to luminescent molecular systems whose light emission could be switched on/off through a chemical (or electrochemical) input.¹³

Our approach fits well the metaphor illustrated in Figure 1: the bulb is a luminescent fragment (e.g., a naphthalene moiety), the switch is a redox-active subunit (e.g., a transition metal center in a given coordinative environment), and the input is provided by a change of the redox potential, which can be achieved, for instance, by adding an oxidizing or reducing agent to the solution.

Redox-Active Metal Centers That Switch Fluorescence On/Off

An organic fluorophore, F, is linked covalently to a multidentate receptor which hosts a metal center, M, as outlined in the scheme in Figure 2. The metal is redox active through the two oxidation states, $M^{(n+1)+}$ and M^{n+} , which are connected by a fast and reversible redox change.

The corresponding reduction potential, $E^{\circ}(M^{(n+1)+}/M^{n+})$, has to be neither too positive nor too negative, thus indicating that the two states have a comparable stability. Each state can or cannot interact with the proximate photoexcited fluorophore through either an *electron-transfer* (eT) or an *energy-transfer* (ET) process. Interaction causes the quenching of light emission by F, as illustrated by the triangular scheme in Figure 2. Favorable combinations for a switching behavior are those in which *one oxidation state quenches the fluorescence and the other*

Luigi Fabbrizzi was born in Florence in 1946. In 1969, he graduated in chemistry at the University of Florence, where, from 1972 to 1980, he was lecturer of inorganic chemistry. In 1980, he was appointed Professor of Inorganic Chemistry at the Faculty of Science of the University of Pavia. His main research interests are related to the supramolecular chemistry of transition metals, with a special regard to the electrochemical and photophysical aspects.

Maurizio Licchelli was born in Lecce, Italy, in 1959. He graduated in chemistry at the University of Pavia in 1983. He was a researcher at Enichem R&D Laboratories in Milan until 1990, when he joined the Department of General Chemistry of the University of Pavia as a Research Associate. His current interests include the design of luminescent molecular sensors for ions and biologically relevant analytes and the photophysics of metal-containing supramolecular systems.

Piersandro Pallavicini was born in Vigevano, Italy, in 1962. He graduated in chemistry at the University of Pavia in 1986. In 1990, he received his Ph.D. degree in chemistry at the Scuola Normale Superiore, Pisa, under the supervision of Professor Fausto Calderazzo. He joined the University of Pavia in 1991, where he is presently a Research Associate. His research interests cover multicomponent coordination compounds and the study of oriented motions at the molecular level.

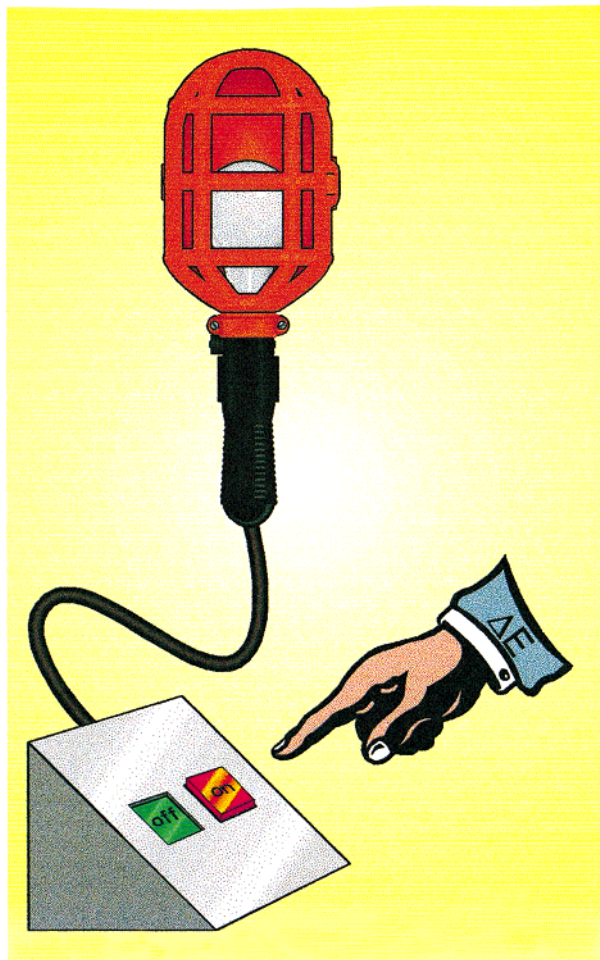
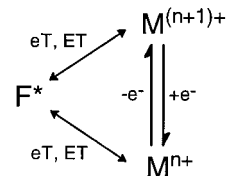
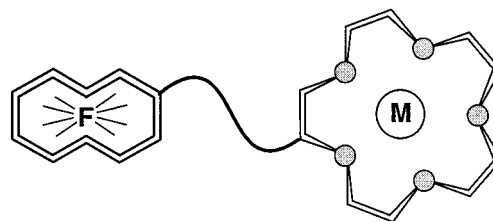


FIGURE 1. Metaphorical sketch of a molecular luminescence switch. The light bulb is the luminescent fragment, the electrical wire is the spacer, and the real switch is a redox-active fragment, whose oxidized form quenches the light emission and the reduced form does not (or vice versa). The input is provided by a variation of the redox potential (ΔE).

does not. In such a situation, the emission by the fluorophore can be switched on/off through the $M^{(n+1)+}/M^{n+}$ couple, chemically (by adding consecutively an oxidizing agent and a reducing agent) or electrochemically (by adjusting the potential of the working electrode at the appropriate values, in an exhaustive electrolysis experiment). Unfavorable combinations are those in which both $M^{(n+1)+}$ and M^{n+} quench the photoexcited fluorophore (light permanently turned off) or do not interact with it (light permanently turned on).

Combining the convenient components and obtaining a working redox switch of fluorescence seemed, at least at the beginning, simply a matter of chance. Fortunately, our first attempt was successful.¹⁴ An anthracene fragment was linked covalently to the 14-ane- S_4 macrocyclic receptor, which hosted a copper center (**1**, Figure 3); the S_4 donor set forms fairly stable complexes with both Cu^{II} and Cu^I , and the potential associated with the electrochemically quasi-reversible Cu^{II}/Cu^I couple inside the tetrathia macrocycle is weakly positive. The Cu^I derivative, dissolved in an MeCN solution, displays a structureless



$F^*-M^{(n+1)+}$ interaction	F^*-M^{n+} interaction	emission output
YES	NO	OFF/ON
NO	YES	ON/OFF
YES	YES	OFF/OFF
NO	NO	ON/ON

FIGURE 2. Mechanism of on/off switching of fluorescence in a two-component light-emitting system, whose active subunit contains a redox-active metal center M , providing two oxidation states, M^{n+} and $M^{(n+1)+}$, of comparable stability (bistable system). Switching behavior is attained when one state quenches the nearby excited fluorophore F^* through an intercomponent process (electron transfer, eT, or energy transfer, ET) and the other does not. There exist two favorable combinations (off/on and on/off) and two unfavorable combinations (off/off and on/on).

emission band at $\lambda = 460$ nm, which originates from the charge-transfer excited state (An-CT*) of the anthracenoic ester fragment. On chemical (with $NOBF_4$) or electrochemical oxidation (working potential, 0.55 V vs Fc^+/Fc), the Cu^{II} derivative was generated in solution, and complete quenching of fluorescence was observed. On reduction to Cu^I (working potential, -0.05 V vs Fc^+/Fc), the emission band at 460 nm was fully restored. Then, consecutive oxidation and reduction at the copper center resulted in turning off/on the light emission by the photoexcited anthracenoic ester fragment, a process which could be carried out indefinitely, at will, as one would expect from a light switch in real life. With regard to the mechanism of the quenching of the An-CT* excited state by Cu^{II} , it was established that it was a result of a fluorophore-to-metal eT process.

The occurrence of such a process can be simply accounted for on a thermodynamic basis: in particular, the free energy change associated with the eT process, $\Delta G^\circ(\text{An-CT}^* \rightarrow Cu^{II})$, which can be calculated through the combination of the pertinent photophysical and electrochemical quantities illustrated in the cycle of Figure 4a, is distinctly negative (-1.87 eV). On the other hand, with regard to the Cu^I derivative, the occurrence of an eT process from Cu^I to An-CT* is thermodynamically disfavored, because of the positive value of $\Delta G^\circ(Cu^I \rightarrow \text{An-CT}^*)$, 0.01 eV (calculated through the thermodynamic cycle of Figure 4b). A closer inspection of the quantities

molecule	couple	switching behaviour	mechanism	distance (Å)
	Cu ^I /Cu ^I	OFF/ON	eT	6.9
	Ni ^{III} /Ni ^{II}	OFF/ON	eT	5.9
	Ni ^{III} /Ni ^{II}	OFF/ON	eT	6.0
	Ni ^{III} /Ni ^{II}	OFF/OFF	eT	6.1
	Cu ^I /Cu ^I	OFF/ON	ET	4.4
	Cu ^I /Cu ^I	OFF/ON	ET	4.3
	Ni ^{III} /Ni ^{II}	OFF/OFF	ET	4.5
	Ni ²⁺ /Ni ⁺ (*)	ON/OFF	eT	-

(*) Ni⁺ = [Ni^{II}(L⁻)]⁺

FIGURE 3. Two-component molecular switches of fluorescence operating through a metal-centered redox couple. The metal center, in a given oxidation state, can quench the emission of the proximate fluorophore through either an eT (electron transfer) or an ET (energy transfer) mechanism. The distances reported are those between the metal center and the carbon atom of the organic fluorophore closest to the metal center, and they were either obtained from X-ray data, when available, or calculated through a semiempirical method. In the case of system **8**, the distance was omitted because, in the reduced form, a Ni^{II}–ligand anion radical species, the electron involved in the eT process moves not from the metal center but from a π orbital of the ligand backbone.

contributing to the ΔG° values indicates that the off/on behavior in the final analysis depends on the very endergonic nature of the one-electron reduction of the anthracene fragment ($An + e^- \rightarrow An^-$, $-eE^\circ = +2.46$ eV), which prevents the occurrence of the $Cu^I \rightarrow An-CT^*$ eT process (fluorescence on). On the other hand, in the case of the $An-CT^* \rightarrow Cu^{II}$ process, the one-electron oxidation of the anthracene fragment ($An \rightarrow An^+ + e^-$, $-eE^\circ = 1.08$ eV) is not endoergonic enough to outweigh the other favorable contributions; thus, the eT process takes place, and fluorescence is off.

The thermodynamic approach outlined above would indicate that the behavior of any redox switch of fluorescence can be predetermined by inserting the pertinent photophysical and electrochemical quantities of the chosen components in the two thermodynamic cycles of the type illustrated in Figure 4. The nature of the fluorophore and of the metal centered redox couple does not matter and can be changed at will. The essential point is that the two ΔG°_{eT} values have an *opposite* sign.

The second redox switch of fluorescence we considered, system **2** in Figure 3, consisted of a control subunit based on the Ni^{III}/Ni^{II} redox couple (hosted by a cyclam-like macrocycle; a cyclic coordinative framework is rec-

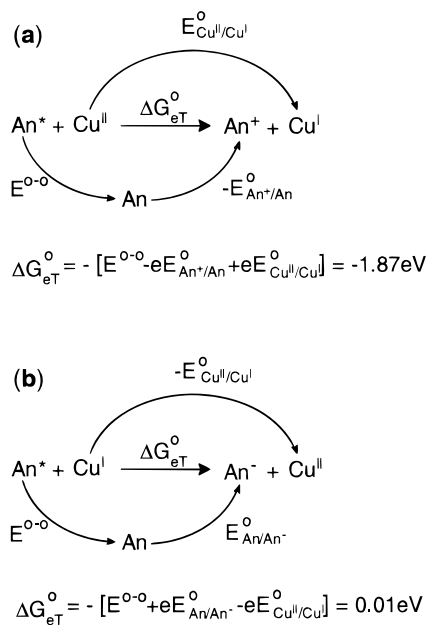


FIGURE 4. Thermodynamic cycles for evaluating the free energy changes, ΔG°_{eT} , associated with the intramolecular photoinduced electron-transfer process in system **1** in its oxidized (a) and reduced (b) forms. The E^{0-0} quantity, the spectroscopic energy, is obtained from the emission spectrum; the E° values, electrode potentials associated with the given redox change, can be determined through voltammetry experiments. The Coulombic term ($e^2/\epsilon r$) has been considered negligible under the present circumstances.

ommended in order to prevent the metal from escaping to the solution) and of a dansyl fluorophore, linked by a sulfonamide spacer.¹⁵ System **2** represents a further example of an off/on switch: the oxidized metal ion, Ni^{III}, quenches the dansyl fluorescence; the reduced ion, Ni^{II}, does not. Quenching is to be ascribed again to a fluorophore-to-metal eT process, and its occurrence is justified thermodynamically: $\Delta G^\circ_{eT}(\text{Dns}^* \rightarrow \text{Ni}^{III}) = -1.93$ eV. On the other hand, the Ni^{II}-to-Dns* eT process is disfavored from a thermodynamic standpoint: $\Delta G^\circ_{eT}(\text{Ni}^{II} \rightarrow \text{Dns}^*) \geq 0.7$ eV. Actually, the luminescence of the dansyl fragment of **2** can be switched on/off electrochemically, in an exhaustive electrolysis experiment on an MeCN solution, by setting the potential of the platinum gauze used as a working electrode alternatively at 0.23 V vs Fc^{+/}Fc (Ni^{III} state, fluorescence off) and at -0.07 V (Ni^{II} state, fluorescence on). The fluorescence quenching/revival can also be induced chemically, in an EtOH solution, through consecutive addition of Na₂S₂O₈ and NaNO₂. In real life, the type of illumination can be changed by unscrewing the bulb and replacing it with a different one. Something similar can be done in the molecular world: for instance, the dansyl luminophore of system **2** (which emits in the visible region, $\lambda = 510$ nm, from a CT excited state) has been replaced in system **3** by a plain naphthalene fragment, which emits UV light, $\lambda = 362$ nm, through its typical $\pi^* \rightarrow \pi$ transition. Also in this case, light emission can be switched on/off at will either chemically or electrochemically, through the Ni^{III}/Ni^{II}.

However, not everything turns out as it should! In system **4**, a nickel center is incorporated inside a dioxo-

cyclamato(2-) ring, a coordinative environment which favors the attainment of high oxidation states; in particular, the potential of the Ni^{III}/Ni^{II} couple is especially low (0.3 V). An anthracene fragment is linked covalently to a carbon atom of the macrocyclic framework, but its fluorescent emission is quenched for *both* Ni^{III} and Ni^{II} derivatives. The frustrating off/off combination results from the occurrence of thermodynamically favored eT processes: An^{*}-to-Ni^{III}, $\Delta G^{\circ}_{eT} = -2.56$ eV, and Ni^{II}-to-An^{*}, $\Delta G^{\circ}_{eT} = -0.40$ eV. The occurrence of the latter process, which is not observed with the other Ni^{III}/Ni^{II}-based switching devices **2** and **3**, is essentially a consequence of the ease of oxidation of the Ni^{II} center, when incorporated by the dioxocyclamato(2-) ring.¹⁶

Besides electron transfer, there exists another mechanism by which a transition metal center can quench a close photoexcited fragment: an energy transfer (ET) process, either of the Dexter type (double electron exchange) or of the Förster type (resonance energy transfer).^{17,18} The occurrence of the ET process requires that the metal possesses empty or half-filled levels of low energy, a common situation for d block metal ions. Such a situation is verified when the metal displays absorption band(s) at a higher wavelength than the fluorophore emission band. Under these circumstances, photonic energy can be transferred from the excited state of the fluorophore to an excited state of the metal, which in most cases undergoes a nonradiative decay, thus quenching fluorescence. On the other hand, metals with a closed-shell electronic configuration do not possess low energy levels and cannot be involved in an ET process. An example is provided by the d¹⁰ cation Zn^{II}. This suggests that a d⁹/d¹⁰ redox couple could work well as an ET fluorescence switch, as the d⁹ cation should quench the nearby fluorophore and the d¹⁰ state should not. A couple displaying the required electronic configuration (perhaps the only one feasible) is Cu^{II}/Cu^I, which we have seen to operate well in the off/on switching system **1** under eT conditions. Indeed, Cu^{II}/Cu^I-based off/on fluorescence switches operating through an ET mechanism exist, and an example is given by system **5**.¹⁶ This system resembles **1** in that it consists of a sulfur-containing macrocycle providing comparable stability for Cu^{II} and Cu^I chelates, covalently linked to an aromatic fluorophore, naphthalene. The typical naphthalene emission is fully displayed by the colorless Cu^I form, but it is quenched in the bright blue Cu^{II} derivative, due to an ET process. We should be happy that the ET mechanism is operating in this system, rather than the eT one. In fact, were the eT mechanism active, we would be in the presence of a frustrating off/off combination, as both the Naphth^{*}-to-Cu^{II} and the Cu^I-to-Naphth^{*} eT processes are thermodynamically favored ($\Delta G^{\circ} = -2.46$ and -0.99 eV, respectively). Other systems in which an ET mechanism operates are illustrated in Figure 3. In particular, in the Ni^{III}/Ni^{II}-based system **6**, both the oxidized and reduced forms have the anthracene fluorescence quenched (off/off), due to an ET mechanism. Notice that the eT rule, if operating, would lead in any

case to the unpleasant off/off situation: An^{*}-to-Ni^{III}, $\Delta G^{\circ}_{eT} = -2.46$ eV; Ni^{III}-to-An^{*}, $\Delta G^{\circ}_{eT} = -0.40$ eV.

Explaining why in some cases the eT mechanism predominates over the ET mechanism and in others the opposite takes place is not straightforward, and the limited number of molecular switches investigated so far does not help the search for a convincing rationalization. An empirical consideration which can be made by looking at the stocklist in Figure 3 is that the ET mechanism is active in those systems in which the fluorophore and the metal center are closer (calculated distance ≤ 4.5 Å, systems **5**, **6**, and **7**) and that the eT mechanism prevails when the metal-fluorophore distance is ≥ 5.9 Å (**1**, **2**, and **3**).

From the point of view of the design, one would prefer to rely on the eT rather than on the ET mechanism, as the latter process works predictably well with only one couple: Cu^{II}/Cu^I. To the contrary, under the eT rule, any M⁽ⁿ⁺¹⁾⁺/Mⁿ⁺ couple can generate, given the proper conditions, the favorable off/on and on/off combinations. In particular, coordination of a transition metal by a suitable receptor can make available different redox couples, whose electrode potential (a key quantity in the thermodynamic balance leading to the off or on behavior) can be modulated through subtle structural modifications of the coordinating framework.

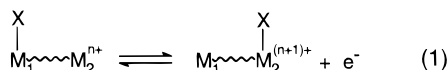
Notice that in the updated stocklist reported in Figure 3, most of the switches are of the off/on type; i.e., in the oxidized form the fluorescence is quenched, and in the reduced form the fluorescence is revived. There is just one switch of the on/off type: **8**, which operates through the [NiL]²⁺/[NiL]⁺ couple. However, the reduced form must be seen as a Ni^{II}-anion radical ligand complex, [Ni^{II}(L^{•-})]⁺. It is the electron delocalized onto the unsaturated portion of the macrocycle that is transferred to the excited fluorophore, thus quenching its emission.¹⁹ Finally, it has to be mentioned that Figure 3 does not include the first example of redox switch of luminescence, whose control unit is based on the quinone/hydroquinone couple and whose luminophore is a [Ru^{II}(bpy)₃]²⁺ fragment.²⁰

Redox-Driven Anion Translocation between Metal Centers

The drastic change of the stereochemical properties that usually follows the one-electron uptake–release by a transition metal is a property that can be utilized in order to promote oriented motions at the molecular level. A nice example is given by Sauvage's disymmetrical copper catenate.²¹ Following the oxidation of Cu^I (electronic configuration, d¹⁰; preferred coordination number, CN = 4) to Cu^{II} (d⁹; CN = 5), one ring of the catenane makes a half-turn with respect to the other. On reduction to Cu^I, the turn is completed. Thus, the Cu^{II}/Cu^I couple can be used to convert chemical or electrochemical energy into controlled motion and is an essential component of a simple yet efficient molecular machine.

Controlled motion can be generated at the molecular level also by making a particle translocate between fixed

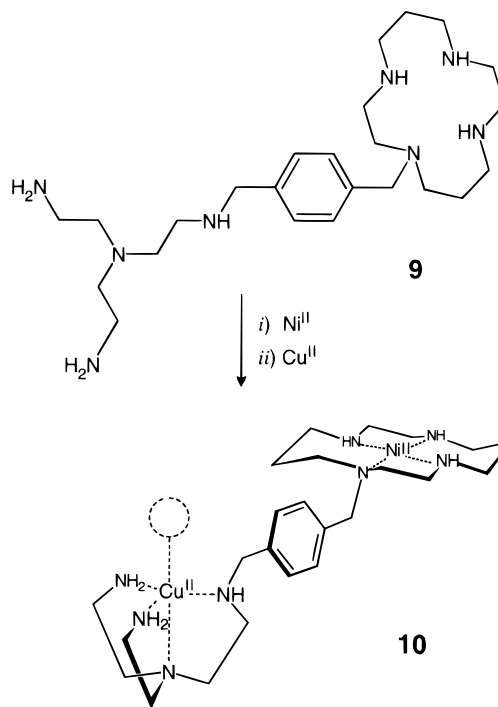
positions, following a prescribed pathway. The particle can be an anion, X^- , and can be made to move between two transition metal centers, M_1 and M_2 , taking advantage of the redox activity of one of them. To define the route, each metal center has to be hosted by a receptor, and the two receptors must be covalently linked through a spacer (which determines the length of the path). Moreover, the two metals should possess the following characteristics: (i) M_2 must undergo a reversible one-electron redox change, $M^{(n+1)+}/M^{n+}$, at a not-too-high, not-too-low potential. (ii) M_1 and M_2 should be coordinatively unsaturated (thus being inclined to bind X^-) and the affinity toward X^- should decrease along the series $M_2^{(n+1)+} > M_1 > M_2^{n+}$. Under these circumstances, the following redox equilibrium is established in solution:



In particular, when M_2 is in its reduced form, M_2^{n+} , X^- prefers to stay on M_1 , but when M_2 is oxidized to $M_2^{(n+1)+}$, X^- moves to the M_2 center. Thus, if the M_1-X and M_2-X coordinative bonds are labile, the X^- anion can be translocated at will, back and forth between M_1 and M_2 , by oxidizing and reducing the M_2 center, either chemically or electrochemically.

A redox change useful for anion translocation purposes is provided by the already mentioned Ni^{III}/Ni^{II} couple, when incorporated in a cyclic tetramine environment of the cyclam type. In the case of the fluorescence switching considered in the previous section, we profited from the different redox tendencies of the two oxidation states: Ni^{III} was able to involve the proximate excited fluorophore in an eT process, and Ni^{II} was not. For anion translocation purposes, we can benefit from the drastic change of the stereochemical preferences associated with the redox change. In particular, the reduced form, $[Ni^{II}(\text{cyclam})]^{2+}$, tends to be square-planar in solution (with the Ni^{II} ion in the low-spin state), and the metal shows a very low tendency to bind anions. On the other hand, the oxidized form (Ni^{III} , low-spin) wants to attain a higher coordination number than 4 and strongly binds anions (e.g., Cl^-) in the axial positions. A good candidate to play the auxiliary role of M_1 is the Cu^{II} complex of the tripodal tetramine tris(2-aminoethyl)amine (tren). In fact, the quadridentate tren ligand imposes on the metal a trigonal bipyramidal stereochemistry, thus leaving one of the axial sites of the coordination polyhedron available for anion coordination. Moreover, $[Cu^{II}(\text{tren})]^{2+}$ has a definite tendency to bind an anion, much higher than $[Ni^{II}(\text{cyclam})]^{2+}$, but distinctly lower than $[Ni^{III}(\text{cyclam})]^{3+}$. This provides the required sequence of affinities: $[Ni^{III}(\text{cyclam})]^{3+} > [Cu^{II}(\text{tren})]^{2+} > [Ni^{II}(\text{cyclam})]^{2+}$.

Thus, the two tetramine receptors, cyclam and tren, were linked by a 1,4-xylyl spacer to give system **9**.²² The peculiar nature of the two tetramine receptor subunits of **9** allowed control of the synthesis of the desired heterodimetallic complex **10** and avoided the attainment of a frustrating statistical mixture. **9** first reacted with 1 equiv



of Ni^{II} , which occupied the most favorable cyclam cavity to give an inert complex species. One equivalent of Cu^{II} was then added: Cu^{II} could compete successfully for the cyclam cavity, but, at room temperature, it could not displace the kinetically stable Ni^{II} center. Thus, Cu^{II} had to be satisfied with coordination by the tren subunit of **9**, and the $[Cu^{II}(\text{tren})\sim Ni^{II}(\text{cyclam})]^{4+}$ heterodimetallic species was obtained. This two-step synthesis stresses the special properties of macrocyclic complexes. First, Ni^{II} is addressed to the cyclam rather than to the tren receptor to profit from the *thermodynamic* macrocyclic effect.²³ When Cu^{II} is added, the transmetalation at the cyclam ring is prevented by the *kinetic* macrocyclic effect,²⁴ thus sending the metal to the tren subunit.

The $[Cu^{II}(\text{tren})\sim Ni^{II}(\text{cyclam})]^{4+}$ system performs the expected mechanical work with the chloride anion. When 1 equiv of Cl^- is added to an MeCN solution of the heterodimetallic complex, the anion goes on the Cu^{II} center. In particular, since the log K value for the 1:1 adduct formation equilibrium is 5.7, in a 10^{-3} M solution of the heterodimetallic complex, 95% of the Cl^- ion is bound to Cu^{II} , while the remaining 5% is dispersed in the solution. The solution has a blue-green color, as a result of an absorption band centered at 460 nm, caused by the $[Cu^{II}(\text{tren})]^{2+}$ fragment of the heterodimetallic complex (Cl^- -to- Cu^{II} CT transition). If, in an experiment of exhaustive electrolysis, the potential of the working electrode is set at 0.40 V vs Fc^+/Fc , the color of the solution turns bright-yellow. This is the color of the $[Ni^{III}(\text{cyclam})Cl]^{2+}$ fragment (intense absorption band at 315 nm). The $Ni^{III}-Cl$ binding constant is $>10^7$; thus, 100% of Cl^- is bound to the trivalent center. Thus, the blue-green-to-bright-yellow color change signals the occurrence of the redox-driven chloride translocation, illustrated by the half-reaction below:

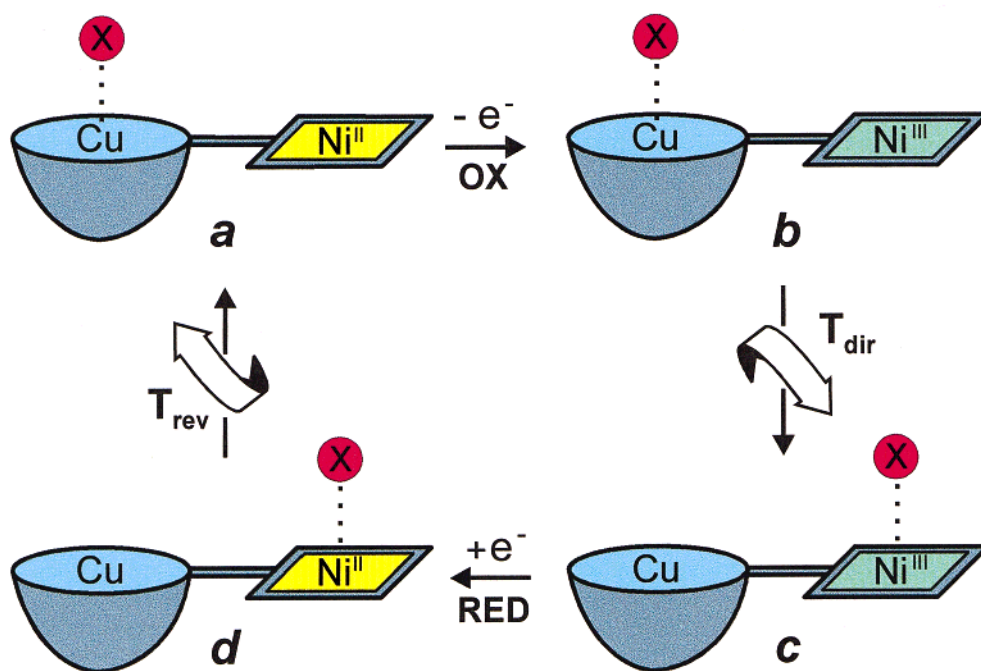
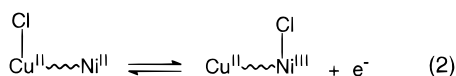


FIGURE 5. Square scheme illustrating the redox-driven translocation of an X^- anion from Cu^{II} to Ni^{III} in a system like **10**, and vice versa. As the transient species **b** has too short a lifetime, the oxidation step, OX, and the direct translocation step, T_{dir} , cannot be distinguished and are perceived as simultaneous. The same happens for the reduction (RED) and reverse translocation (T_{rev}) steps.



The process is fully reversible: on setting the potential of the working electrode at 0.00 vs Fc^+/Fc , Ni^{III} is reduced to Ni^{II} , Cl^- moves back to the Cu^{II} center, and the solution takes its original blue-green color. Due to the great stability of both reduced and oxidized forms of the heterodimetallic complex, the Cl^- anion can be moved back and forth between copper and nickel centers at will by switching the value of the potential of the working electrode between 0.40 and 0.00 V.

The intimate mechanism of the anion translocation is illustrated in Figure 5. First, Ni^{II} undergoes oxidation to Ni^{III} (OX process). Then, Cl^- moves from Cu^{II} to Ni^{III} (direct translocation, T_{dir}). The T_{dir} process is too fast to be characterized spectroscopically or electrochemically, and the transient species **b** can be only hypothesised, not identified. A relevant question is whether, in process T_{dir} , the Cl^- anion comes from the proximate Cu^{II} center within the same heterodimetallic complex (*intramolecular* event) or from a different dimetallic complex in solution (a less valuable *intermolecular* process). It has been demonstrated that the T_{dir} step must be intramolecular, as the uptake of a Cl^- ion by Ni^{III} from solution is a very disfavored process from an entropic point of view.²² Roughly speaking, it is much easier and more convenient to take the desired object, Cl^- , when it is positioned at 7.5 Å (the calculated Ni–Cu distance in the heterodimetallic system) than to seek it in the bulk solution (average distance between the Cu–Ni complexes at a 10^{-3} M concentration, 117 Å). The square scheme in Figure 6 is completed by the reduction of Ni^{III} to Ni^{II} (RED process)

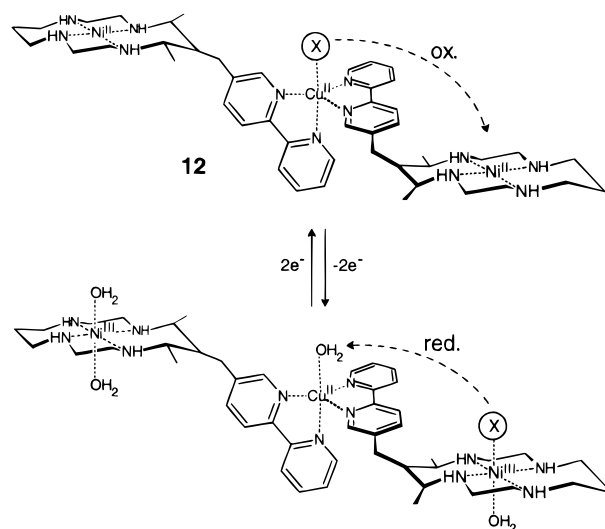
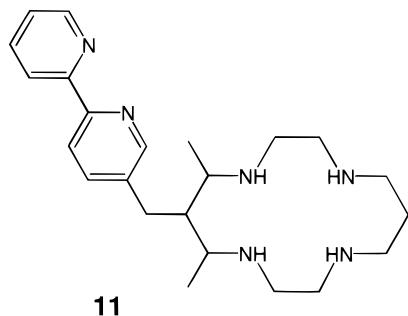


FIGURE 6. Electrochemically triggered anion translocation in a multicentric supramolecular coordination compound. On Ni^{II} -to- Ni^{III} oxidation, the X^- anion moves from Cu^{II} to one of the two available proximate trivalent centers. Following the Ni^{III} -to- Ni^{II} reduction, X^- moves back from the periphery to the center. As the process takes place in water, the axial position on Cu^{II} , when left vacant due to X^- translocation, is occupied by an H_2O molecule.

and the reverse translocation of Cl^- to the Cu^{II} center (T_{rev}). Again, due to the extremely fast nature of T_{rev} , the two formally consecutive processes are perceived as simultaneous. It should be noted that the very high rate of both T steps is related to the labile nature of the Cu^{II} – Cl and Ni^{III} – Cl bonds and accounts for the quick reversibility of the translocation process.

The choice of the pair of metals is not trivial. In the case of the previously considered tren–cyclam conjugate,

the $\text{Cu}^{\text{II}}(\text{tren})\text{-Ni}^{\text{II}}(\text{cyclam})$ combination seems to be the only one operating properly. For instance, the inversion of the two metal centers, $\text{Ni}^{\text{II}}(\text{tren})\text{-Cu}^{\text{II}}(\text{cyclam})$, does not work. When encircled by the cyclam receptor, Cu^{II} can undergo one-electron oxidation, even if at a rather positive potential,²⁵ but the Cu^{III} center that forms, having a d^8 electronic configuration, likes being square planar and does not allow the required sequence of anion affinities to be established.



The copper–nickel couple works well in the heterodimetallic system based on molecule **11**. Here, a 2,2'-bipyridine fragment is linked covalently to the carbon backbone of a $\text{Ni}^{\text{II}}(\text{cyclam})$ subunit. Two bpy fragments bind a Cu^{II} center, giving rise to the trimetallic system depicted in Figure 6. The system that forms, **12**, can be rightly considered a *supramolecule*, as it consists of three distinct subunits held together by noncovalent interactions. The trimetallic system **12** fulfils the requirements for a redox-driven anion translocation. The redox change driving the anion translocation is again the $\text{Ni}^{\text{II}}/\text{Ni}^{\text{III}}$ couple inside the cyclam ring. The central $\text{Cu}^{\text{II}}(\text{bpy})_2$ fragment acts as an auxiliary subunit, as Cu^{II} wants to achieve five-coordination and gives a fairly stable 1:1 adduct in aqueous solution with an inorganic anion X^- (Cl^- , NCO^-). Thus, when 1 equiv of X^- is added to an aqueous solution of **12** in its reduced form, $\text{Ni}^{\text{II}}\sim\text{Cu}^{\text{II}}\sim\text{Ni}^{\text{II}}$, the anion goes on the Cu^{II} ion at the core of the system. Following the Ni^{II} -to- Ni^{III} electrochemical oxidation (the two metal centers display independent redox activity and are oxidized at the same potential), the anion moves to the periphery to bind one of the $\text{Ni}^{\text{III}}(\text{cyclam})$ subunits. Thus, the covalently linked tren–cyclam conjugate **10** and the supramolecular system **12** display a similar behavior. However, in system **12**, the Cu^{II} -to- Ni^{III} translocation process profits from a statistical factor of 2, as the X^- anion can choose among two equivalent sites.

Both investigated heterometallic systems consist of a fixed framework and a movable part (X^-) and are able to convert energy (of electrochemical nature) into a controlled motion. Thus, they can be classified as a new type of molecular machine, an addition to the previously reported catenane- and rotaxane-based systems.^{2,3} The motive power is provided by the $\text{Ni}^{\text{II}}/\text{Ni}^{\text{III}}$ redox couple within a tetramine macrocycle. From the point of view of the efficiency, the supramolecular system **12** can be considered as a less valuable machine, as it uses two

engines to do the same work as the single-engine tren–cyclam system **10**.

Conclusions

The work described in the previous sections belongs to that *dynamic* branch of supramolecular chemistry aimed at the design of devices capable of exerting functions of varying nature at the molecular level. While this research field is expected to evolve to a new technology based on single molecules, it can be considered at present a useful and beneficial exercise which helps to define new concepts of basic chemistry and to develop new ideas. Transition metals are irreplaceable components of the dynamic supramolecular chemistry tool box, in view of their unique electronic properties, as we tried to illustrate in this paper. A further fascinating role played by transition metals in supramolecular chemistry is associated with their ability to organize multicomponent assemblies of varying complexity such as double and triple helices, racks, and grids.²⁷ Since the structural features of the assembly are related to the stereochemical preferences of the metal, a change of its oxidation state can cause a drastic variation of the supramolecular structure. A simple yet intriguing example refers to the electrochemically switched assembling–disassembling of a double helix through the $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ couple: two Cu^{I} centers (preferred coordination geometry, tetrahedral) organize two quadridentate strands in a double helicate, whereas the Cu^{II} center unfolds the helix to give two mononuclear species and to profit from a distorted tetragonal stereochemistry.^{28,29} Intriguing effects can be foreseen if metal-centered redox switching is applied to supramolecular assemblies of greater complexity.

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References

- (1) Lehn, J.-M. *Supramolecular Chemistry, Concepts and Perspectives*; VCH: Weinheim, 1995; pp 89–138.
- (2) Balzani, V.; Gómez-López, M.; Stoddart, J. F. *Molecular Machines*. *Acc. Chem. Res.* **1998**, *31*, 405–414.
- (3) Sauvage, J.-P. *Transition Metal Containing Rotaxanes and Catenanes in Motion: Toward Molecular Machines and Motors*. *Acc. Chem. Res.* **1998**, *31*, 611–619.
- (4) Kelly, T. R.; Bowyer, M. C.; Bhaskar, K. V.; Bebbington, D.; Garcia, A.; Lang, F.; Kim, M. H.; Jette, M. P. *A Molecular Brake*. *J. Am. Chem. Soc.* **1994**, *116*, 3657–3658.
- (5) Clayden, J.; Pink, J. H. *Concerted Rotation in a Tertiary Aromatic Amide: Towards a Simple Molecular Gear*. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1937–1939.
- (6) Kelly, T. R.; Tellitu, I.; Sestelo, J. P. *In Search of Molecular Ratchets*. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1866–1868.

- (7) Franceschi, F.; Solari, E.; Floriani, C.; Rosi, M.; Chiesi-Villa, A.; Rizzoli, C. Molecular Batteries Based on Carbon–Carbon Bond Formation and Cleavage in Titanium and Vanadium Schiff Base Complexes. *Chem. Eur. J.* **1999**, *5*, 708–721.
- (8) Ishow, E.; Credi, A.; Balzani, V.; Spadola, F.; Mandolini, L. A Molecular-Level Plug/Socket System: Electronic Energy Transfer from a Binaphthyl Unit Incorporated into a Crown Ether to an Anthracenyl Unit Linked to an Ammonium Ion. *Chem. Eur. J.* **1999**, *5*, 984–989.
- (9) de Silva, A. P.; Gunaratne, H. Q. N.; McCoy, C. P. A Molecular Photoionic AND Gate Based on Fluorescent Signaling. *Nature* **1993**, *364*, 42–44.
- (10) de Silva, A. P.; Gunaratne, H. Q. N.; Maguire, G. E. M. ‘Off-On’ Fluorescent Sensors for Physiological Levels of Magnesium Ions Based on Photoinduced Electron Transfer (PET), Which Also Behave as Photoionic OR Logic Gates. *Chem. Commun.* **1994**, 1213–1214.
- (11) de Silva, A. P.; Gunaratne, H. Q. N.; McCoy, C. P. Molecular Photoionic AND Logic Gates with Bright Fluorescence and “Off-On” Digital Action. *J. Am. Chem. Soc.* **1997**, *119*, 7891–7892.
- (12) Credi, A.; Balzani, V.; Langford, S. J.; Stoddart, J. F. Logic Operations at the Molecular Level. An XOR Gate Based on a Molecular Machine. *J. Am. Chem. Soc.* **1997**, *119*, 2679–2681.
- (13) Fabbrizzi, L.; Poggi, A. Sensors and Switches from Supramolecular Chemistry. *Chem. Soc. Rev.* **1995**, *24*, 197–202.
- (14) De Santis, G.; Fabbrizzi, L.; Licchelli, M.; Mangano, C.; Sacchi, D. Redox Switching of Anthracene Fluorescence through the Cu^{II}/Cu^I Couple. *Inorg. Chem.* **1995**, *34*, 3581–3582.
- (15) De Santis, G.; Fabbrizzi, L.; Licchelli, M.; Sardone, N.; Velders, A. H. Fluorescence Redox Switching Systems Operating through Metal Centres: the Ni^{III}/Ni^{II} Couple. *Chem. Eur. J.* **1996**, *2*, 1243–1250.
- (16) Bergonzi, R.; Fabbrizzi, L.; Licchelli, M.; Mangano, C. Molecular Switches of Fluorescence Operating through Metal Centred Redox Couples. *Coord. Chem. Rev.* **1998**, *170*, 31–46.
- (17) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*, Ellis Horwood: Chichester, 1991; pp 71–73.
- (18) Suppan, P. *Chemistry and Light*; The Royal Society of Chemistry: Cambridge, 1994; pp 66–68.
- (19) Fabbrizzi, L.; Licchelli, M.; Sacchi, D. Unpublished results.
- (20) Gouille, V.; Harriman, A.; Lehn, J.-M. An Electrophotoswitch: Redox Switching of the Luminescence of a Bipyridine Metal Complex. *J. Chem. Soc., Chem. Commun.* **1993**, 1034–1036.
- (21) Livoreil, A.; Dietrich-Buchecker, C. O.; Sauvage, J.-P. Electrochemically Triggered Swinging of a [2]-Catenate. *J. Am. Chem. Soc.* **1994**, *116*, 9399–9400.
- (22) Fabbrizzi, L.; Gatti, F.; Pallavicini, P.; Zambarbieri, E. Redox Driven Intramolecular Anion Translocation between Transition Metal Centres. *Chem. Eur. J.* **1999**, *5*, 682–690.
- (23) Cabbiness, D. K.; Margerum, D. W. Macrocyclic Effect on the Stability of Copper(II) Tetramine Complexes. *J. Am. Chem. Soc.* **1969**, *91*, 6540–6541.
- (24) Cabbiness, D. K.; Margerum, D. W. Effect of Macrocyclic Structures on the Rate of Formation and Dissociation of Copper(II) Complexes. *J. Am. Chem. Soc.* **1970**, *92*, 2151–2153.
- (25) Fabbrizzi, L. The Stabilization of High Oxidation States of Metals Through Coordination by Poly-aza Macrocycles. *Comments Inorg. Chem.* **1985**, *4*, 33–54.
- (26) De Santis, G.; Fabbrizzi, L.; Iacopino, D.; Pallavicini, P.; Perotti, A.; Poggi, A. Electrochemically Switched Anion Translocation in a Multicomponent Coordination Compound. *Inorg. Chem.* **1997**, *36*, 827–832.
- (27) Reference 1, pp 144–160.
- (28) Gisselbrecht, J.-P.; Gross, M.; Lehn, J.-M.; Sauvage, J.-P.; Ziessel, R.; Piccinni-Leopardi, C.; Arrieta, J. M.; Germain, G.; Meersche, M. V. p-Quaterpyridine Complexes: Crystal Structure of the Mononuclear Cu^{II} Complex. Electrochemical Studies of the Monomeric Cu^{II} and Dimeric Cu^I Complexes, of Their Interconversion, and of the bis-Ru^{II}(bpy)₂ Complex. *Nouv. J. Chem.* **1984**, *8*, 661–667.
- (29) Amendola, V.; Fabbrizzi, L.; Linati, L.; Mangano, C.; Pallavicini, P.; Pedrazzini, V.; Zema, M. Electrochemically Controlled Assembling/Disassembling Processes with a bis-imine bis-quinoline Ligand and the Cu^{II}/Cu^I Couple. *Chem. Eur. J.*, in press.

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