

Molecular Machines Based on Metal Ion Translocation[†]

VALERIA AMENDOLA, LUIGI FABBRIZZI,*
CARLO MANGANO, AND
PIERSANDRO PALLAVICINI

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

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ABSTRACT

Transition metal ions can be moved reversibly between the two coordinatively unequivalent compartments A and B of a ditopic ligand, using as an input the variation of a bulk solution parameter, either pH or redox potential. In a redox-driven translocation, the metal moves reversibly from A to B on cycling between two consecutive oxidation states (e.g., Cu^{II}/Cu^I; Fe^{III}/Fe^{II}) by means of auxiliary oxidation and reduction reactions. In a pH-driven process, one compartment displays also acid–base properties (AH_n ⇌ Aⁿ⁻ + nH⁺), and the Mⁿ⁺ ion is translocated between B and Aⁿ⁻ through consecutive addition of base and acid.

Introduction

Mechanical work can be produced at the molecular level through the controlled motion of a chosen component occurring within a molecular or a supramolecular system. The envisaged system should contain both a *mobile* part and a *stationary* part, and an external operator should be able, by means of a given input, to induce the displacement of the movable part with respect to the immovable one.¹ Most of the investigated systems operate in solution, where the so-called mobile and stationary fragments are

Valeria Amendola was born in Milan in 1974. In 1997, she graduated in chemistry from the University of Pavia. From 1997 to 2000 she worked as a Ph.D. student in the Dipartimento di Chimica Generale, University of Pavia, in the research group of Professor Luigi Fabbrizzi, where she was involved in the study of chemically and electrochemically controlled molecular motions. Presently, she holds a postdoctoral position at the University of Pavia, and continues her research on transition metal-based molecular machines and devices.

Luigi Fabbrizzi was born in Florence in 1946. In 1969, he graduated in chemistry from the University of Florence, where from 1972 to 1980, he was lecturer of inorganic chemistry. Since 1980, he has been Professor of Inorganic Chemistry at 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, and to the design of luminescent molecular sensors for anions and biologically relevant analytes.

Carlo Mangano was born in Pavia in 1965. He graduated in chemistry from the University of Pavia in 1989. In 1994 he received his Ph.D. degree in chemistry from the University of Pavia, under the supervision of Professor Luigi Fabbrizzi. After that he joined the University of Pavia, where is currently Graduated Technical Assistant. His research area covers the synthesis of multicomponent coordination compounds, polytopic ligands, and luminescent molecular sensors.

Piersandro Pallavicini was born in Vigevano in 1962. He graduated in chemistry from the University of Pavia in 1986. In 1990, he received his Ph.D. degree in chemistry from 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, the study of oriented motions at the molecular level, and the control of self-assembling/disassembling processes of transition metal-containing superstructures.

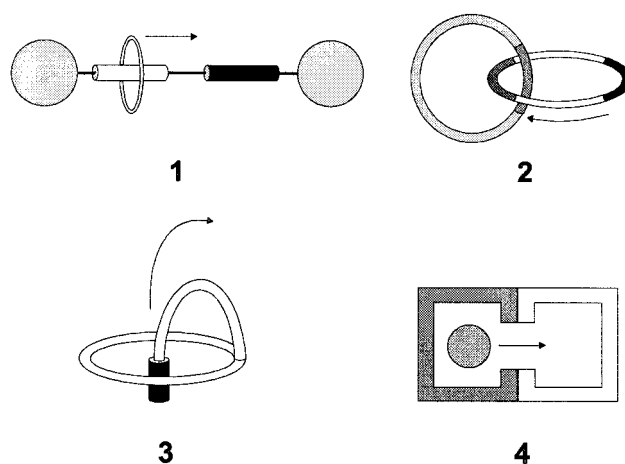


FIGURE 1. Systems containing a mobile part and a stationary part, suitable for carrying out controlled molecular motions: **1**, two-station rotaxanes; **2**, asymmetric 2-catenanes; **3**, rings with an appended movable side chain; **4**, systems in which a particle can move from one compartment to the other. Systems **1–4** convert the energy of an auxiliary reaction (redox or acid–base) into mechanical work and can be therefore considered “molecular machines”.

both in motion; however, one of the fragments (in general the bulkier) is arbitrarily considered motionless, and the other is said to move with respect to it. In solution, the external input promoting the molecular motion can be the variation of a bulk parameter, such as the pH or the redox potential. First examples of controlled molecular motions came from supramolecular chemistry and involved systems in which the mobile and the motionless parts were held together by noncovalent interactions.^{2,3} Some of the investigated systems are roughly sketched and classified in Figure 1.

System **1** is a rotaxane, held together by π -donor–acceptor interactions: in particular, a π -acceptor wheel can be moved between two π -donor segments placed along the axle, by selectively altering their donating properties through an auxiliary reaction of either acid–base or redox nature.² System **2** is a 2-catenane containing two asymmetric coordinating wheels, which can be held together by the metal–ligand interactions with a copper center. The half-turn of a wheel with respect to the other follows the Cu^{II}/Cu^I redox change, which is being induced by auxiliary oxidation and reduction reactions.³ Systems **1** and **2** are quite general, and their dynamic behavior is independent of the type of noncovalent interactions: for instance, a two-station rotaxane of type **1**, based on metal–ligand interactions and still benefiting from the Cu^{II}/Cu^I redox change, has been more recently designed.⁴ On the other hand, molecular motions can be induced in catenanes of type **2**, held together by π -donor–acceptor interactions, through a redox input.^{5,6} Movements in π -systems of both types **1** and **2** are not very complicated from a kinetic point of view and are, in general, fast. On the other hand, systems held together by metal–ligand

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* To whom correspondence should be addressed. E-mail: luigi.fabbrizzi@unipv.it.

interactions may suffer from the kinetic complications arising from the stereochemical modifications associated with the change of the electronic configuration of the metal center, when oxidized or reduced.

A further system suitable for producing controllable molecular motions is illustrated by structure **3** in Figure 1. In this case, a flexible side chain (the movable fragment) is covalently linked to a ring (the stationary part). If the ring is a quadridentate macrocycle and encircles a metal center (e.g., Ni^{II}), the pendant arm, which contains a donor atom at its end (e.g., an amine nitrogen atom), folds to coordinate the metal; however, on acidification, the side chain is protonated and unfolds quickly, due to the repulsive electrostatic interaction between the ammonium group and the Ni²⁺ cation.⁷ On addition of base, the ammonium group is neutralized, and the motion of the pendant arm is reversed. In another version, the ring displays π -acceptor properties, and the side chain contains a terminal π -donor fragment: π -acceptor features can be modified through auxiliary oxidation and reduction processes, which induce fast and reversible threading/dethreading of the side chain into/from the ring.⁸

All of the considered systems contain a movable part, whose motion can be reversibly and repeatedly carried out: they convert energy (that of an auxiliary chemical reaction) into mechanical work and can be therefore considered *machines* operating at the molecular level.^{9,10} Whether the mobile and stationary fragments are held together by noncovalent (π -donor–acceptor, metal–ligand for systems **1** and **2**) or covalent interactions (system **3**), the movability refers in any case to the breaking/making of noncovalent interactions, which explains the generally observed high rate of the molecular motions and justifies the analogy with the machines of the macroscopic world.

However, there exists another way to induce controlled movements at the molecular level, thus converting the energy of a chemical reaction into mechanical work. This can be done by moving a particle (e.g., a monatomic ion) between two distinct sites of a ditopic system, following a predetermined pathway. This new type of molecular machine is sketched in Figure 1 (system **4**). Again, to guarantee fast reversibility, the interaction of the movable particle with either compartment must be noncovalent and labile. Such a feature can be achieved when the particle is a d block metal ion and each compartment is able to establish selective coordinative interactions with it. Examples have been reported in which a 3d metal center is reversibly displaced between two coordinatively unequal compartments of a ditopic ligand, benefiting from an auxiliary reaction of either oxidation–reduction or acid–base nature: these processes are called redox- and pH-driven translocations, respectively.¹¹

Redox-Driven Translocation of a Metal Center

To profit from an auxiliary oxidation and reduction reaction, the movable metal center should possess two consecutive oxidation states of comparable stability (a

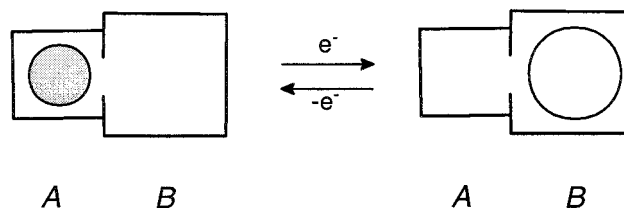
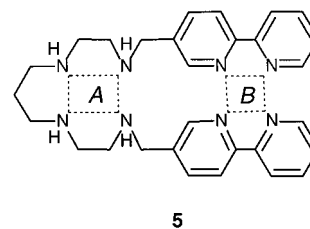


FIGURE 2. Redox-driven translocation of a metal ion. The oxidized cation, $M^{(n+1)+}$ (smaller sphere), has a *hard* nature and likes staying in the *hard* compartment A. The reduced cation, M^{n+} (larger sphere), of *soft* characteristics, prefers to reside in the *soft* compartment B. The metal center can be reversibly translocated between A and B, through the $M^{(n+1)+}/M^{n+}$ redox cycle, coupled to an auxiliary oxidation–reduction process (which can be carried out either chemically or electrochemically).

quite common feature in transition metal chemistry), i.e., M^{n+} and $M^{(n+1)+}$, and the $M^{(n+1)+}/M^{n+}$ change should be reversible, in a chemical sense. On these bases, a ditopic ligand should be designed, in which one compartment (denoted as A in Figure 2) displays a selective affinity toward the oxidized metal center, $M^{(n+1)+}$, whereas the other compartment, denoted as B, shows a higher affinity toward the reduced cation, M^{n+} . On the basis of the oversimplified presumption that the oxidized cation is *hard* and the reduced one is *soft*, the ditopic system should contain a hard (A) compartment and a soft (B) compartment. Thus, the hard cation $M^{(n+1)+}$ stays in the hard compartment A, but when the metal center is reduced to its soft version M^{n+} , it moves to the soft compartment B. Therefore, the metal center can be translocated at will between A and B in a repeatable way, through the $M^{(n+1)+}/M^{n+}$ redox cycle, which can be performed either chemically or electrochemically.

The rate of the process in either direction depends (i) on the intrinsic rate of the electron transfer at the metal center (which is known) and (ii) on the relative easiness of the stereochemical rearrangements, which may be associated with the translocation: in particular, each compartment, following the redox change, has to reorganize in order to offer the metal the most favorable coordinative arrangement; the relevance of this kinetic effect is not easily predictable.

An example which fits well the mechanistic scheme of Figure 2 is provided by the ditopic octadentate ligand **5**.¹²



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The system, which operates through the $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ couple, contains a compartment A, consisting of four secondary amine groups, suitable for the coordination of the *border-line* cation Cu^{2+} (d^9 electronic configuration) and a bis-2,2'-bipyridine compartment (B), which exhibits a pronounced affinity toward the *soft* cation Cu^{I} (d^{10}). The

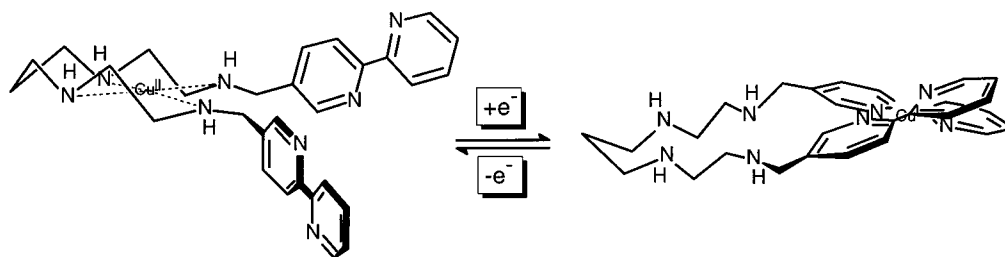


FIGURE 3. Redox-driven translocation of a copper center, based on the $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ change. The Cu^{II} ion stays in the tetraamine compartment of the ditopic ligand **5**, whereas the Cu^{I} ion prefers to occupy the bis(2,2'-bipyridine) compartment. The fast and reversible translocation of the metal between the two compartments can be carried out through auxiliary redox processes (reduction of Cu^{II} with ascorbic acid; oxidation of Cu^{I} with H_2O_2).

ditopic system **5** is flexible enough to fulfill the stereochemical requirements of each metal oxidation state (square coordination for Cu^{II} , tetrahedral for Cu^{I}) without suffering any steric constraint.

The translocation process, illustrated in Figure 3, is fast and reversible and can be followed both visually and spectrophotometrically. As a matter of fact, an MeCN solution containing equimolar amounts of **5** and Cu^{II} is blue-violet (d–d absorption band: $\lambda_{\text{max}} = 548 \text{ nm}$, $\epsilon = 120 \text{ M}^{-1} \text{ cm}^{-1}$), which indicates that the oxidized cation resides in the tetraamine compartment. On addition of a reducing agent (ascorbic acid), the solution takes the brick-red color typically observed with the $[\text{Cu}^{\text{I}}(\text{bpy})_2]^+$ chromophore (bpy = 2,2'-bipyridine; MLCT transition: $\lambda_{\text{max}} = 430 \text{ nm}$, $\epsilon = 1450 \text{ M}^{-1} \text{ cm}^{-1}$), indicating that the $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ reduction process has taken place and that the metal center has translocated fast to the soft (bpy)₂ compartment. On addition of an oxidizing agent (e.g., H_2O_2), the solution takes again its original blue-violet color, indicating that the metal center (as Cu^{II}) has moved back to the tetraamine compartment.

The first example of redox-driven translocation of a metal center was based on a different couple, $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$, and took place in ditopic ligands containing (i) a tris-hydroxamate compartment (suitable for the Fe^{III} cation) and (ii) a (bpy)₃ compartment (which shows an especially high affinity toward Fe^{II} , d⁶ low spin).¹³ One of the investigated systems is sketched in Figure 4. Also in this case, the translocation was driven through auxiliary redox reactions (reduction of Fe^{III} with ascorbic acid, oxidation of Fe^{II} with peroxydisulfate) and could be followed both visually (color change from pale brown, Fe^{III} state, to red-violet, Fe^{II} state) and spectrophotometrically. However, the translocation process was rather slow: it ranged from minutes to hours, depending on the direction and the nature of the ligand's framework, due to some severe steric rearrangements the structurally complex ditopic system had to experience in the course of the metal transfer. Analogous redox-driven translocation processes based on the $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ couple have been more recently described for a three-strand ditopic ligand, whose A compartment contained three salicylamide groups, and whose B compartment consisted of three bpy fragments.¹⁴

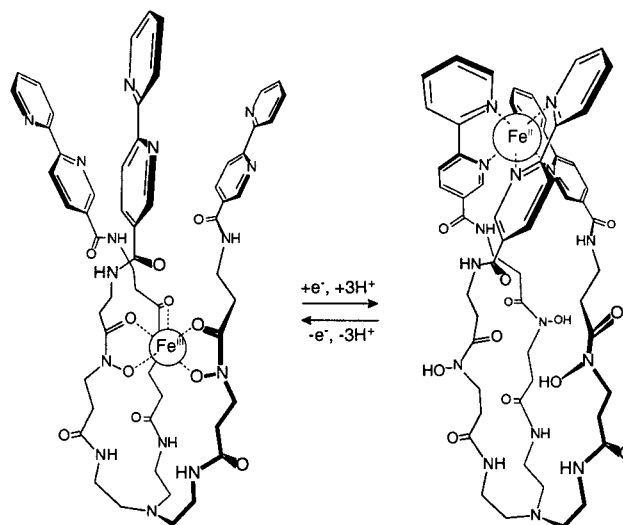


FIGURE 4. Redox-driven translocation of an iron center within a ditopic system containing a *hard* compartment (the tris(hydroxamate) donor set, lower level, which shows a strong affinity for Fe^{III}) and a *soft* compartment (tris(2,2'-bipyridine) donor set, upper level, suitable for the coordination of the low-spin Fe^{II} ion). Reduction of Fe^{III} with ascorbic acid and oxidation of Fe^{II} with $\text{S}_2\text{O}_8^{2-}$ induces the reversible (and slow) metal translocation from one level to the other. Notice that the uptake/release of one electron by the metal center is accompanied by the uptake/release of three hydrogen ions at the three hydroxamate/hydroxamic groups.

pH-Driven Translocation of a Metal Center

Instead of modifying the metal center by changing its oxidation state, one could try to modify, through a given input, the ditopic ligand, or, more precisely, one of its compartments, to induce the translocation of the intact M^{n+} cation. This can be done by designing a compartment (e.g., A), which displays both coordinating tendencies and Brønsted acid–base properties. As an example, the envisaged compartment should be able to exist both in a protonated form, AH_n , and in a fully deprotonated form, A^{n-} , whereas the second compartment, B, should not show any acid–base feature. Then, it should happen that the coordinating tendencies of the varying compartments decrease along the series $\text{A}^{n-} > \text{B} > \text{AH}_n$. Under these circumstances, changing the protonation state of the $\text{AH}_n/\text{A}^{n-}$ compartment will induce metal translocation.

In particular, as illustrated in Figure 5, when the pH-sensitive compartment is in the AH_n form, M^{n+} will stay in B, but when the AH_n acid is deprotonated to give A^{n-} ,

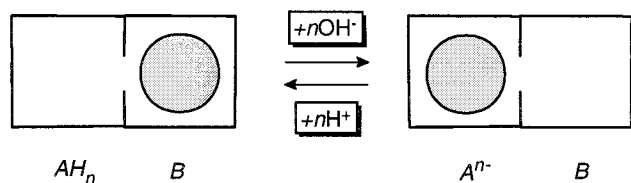
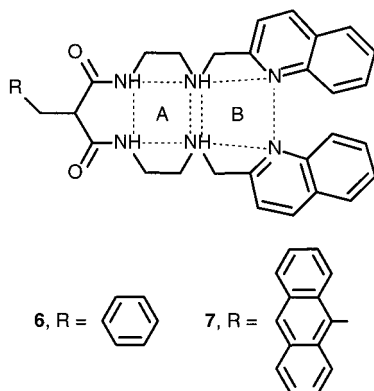


FIGURE 5. pH-driven translocation of a metal ion M^{n+} between the two compartments A and B of a ditopic system. Requirements for metal translocation are the following: (i) compartment A must present also Brønsted acid–base behavior, according to the equilibrium $AH_n \rightleftharpoons A^{n-} + nH^+$; (ii) the affinity sequence toward M^{n+} must decrease along the sequence $A^{n-} > B > AH_n$. Under these circumstances, the displacement of the acid–base equilibrium, achieved through appropriate pH variations, makes M^{n+} translocate reversibly between the two compartments.

M^{n+} will move to the deprotonated compartment. Thus, the auxiliary reactions driving the reversible translocation process are (i) $AH_n + nOH^- \rightleftharpoons A^{n-} + nH_2O$ and (ii) $A^{n-} + nH^+ \rightleftharpoons AH_n$. It will be shown that, in a protic medium, such acid–base reactions can be carried out through moderate pH changes.



An example of pH-driven metal translocation is provided by system **6**, also indicated as LH_2 , in which an AH_2 compartment is present, which consists of two amine groups and two amide groups.¹⁵ Amide nitrogen atoms display very poor or nil coordinating tendencies toward transition metals. Thus, compartment AH_2 is avoided by the metal, which prefers to reside in the more comfortable compartment B, offering two amine groups and two quinoline nitrogen atoms. However, in the presence of divalent metal ions late in the 3d series (e.g., Ni^{II} , Cu^{II}), secondary amide groups, $-(CO)NH$, may deprotonate, giving rise to the strongly donating group $-(CO)N^-$. In this situation, the M^{n+} ion will move to the more appealing A^{2-} compartment.

Some things are especially evident in the case of the Ni^{II} ion. In a solution containing equimolar amounts of **6** and Ni^{II} , adjusted to $pH = 7.5$, the dominating species is the doubly positively charged complex $[Ni^{II}(LH_2)]^{2+}$, which shows a pale violet color and is high spin. This indicates that the Ni^{II} center resides in compartment B, where it exhibits octahedral stereochemistry, with two water molecules completing six coordination. On the other hand, if the pH is brought to ≥ 9 , the neutral species $[Ni^{II}(L)]$ forms at 100%, and the solution shows a bright yellow color (d–d

absorption band: $\lambda_{max} = 450 \text{ nm}$, $\epsilon = 103 \text{ M}^{-1} \text{ cm}^{-1}$). Such spectral features are typical for a square Ni^{II} low-spin complex, when coordinated by a strongly donating quadri-dentate ligand, i.e., compartment A (in its doubly negative form A^{2-}), which offers two deprotonated amide groups and two amine nitrogen atoms. Thus, on increasing the pH from 7.5 to 9.5, the Ni^{II} ion is translocated from compartment B to compartment A (which has become A^{2-}), changing its spin state. On the other hand, when the pH is brought back to 7.5, Ni^{II} leaves compartment A (which becomes AH_2) and moves back to B. The process can be repeated many times without degradation, through alternate addition of a few drops of standard acid and base and is visually perceived through a sharp color change: from pale violet to bright yellow and vice versa. Quite interestingly, the rate of B-to-A translocation is distinctly higher than that of the reverse A-to-B process: lifetimes τ for the two first-order processes are 0.25 ± 0.01 and $2.2 \pm 0.1 \text{ s}$, respectively. The difference in the rates of direct and reverse processes can be explained on the basis of classical arguments of inorganic kinetics.¹⁶ The translocation process in either direction must involve an initial dissociative step. The rate of metal–ligand dissociation can vary significantly with the spin state of the metal center: in particular, high-spin Ni^{II} is labile (which accounts for a fast dissociation from compartment B), whereas low-spin Ni^{II} is relatively inert (which justifies the slower dissociation from compartment A^{2-}).

Equipping the framework of the ditopic ligand with a fluorescent fragment may allow the translocation process to be signaled through a drastic change of the light emission, which is switched on/off depending on the direction of the metal transfer.¹⁵ Such a goal has been achieved with system **7**, in which an anthracene subunit (An) has been covalently linked, through a $-CH_2-$ spacer, to the carbon atom joining the amide groups of compartment A. The behavior in solution of the $Ni^{II}/\mathbf{7}$ system is very similar to that previously described for the $Ni^{II}/\mathbf{6}$ system: at $pH = 7$ the $[Ni^{II}(LH_2)]^{2+}$ species dominates, in which the Ni^{II} center (high spin) is located in compartment B. In this situation, the anthracene fragment displays its full fluorescence. On bringing the pH to ≥ 9 , the Ni^{II} ion moves to the A^{2-} compartment, where it assumes a low-spin configuration, and anthracene fluorescence is completely quenched. The process is sketched in Figure 6. At a first glance, one could ascribe this behavior to a mere distance effect: when in compartment A, the transition metal interferes with the close fluorophore, quenching its emission. Interference vanishes (and fluorescence is restored) when the metal is moved to the more distant compartment B. However, the correct interpretation is more subtle and refers to the mechanism of the quenching process. In particular, it has been observed that the photoexcited anthracene fragment An^* is quenched through a Ni^{II} -to- An^* electron transfer (ET) process.¹⁵

The feasibility of such an ET process can be accounted for on a thermodynamic basis. In particular, the corresponding free energy change, ΔG_{ET}° , can be calculated through the thermodynamic cycle shown in Figure 7, by

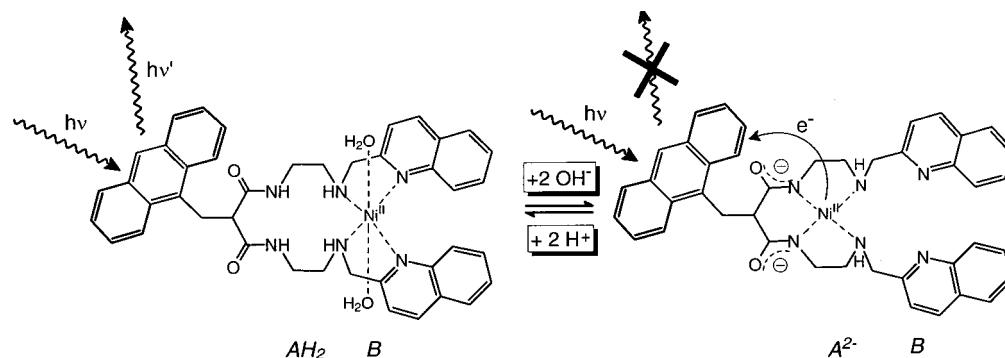


FIGURE 6. pH-driven translocation of the Ni^{II} ion within the ditopic system **7**, which is signaled by quenching/revival of the emission of a fluorescent reporter (the anthracene substituent). When Ni^{II} resides in compartment A²⁻, the emission is fully quenched, due to the occurrence of a metal-to-fluorophore electron transfer (ET) process; when Ni^{II} moves to compartment B, the ET mechanism vanishes and fluorescence is restored.

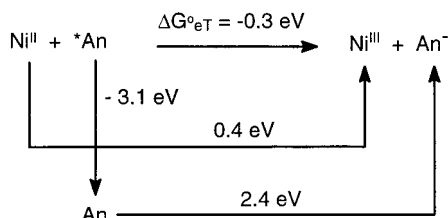


FIGURE 7. Thermodynamic cycle for calculating the $\Delta G^{\circ}_{\text{ET}}$ value associated with the intramolecular electron transfer from the nickel(II) ion to the photoexcited anthracene substituent within system **7**. The process takes place ($\Delta G^{\circ}_{\text{ET}} = -0.3$ eV) when Ni^{II} stays in the A²⁻ compartment, whose donor set favors the oxidation to Ni^{III} (moderately positive value of the Ni^{III}/Ni^{II} electrode potential), but does not take place when Ni^{II} resides in compartment B, due to its scarce tendency to promote metal oxidation (very positive value of the Ni^{III}/Ni^{II} electrode potential).

combining the appropriate photophysical (E^{0-0}) and electrochemical quantities ($FE^{\circ}_{\text{Ni}^{\text{III}}/\text{Ni}^{\text{II}}}$, $FE^{\circ}_{\text{An}/\text{An}^-}$): in particular, $\Delta G^{\circ}_{\text{ET}} = -E^{0-0} + FE^{\circ}_{\text{Ni}^{\text{III}}/\text{Ni}^{\text{II}}} - FE^{\circ}_{\text{An}/\text{An}^-}$. E^{0-0} , the photonic energy of An* (3.1 eV), and $FE^{\circ}_{\text{An}/\text{An}^-}$, the electrode potential associated with the reduction of the anthracene fragment (-2.4 V, $FE^{\circ}_{\text{An}/\text{An}^-} = -2.4$ eV), are common quantities for both [Ni^{II}(L)] and [Ni^{II}(LH₂)]²⁺ complexes. Thus, the key parameter is $E^{\circ}_{\text{Ni}^{\text{III}}/\text{Ni}^{\text{II}}}$, the electrode potential associated with the Ni^{III}/Ni^{II} couple, which expresses the easiness of the access to the Ni^{III} state. Coordination of Ni^{II} by the strongly donating A²⁻ set, in the [Ni^{II}(L)] species, raises the energy of the antibonding level (essentially metal centered) from which the electron is abstracted on oxidation, thus making the attainment of a +3 oxidation state not too difficult and the value of $E^{\circ}_{\text{Ni}^{\text{III}}/\text{Ni}^{\text{II}}}$ (0.4 V, $FE^{\circ}_{\text{Ni}^{\text{III}}/\text{Ni}^{\text{II}}} = 0.4$ eV) not positive enough to balance the favorable contribution of the photonic energy E^{0-0} ; as a consequence, $\Delta G^{\circ}_{\text{ET}}$ is distinctly negative (-0.3 eV), and the ET process is thermodynamically favored.¹⁷ In contrast, the ligand field exerted by compartment B, in the [Ni^{II}(LH₂)]²⁺ complex, is not strong enough to allow an easy attainment of the Ni^{III} state: the $E^{\circ}_{\text{Ni}^{\text{III}}/\text{Ni}^{\text{II}}}$ value is very positive and cannot be compensated by E^{0-0} ; thus, $\Delta G^{\circ}_{\text{ET}} \gg 0$, and the ET process cannot take place. In conclusion, a metal's ability to interfere with the photoexcited fluorophore essentially depends on the more or less pronounced

coordinating tendencies of each compartment, even if a minor contribution due to the distance cannot be excluded.

As far as the rate of the translocation is concerned, for system **7** it is also observed that the B-to-A movement, involving high-spin Ni^{II}, is considerably faster than the reverse process, which refers to low-spin Ni^{II}: τ values for the two first-order processes are 12 ± 1 and 66 ± 12 s, respectively. The unexpected point is that rates in either direction are much lower for system **7**, which bears an anthracenyl substituent, than for system **6**, equipped with the less hindering benzyl group. This behavior has been related to the intimate mechanism of the translocation, which cannot be supposed to occur through the "long jump" of the metal ion from one compartment to the other. Better, it is suggested that the ditopic system, either **6** or **7**, thermally folds like an open book whose spine is represented by the ideal vertical segment connecting the two secondary amine nitrogen atoms. Metal translocation takes place when the two "facing pages" of the book (each containing one compartment) have been brought to an adequately short distance. The presence of a bulky substituent such as the anthracenyl group makes book folding sterically more difficult and raises the energy of the transition state, thus reducing the rate of the overall metal translocation. This feature provides the unique opportunity of controlling by design metal translocation rates in systems such as **6** and **7**, i.e., by appending to the ligand framework substituents of chosen bulkiness.

System Ni^{II}/7 is a dynamic molecular switch of fluorescence which shows some similarity with light switches of everyday life: in fact, the light of a bulb (the anthracene unit) can be turned on/off at will, repeatedly, through a mechanical act (the displacement of a metal ion between two defined positions), which is induced by an external operator.^{18,19}

Conclusions

Systems which can exist in two forms differing in the position of the mobile subunit can give rise to switchable digital states "1" and "0" and may represent the elementary components of a computer operating on the activity

of single molecules. Indeed, Stoddart's redox-active rotaxanes and catenanes (belonging to classes **1** and **2** in Figure 1, and held together by π -donor-acceptor interactions) have been recently assembled in monolayers sandwiched between electrodes, to form logic gates, whose "1" and "0" states can be switched by using an applied voltage,^{20,21} which demonstrates that the design of a "chemical computer" can no longer be considered a dream or an extremely long-term project.²² The utilization of two-state systems containing metal centers, like those described in this Account, has to be explored for the application. Transition metals bring several properties which may be useful from the point of view of the design of switchable systems, of signal generation and information processing, at the molecular level. We have seen that these properties can be drastically modified when the metal is moved between coordinatively nonequivalent compartments, under a variety of stimuli: they include, among the others, (i) change of stereochemistry and of the coordination number, (ii) change of the color and of the optical properties, (iii) variation of the magnetic features, through spin interconversion equilibria, and (iv) the capability of selective intramolecular interaction with proximate light-emitting fragments. It is hoped that transition metals together with the well-established concepts of a more than centenarian discipline—coordination chemistry—will be increasingly utilized for the construction of two-state molecular devices displaying a dynamic activity.

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