Transition metal complexes as molecular machine prototypes

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The field of molecular machines, *i.e.* multicomponent systems able to undergo large amplitude motions under the action of an external signal, has experienced a spectacular development since the beginning of the 1990s. Transition metal complexes have played an important role in this context, often as components of catenanes and rotaxanes. The present *tutorial review* will discuss a few systems of this type, taken from the contributions of our group or from others. The stimulus responsible for the controlled motion of the machine can be chemical, electrochemical, or photochemical. Examples of these three categories will be considered.

1 Introduction

In the course of the last 15 years, a new field has experienced a spectacular development: the elaboration of dynamic molecular systems for which large amplitude motions can be induced and controlled from the outside.[1] In this research area, the molecules, often referred to as "molecular machines", display two or several distinct geometries that can be interconverted into one another in a reversible way by various processes.

The rapid growth of this field can be linked to the discovery and a better understanding of numerous dynamic biological systems (motor proteins) whose controlled motions correspond to important biological functions. Such biological motors have been studied in great detail[2] and, for several of them, it has even been possible to visualize their movement while they are in action.[3] Classical examples are ATP synthase, a rotary motor, the actin–myosin complex of the striated muscle, acting as a linear motor, or the kinesins, essential motor proteins able to "walk" on the microtubules and to transport important molecular components of the cell over large distances.

In the present *tutorial review*, we will focus mostly on transition metal-containing molecular machines, but purely organic systems are equally important. The contributions of

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Benoît Champin

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Pierre Mobian

Pierre Mobian was born in 1976 in Strasbourg and studied Chemistry at the University Louis Pasteur of Strasbourg. After a brief period spent in Cambridge, England, working under the supervision of Jeremy K. M. Sanders, he joined the group led by Dr Jean-Pierre Sauvage in 1999, where he obtained his PhD in 2003 working in the field of light-driven molecular machines. Then, he was a postdoc at the University of Geneva, working with Prof. Lacour on the resolution of organic cations. He is now a postdoctoral fellow in the group of Dr Jean-Pierre Sauvage, working in the field of molecular machines grafted on gold surfaces.

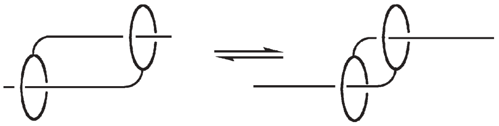


Fig. 1 Gliding of the filaments in a rotaxane dimer: interconversion of the stretched geometry and the contracted conformation.

Balzani, Stoddart, Leigh, Harada and others and their co-workers, using catenanes or rotaxanes, represent real breakthroughs.[4–8] Similarly, the non-interlocking systems proposed by Feringa, Kelly and others are particularly novel and can also be regarded as pioneering contributions.[9,10] The photochemical isomerisation of C=C double bonds is a useful process which has been utilized to set molecular fragments in motion within a given molecule.[11]

The use of transition metal complexes is particularly attractive since metal centres are often electroactive, allowing them to induce rearrangements *via* a metal-localized redox signal, thus circumventing any potential difficulty associated with the generation of organic radicals. In addition, the structure of some transition metal complexes can be profoundly modified by modifying the pH of the medium or by generating a dissociative excited state, thus allowing some parts of the compounds to be set in motion using a chemical signal or a photonic impulse.

It should be noted that the coverage in the present *tutorial review* is by no means exhaustive. We have, rather, selected a few representative examples in the recent literature but our choice is, of course, arbitrary and reflects the scientific interests of our group.

2 Molecular motions triggered by a chemical signal

2.1 Contraction/stretching process of a muscle-like rotaxane dimer[12]

Linear machines and motors are essential in many biological processes such as, in particular, contraction and stretching of the skeletal muscles. In relation to "artificial muscles", one-dimensional molecular assemblies able to undergo stretching and contraction motions thus represent an exciting target.

A multicomponent system able to contract or stretch under the action of an external chemical signal was designed and made in our group a few years ago. The system is based on a symmetrical, doubly-threaded topology as represented in Fig. 1. The motion is easy to visualize: both "strings" (mimicking the myosin-containing thick filament and the actin thin filament of the striated muscle) move along one another but stay together thanks to the rotaxane nature of the system.

The copper-complexed rotaxane dimer $\mathbf{1}^{2+}$ was synthesized (more than 20 steps from commercially available compounds). As shown in Fig. 2, each "filament" contains both a bidentate chelate (coordinated to copper(I) in compound $\mathbf{1}^{2+}$) and a tridentate chelate of the terpy (2,2′:6′,2″-terpyridine) type, which is free in the copper(I) complex $\mathbf{1}^{2+}$. The rotaxane dimer was set in motion by exchanging the complexed metal centres. The free ligand, obtained in quantitative yield by reacting the 4-coordinate copper(I) complex $\mathbf{1}^{2+}$ (stretched geometry) with an excess of KCN, was subsequently re-metalated with $Zn(NO_3)_2$, affording quantitatively the 5-coordinate Zn^{2+} complex $\mathbf{2}^{4+}$ in the contracted situation (Fig. 2). The reverse motion, leading back to the extended situation $\mathbf{1}^{2+}$, could be induced easily upon addition of excess $Cu(CH_3CN)_4{}^+$. From CPK model estimations, the length of the organic backbone changes from 85 to 65 Å between both situations.

2.2 Molecular machines based on metal ion translocation

Molecular machines could also enter the field of molecular recognition by acting as receptors with a useful implemented function: to recognize and bind a substrate only when the proper external stimulus is applied. The molecular machine of Fabbrizzi, Pallavicini *et al.*[13] behaves as such a receptor and merges the advantages of the lock-and-key principle (selectivity) with those of its adaptive behaviour, that is, activation in the presence of substrates. Moreover, a drastic colour

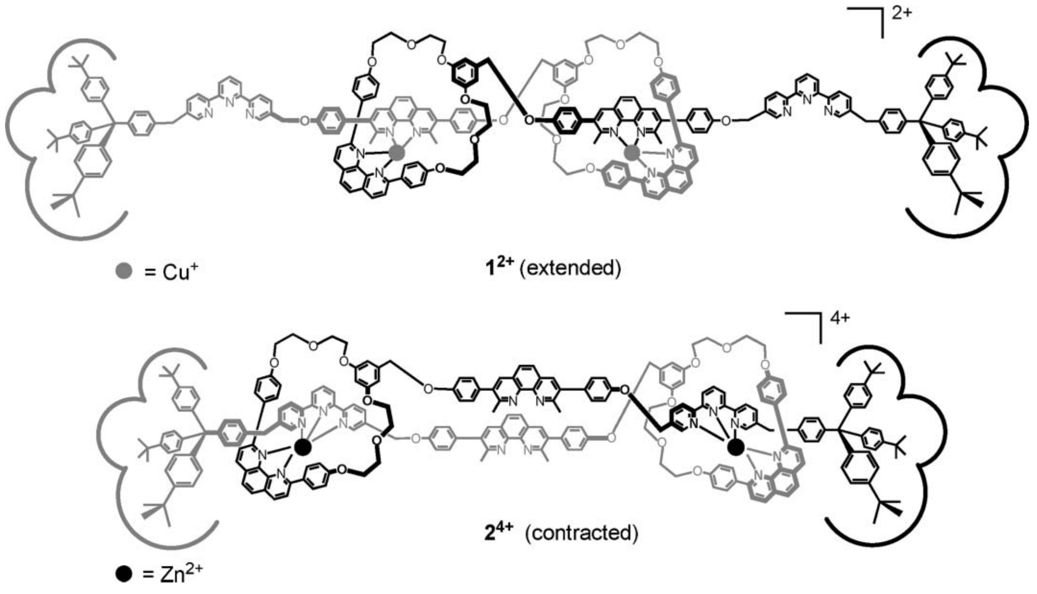


Fig. 2 The two states of the muscle-like molecule.

change associated with movement and recognition events turns this system into a very efficient colorimetric sensor.

Macrocycle LH_4 contains two couples of polydentate compartments capable of binding copper(II) ions and comprises two diamide-diamine tetradentate and two pyridine-diamine (PDA) tridentate binding sets which share the four secondary amino groups.[14] Two distinct colours and types of bands are observed as a function of pH.

At low pH (3–6) the amide groups are protonated, thus they are non-coordinating and the two copper(II) ions are coordinated by the two available separated tridentate PDA units. This form is the complex **4^{4+}**, $[Cu_2(LH_4)]^{4+}$, in which each copper(II) is tricoordinated by the ligand (λ_{max} = 660 nm, deep blue), with the other coordination positions occupied by water.[14]

On raising the pH (6–9) two water molecules are deprotonated to give the blue species $[Cu_2(LH_4)(OH)_2]^{2+}$ and $[Cu_2(LH_4)(OH)]^{3+}$. But if the pH is raised above 10.5 the four amide protons are released and each copper(II) moves inside one of the two deprotonated diamide-diamine moieties to give the neutral complex **3**, $[Cu_2(L)]$ (Fig. 3).[14] This is reflected by a purple-pink solution.

This system was modified into a molecular receptor recognizing specifically the substrate imidazole.

The lock-and-key principle could be achieved in this system with imidazole. In a sharp pH range ($10.0 < pH < 10.4$) and in the absence of imidazole, the $[Cu_2(L)]$ species **3** is predominant in its closed form (95%) whereas in the presence of imidazole, it represents 10% of the mixture and the $[Cu_2(LH_4)(Im^-)]^{3+}$ species **5^{3+}** forms around 90% (Fig. 4). The species contains a bridging imidazolate anion and forms thanks to the particularly stable $[Cu(II)–Im^-–Cu(II)]$ disposition.[14] Therefore, in this system, it is the substrate itself which makes the cations translocate and causes the system to open, thus allowing binding to take place. This recognition is associated with an obvious colour change, thus providing a signal for selective inclusion.

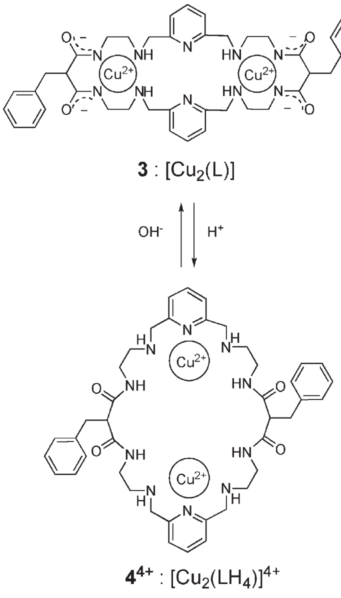


Fig. 3 pH dependent intramolecular translocation of the Cu^{2+} ions.

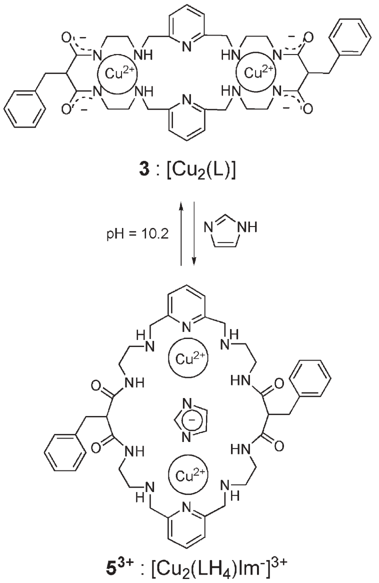


Fig. 4 The imidazole-induced translocation equilibrium at pH 10.2.

It should be noted that many systems not containing transition metals, but where molecular motions are also driven by a chemical reaction, have been reported recently in the literature.[4]

3 Electrochemically controlled molecular motions

3.1 Transition metal-complexed catenanes and rotaxanes

A copper-complexed [2]catenane in motion with three distinct geometries. Multistage systems seem to be uncommon, although they are particularly challenging and promising in relation to nano-devices aimed at important electronic functions and, in particular, information storage.[15] Among the few examples that have been reported in recent years, three-stage catenanes are particularly significant since they lead to unidirectional rotary motors.[7] In the mid-1990s, our group described a particular Cu-complexed [2]catenane which represents an example of such a multistage compound.[16] The molecule displays three distinct geometries, each stage corresponding to a different coordination number of the central complex (CN = 4, 5, or 6). The principle of the three stage electrocontrollable catenane is represented in Fig. 5.

Similarly to the very first and simpler catenane made in our group, for which a large amplitude motion can deliberately be triggered by an external signal,[17] the gliding of the rings in the present system relies on the important differences in stereochemical requirements for coordination of Cu(I) and Cu(II). For the monovalent state the stability sequence is CN = 4 > CN = 5 > CN = 6. On the contrary, divalent Cu is known to form stable hexacoordinate complexes, with pentacoordinate systems being less stable and tetrahedral Cu(II) species being even more strongly disfavoured.

The synthesis of the key catenane $[Cu(I)N_4]^+$ = **6_4^+** (Fig. 6a) (one should notice that, as usual, the subscripts 4, 5 and 6 indicate the coordination number of the copper centre) derives from the usual three-dimensional template strategy.[18]

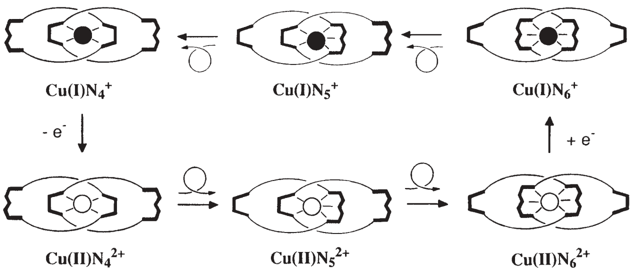
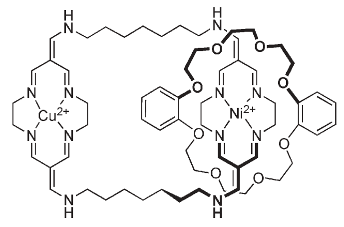


Fig. 5 A three-configuration Cu(I) catenane whose general molecular shape can be modified dramatically by oxidizing the central metal (Cu(I) to Cu(II)) or reducing it back to the monovalent state. Each ring of the [2]catenane incorporates two different coordinating units: the bidentate dpp unit (dpp = 2,9-diphenyl-1,10-phenanthroline) is symbolized by a U whereas the terpy fragment is indicated by a stylized W. Starting from the tetracoordinate monovalent Cu complex (Cu(I)N$_4^+$; top left) and oxidizing it to the divalent state (Cu(II)N$_4^{2+}$), a thermodynamically unstable species is obtained which should first rearrange to the pentacoordinate complex Cu(II)N$_5^{2+}$ by gliding of one ring (left) within the other and, finally, to the hexacoordinate stage Cu(II)N$_6^{2+}$ by rotation of the second cycle (right) within the first one. Cu(II)N$_6^{2+}$ is expected to be the thermodynamically stable divalent complex. The double ring-gliding motion following oxidation of Cu(I)N$_4^+$ can be inverted by reducing Cu(II)N$_6^{2+}$ to the monovalent state (Cu(I)N$_6^+$; top right), as represented on the top line of the figure.



7^{4+}

Fig. 7 Heterodinuclear [2]catenane **7^{4+}**.

The visible spectrum of this deep red complex shows a metal-to-ligand charge transfer (MLCT) absorption band ($\lambda_{\max}$ = 439 nm, ε = 2570 mol^{-1} L cm^{-1}, MeCN). Cyclic voltammetry of a MeCN solution shows a reversible redox process at +0.63 V (*vs.* SCE). Both the CV data and the UV-vis spectrum are similar to those of other related species.[17,18]

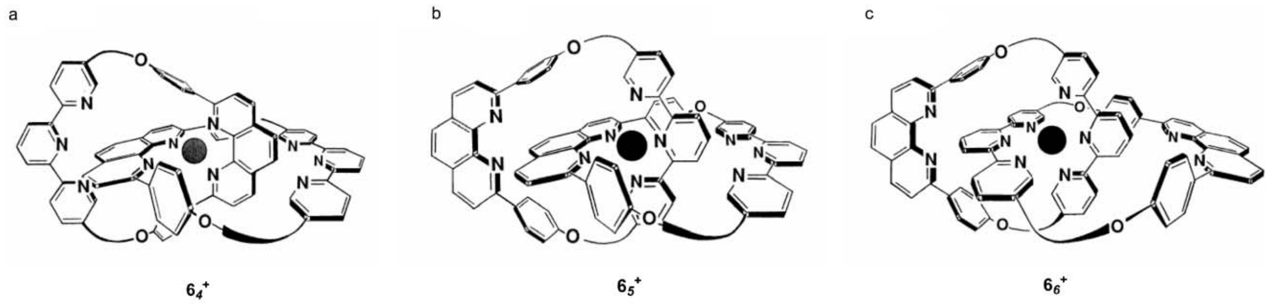
When either the **6$_6^{2+}$** solution resulting from this process or a solution prepared from a sample of isolated solid **6$_6^{2+}$**(BF$_4^-$)$_2$ were electrochemically reduced at −1 V, the tetracoordinate catenane was quantitatively obtained. The cycle depicted in Fig. 5 was thus completed. The changeover process for the monovalent species is faster than the rearrangement of the Cu(II) complexes, as previously observed for the previously reported simpler catenane.[17] In fact, the rate is comparable to the CV time scale and three Cu species are detected when a CV of a MeCN solution of **6$_6^{2+}$**(BF$_4^-$)$_2$ is performed. The waves at +0.63 V and −0.41 V correspond, respectively, to the tetra- and hexacoordinate complexes mentioned above. By analogy with the value found for the previously reported copper-complexed catenane,[17] the wave at −0.05 V is assigned to the pentacoordinate couple (Fig. 6b).

Intramolecular motion within a heterodinuclear bis-macrocycle transition-metal complex. Wozniak and co-workers described recently the first heterodinuclear bis-macrocyclic transition-metal complex **7^{4+}** (Fig. 7) that exhibits potential-driven intramolecular motion of the interlocked crown-ether unit.[19] Although the system contains transition metals, the main interaction between the various subunits, which also allowed the construction of the catenane **7^{4+}**, is an acceptor–donor interaction of the charge transfer type.

The reported heterodinuclear catenane should allow a controlled translocation of the crown-ether unit back and forth between two different metal centres in response to an external stimulus, specifically a potential applied to the electrode (Fig. 8).

The present system can be set in motion using two consecutive redox signals. The main feature of the machine-like catenane is that the preferred conformation will be such that the most electro-deficient transition metal macrocyclic complex will lie in between the two aromatic donor fragments of the crown ether.

The bis-macrocyclic ring is positively charged because of the presence of Ni(II) and Cu(II). The crown ether and the bis-azamacrocyclic ring form a sandwich-like structure in such a way that one of the crown ether aromatic rings is located between the two metal-coordinated macrocyclic rings. The second aromatic ring is located almost parallel to the previous one outside the two linked macrocycles.



Cu(II)/Cu(I): E$_{1/2}$ = +0.63V vs SCE

Cu(II)/Cu(I): E$_{1/2}$ = -0.05V vs SCE

Cu(II)/Cu(I): E$_{1/2}$ = -0.41V vs SCE

Fig. 6 The three forms of the copper-complexed catenane, each species being either a monovalent or a divalent complex. (a) 4-Coordinate complex; (b) 5-coordinate complex; (c) 6-coordinate complex.

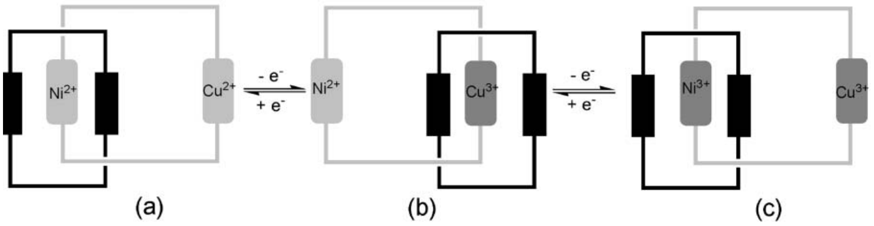


Fig. 8 Schematic representation of electrochemically controlled molecular motion.[19]

As nickel(II) is a better acceptor than copper(II), the situation at the beginning of the process is the one depicted in Fig. 8a. Then, upon oxidation of the molecule, the copper(II) centre turns into copper(III) since oxidation of the nickel(II) centre is more difficult. But, Cu(III) being, of course, a better acceptor than Ni(II), the crown ether relocates from the nickel(II) centre to the copper(III) centre (Fig. 8b). By increasing the potential, the nickel(II) centre is finally oxidized, and the new nickel(III) centre is, as expected, a stronger acceptor than the copper(III) centre. Hence, the crown ether ring moves for the second time, yielding the third situation (Fig. 8c).

A fast-moving electrochemically driven machine based on a pirouetting copper-complexed rotaxane[20]. The rate of the motion in artificial molecular machines and motors is obviously an important factor. Depending on the nature of the movement, it can range from microseconds, as in the case of organic rotaxanes acting as light-driven molecular shuttles,[21] to seconds, minutes or even hours in other systems involving threading–unthreading reactions[22,23] or metal-centred redox processes based on the Cu(II)/Cu(I) couple.[17]

In order to increase the rates of the motions, a new rotaxane in which the metal centre is as accessible as possible was prepared, the ligand set around the copper centre being, thus, sterically little hindering compared to previous related systems. Ligand exchange within the coordination sphere of the metal is thus facilitated as much as possible. The two forms of the new bistable rotaxane, $\mathbf{8_4}^+$ and $\mathbf{8_5}^{2+}$, are depicted in Fig. 9 (as usual, the subscripts 4 and 5 indicate the coordination number of the copper centre). The molecular axis contains a "thin" 2,2′-bipyridine motif, which is less bulky than a 1,10-phenanthroline fragment and thus is expected to spin more readily within the cavity of the ring. In addition, the bipy chelate does not bear substituents in an α-position to the nitrogen atoms. $\mathbf{8_4}^+$ rearranges to the 5-coordinate species $\mathbf{8_5}^{2+}$ after oxidation and *vice versa*. The electrochemically driven motions were studied by cyclic voltammetry (CV).

A lower limit for the rate constant k of the process can be estimated as >500 s^{-1} (or $\tau < 2$ ms, with $\tau = k^{-1}$).

$$\mathbf{8_5}^{+} \xrightarrow{k>500\,\mathrm{s}^{-1}} \mathbf{8_4}^{+}$$

The rearrangement rate for the 4-coordinate Cu(II) complex is smaller than for the monovalent complex. It is nevertheless several orders of magnitude larger than in related catenanes or rotaxanes with more encumbering ligands:

$$\mathbf{8_4}^{2+} \xrightarrow{5\,\mathrm{s}^{-1}} \mathbf{8_5}^{2+}$$

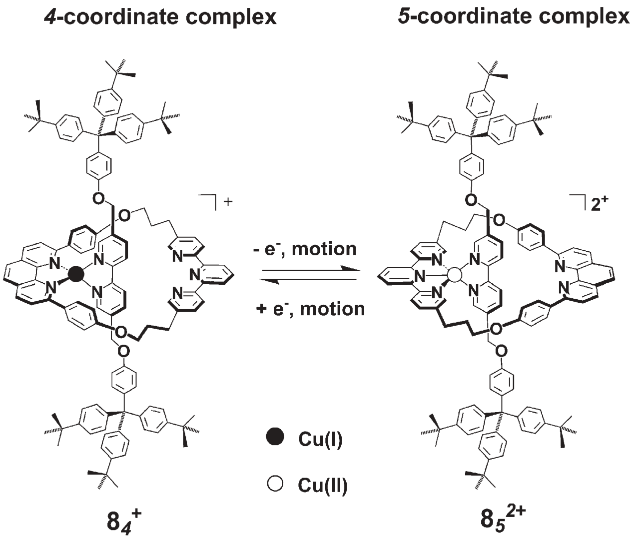


Fig. 9 Electrochemically induced pirouetting of the ring in rotaxane $\mathbf{8}^{n+}$; the bidentate chelate and the tridentate fragment are alternatively coordinated to the copper centre.

This example shows that subtle structural factors can have a very significant influence on the general behaviour (the rate of movement, in particular) of copper(II)/(I)-based molecular machines.

3.2 Other related non-interlocking systems

The first example of redox-driven translocation of a metal centre was based on the couple Fe(III)/Fe(II) and took place in ditopic ligands containing a tris-hydroxamate compartment,[24,25] suitable for the Fe(III) cation, and three bipyridine functions which show a very high affinity towards Fe(II). The translocation was driven through auxiliary redox reactions: reduction of Fe(III) with ascorbic acid and oxidation of Fe(II) with peroxydisulfate. The translocation could be followed both visually and spectrophotometrically (Fig. 10).

A ditopic ligand was designed in which one compartment displays a selective affinity towards the oxidized metal centre $M^{(n+1)+}$ whereas the other compartment shows a higher affinity towards the reduced cation M^{n+}. On the basis of the assumption that the oxidized cation is hard and the reduced one is soft, the ditopic system should contain a hard compartment (A) and a soft compartment (B). Thus, the hard cation stays in the hard compartment. When the metal centre is reduced to its soft version M^{n+}, it moves to the soft compartment B. Therefore, the metal centre can be translocated at

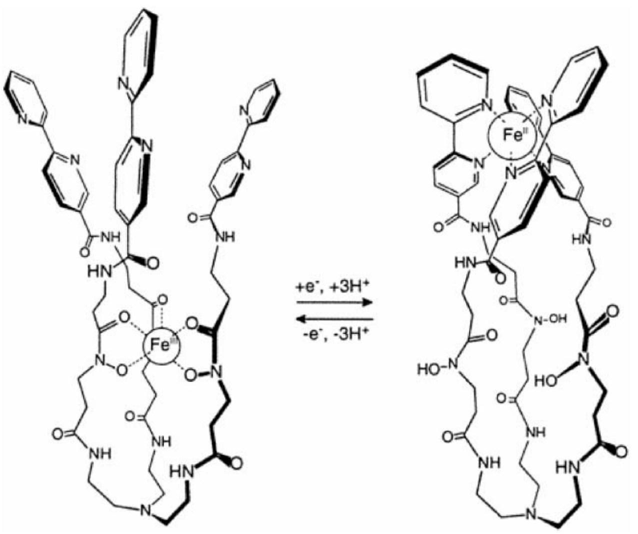


Fig. 10 Redox-driven translocation of an iron centre within a ditopic system containing a hard and a soft compartment.

will between A and B in a repeatable way upon reduction and oxidation of the metal centre in an electrochemical way.

Another example which fits the same mechanistic scheme is provided by the octadentate ligand **9**.[26] The system operates through the Cu(II)/Cu(I) couple. It contains the hard compartment A, consisting of four amine groups, and the soft compartment B, with two 2,2′-bipyridine functions. (Fig. 11)

The translocation process is fast and reversible and can be followed both visually and spectrophotometrically. An MeCN solution containing equimolar amounts of **9** and Cu(II) is blue-violet (d–d absorption band; λ_{max} = 548 nm, ε = 120 M^{-1} cm^{-1}), which indicates that the oxidized cation resides in the tetramine compartment. On addition of a reducing agent (ascorbic acid), the solution takes the brick-red colour typically observed with the [Cu^{I}(bpy)$_2$]$^+$ chromophore (MLCT transition, λ_{max} = 430 nm, ε = 1450 M^{-1} cm^{-1}), indicating that the Cu(II)/Cu(I) reduction process has taken place and that the metal centre has translocated fast to the soft (bpy)$_2$ compartment. On addition of an oxidizing reagent, the solution takes again its original blue-violet colour, indicating that the metal centre (now Cu(II)) has moved back to the tetramine compartment.

4 Light-driven molecular machines

4.1 Photoinduced decoordination and thermal recoordination of a ring in a ruthenium(II)-containing [2]catenane[27]

Our group has recently described multicomponent ruthenium(II) complexes in which one part of the molecule can be set in motion photochemically.[28] Among the light-driven molecular machine prototypes that have been described in the course of the past few years, a very distinct family of dynamic molecular systems takes advantage of the dissociative character of ligand-field states in Ru(diimine)$_3^{2+}$ complexes.[29] In these compounds, one part of the system is set in motion by photochemically expelling a given chelate, the reverse motion being performed simply by heating the product of the photochemical reaction so as to regenerate the original state. In these systems, the light-driven motions are based on the formation of dissociative excited states. Complexes of the [Ru(diimine)$_3$]$^{2+}$ family are particularly well adapted to this approach. If distortion of the coordination octahedron is sufficient to significantly decrease the ligand field, which can be realized by using one or several sterically hindering ligands, the strongly dissociative ligand-field state (^{3}d–d* state) can be efficiently populated from the ^{3}MLCT state to result in expulsion of a given ligand. The principle of the whole process is represented in Fig. 12.

It is thus essential that the ruthenium(II) complexes that are to be used as building blocks of the future machines contain sterically hindering chelates so as to force the coordination sphere of the metal to be distorted from the perfect octahedral geometry.

The [2]catenanes **10^{2+}** and **11^{2+}** were synthesized[30] using an octahedral ruthenium(II) centre as template. Compound **10^{2+}** consists of a 50-membered ring which incorporates two phen units and a 42-membered ring which contains the bipy chelate. Compound **11^{2+}** contains the same bipy-incorporating ring as **10^{2+}**, but the other ring is a 63-membered ring. Clearly, from CPK model considerations, **11^{2+}** is more adapted than **10^{2+}** to molecular motions in which both constitutive rings would move with respect to one another, since the situation is relatively tight for the latter catenane. The light-induced motions and the thermal back reactions carried out with **10^{2+}** or **11^{2+}** are represented in Fig. 13. They are both quantitative, as shown by UV-vis measurements and by ^{1}H NMR spectroscopy.

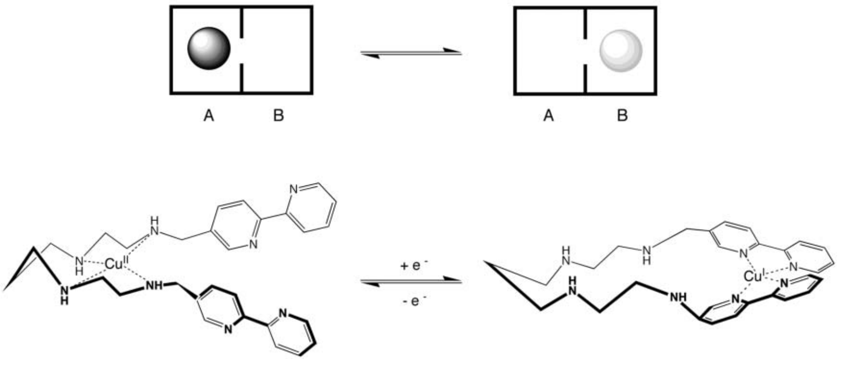


Fig. 11 Redox-driven translocation of a copper centre based on the Cu(II)/Cu(I) change.

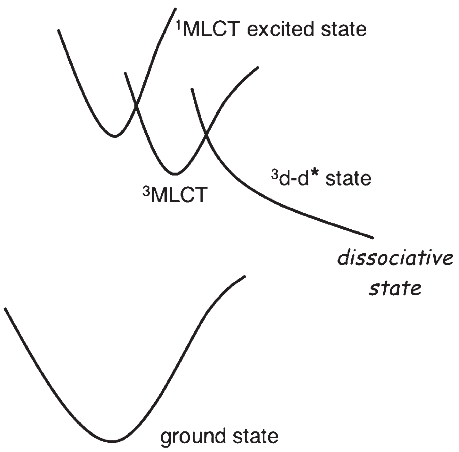


Fig. 12 The ligand-field state ^{3}d–d* can be populated from the ^{3}MLCT state, provided the energy difference between these two states is not too large: formation of this dissociative state leads to dissociation of a ligand.

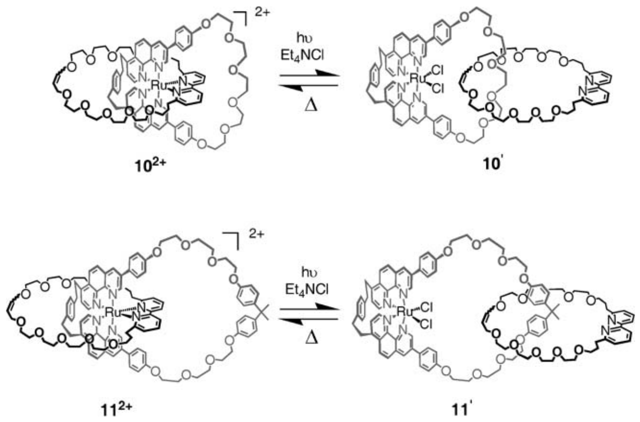


Fig. 13 Catenanes $\mathbf{10^{2+}}$ or $\mathbf{11^{2+}}$ undergo a complete rearrangement on visible light irradiation: the bipy-containing ring is efficiently decoordinated in the presence of Cl^-. By heating the photo-products **10′** or **11′**, the starting complexes $\mathbf{10^{2+}}$ or $\mathbf{11^{2+}}$ are quantitatively regenerated.

The photoproducts, [2]catenanes **10′** and **11′**, contain two disconnected rings since the photochemical reaction leads to decomplexation of the bipy chelate from the ruthenium(II) centre. In a typical reaction, a degassed CH_2Cl_2 solution of $\mathbf{11^{2+}}$ and $NEt_4^+Cl^-$ was irradiated with visible light, at room temperature. The colour of the solution rapidly changed from red ($\mathbf{11^{2+}}$: λ_{max} = 458 nm) to purple (**11′**: λ_{max} = 561 nm) and after a few minutes the reaction was complete. The recoordination reaction **11′** → $\mathbf{11^{2+}}$ was carried out by heating a solution of **11′**. It is hoped that, in the future, an additional tuneable interaction between the two rings of the present catenanes, **10′** or **11′** will allow better control over the geometry of the whole system. In parallel, two-colour machines will be elaborated, for which both motions will be driven by photonic signals operating at different wavelengths.

4.2 A photochemically driven molecular-level abacus

Recently, Credi *et al.* reported[31] the design, synthesis and machine-like performance of a [2]rotaxane, in which the ring component can be induced to move, that is switch between two different recognition sites or "stations" of the dumbbell-shaped component, by light excitation (Fig. 15). Such a molecule exhibits an abacus-like structure and, since it behaves according to binary logic, it could, in principle, be used for information processing at the molecular level.

The design principles at the basis of the light-driven molecular machines developed by this group[32] have been employed to obtain the rotaxane $\mathbf{12^{6+}}$ (Fig. 14),[31] specifically designed to achieve photoinduced ring shuttling.

This compound is made of a π-electron-donating macrocycle as the ring **R**, and a dumbbell-shaped component which contains (i) a $[Ru(bpy)_3]^{2+}$-type complex (**P**) as one of its stoppers, (ii) a 4,4′-bipyridinium unit ($\mathbf{A_1}$) and a 3,3′-dimethyl-4,4′-bipyridinium unit ($\mathbf{A_2}$) as electron-accepting stations, (iii) a *p*-terphenyl-type ring system as a rigid spacer (**S**), and (iv) a tetraarylmethane group as the second stopper (**T**). The stable translational isomer of rotaxane $\mathbf{12^{6+}}$ is the one in which the **R** component encircles the $\mathbf{A_1}$ unit, in keeping with the fact that this station is a better electron-acceptor than the other one.

Two working schemes have been devised for the photoinduced switching of **R** between stations $\mathbf{A_1}$ and $\mathbf{A_2}$: (i) a mechanism based fully on processes which only involve the rotaxane components, that is an intramolecular mechanism, and (ii) a mechanism which requires the help of external reactants, that is a sacrificial mechanism (Fig. 15).

The results obtained[31] have shown that the photochemically driven switching can be performed successfully by the sacrificial mechanism, which is based on the following operations:

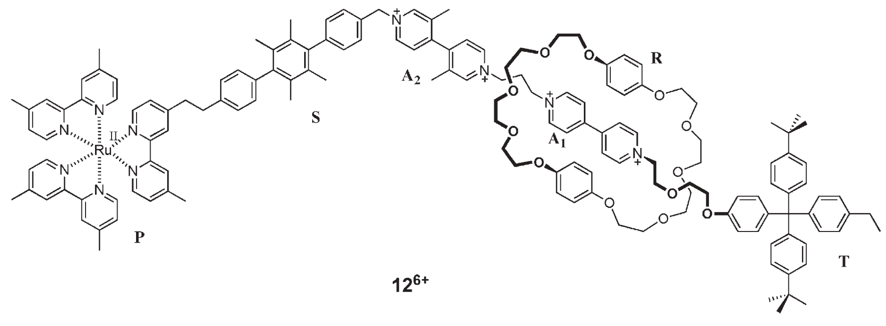


Fig. 14 Chemical structure of rotaxane $\mathbf{12^{6+}}$.

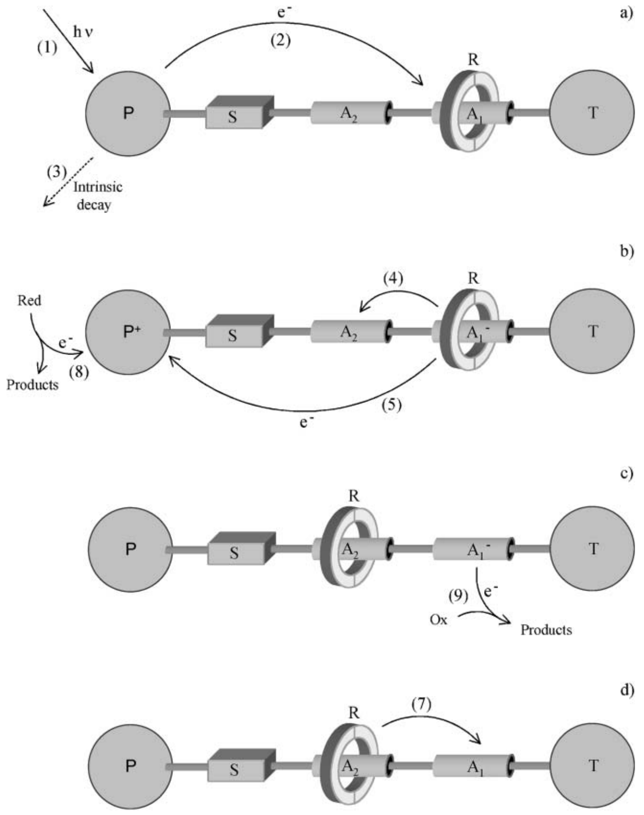


Fig. 15 Working scheme employing a sacrificial mechanism for the light-driven switching of the ring **R** between the two stations $\mathbf{A_1}$ and $\mathbf{A_2}$. The dotted lines indicate processes that compete with those needed to make the machine work: steps (3) and (5).

(a) Destabilization of the stable translational isomer: light excitation of the photoactive unit **P** (step 1) is followed by the transfer of an electron from the excited state to the $\mathbf{A_1}$ station, which is encircled by the ring **R** (step 2), with the consequent ''deactivation'' of this station; such a photoinduced electron-transfer process has to compete with the intrinsic decay of **P*** (step 3).

(b) Ring displacement after scavenging of the oxidized photoactive unit: if the solution contains a suitable reductant, Red (triethanolamine (TEOA), which is a very good scavenger of oxidized Ru–polypyridine complexes), a fast reduction of Red with $\mathbf{P^+}$ (step 8) competes successfully with the back electron transfer reaction (step 5). In such a case, the displacement of the ring to $\mathbf{A_2}$ (step 4), even if it is slow, can take place because the originally occupied station remains in its reduced state $\mathbf{A_1}^-$.

(c) Electronic reset: after an appropriate time, restoration of the electron-acceptor power of the $\mathbf{A_1}$ station can be obtained by oxidizing $\mathbf{A_1}^-$ with a suitable oxidant Ox (dioxygen in that case) (step 9).

(d) Nuclear reset: as a consequence of the electronic reset, back movement of the ring from $\mathbf{A_2}$ to $\mathbf{A_1}$ takes place (step 7).

Many investigations are still being carried out in this field.[33] Such mechanical motions with a ''power stroke'' and a ''recovery stroke'', which are reminiscent of the workings of a simple piston, have also been reported in other systems not containing transition metals.[21]

5 Conclusion and prospective outlook

In this *tutorial review*, we have discussed a few examples of transition metal-containing molecular machines, either of the catenane and rotaxane family or not containing interlocking or threading rings. The input can be electrochemical, and it is thus specific of given transition metal complexes. The systems can be oxidized or reduced at the metal: Cu(II)/Cu(I) or Ni(III)/Ni(II) in the examples discussed here. Alternatively, a photonic stimulus can be used to set the system in motion. Here again, the role of the metal centre is essential since the excited state responsible for the absorption of light is an MLCT excited state but this state is rapidly converted to a dissociative ligand-field (LF) state, which is responsible for the first step of the movement. The third type of stimulus which has been used is chemical. A metal exchange reaction or a recognition reaction allows the shape of a compound to be modified very significantly: stretching–contraction of a rod-like molecule or reorganization of a ring-like compound (similar to inflating or deflating the ring).

It is still not sure whether the field will lead to applications in a short term prospective outlook, although spectacular results have been obtained in the course of the past few years in relation to information storage and processing at the molecular level.[34] Apart from this important field, other applications could of course be envisaged: nanomachines for medical applications such as valves and pumps, molecular devices able to sort molecules, active molecular carriers, able to transport selectively given molecules across a membranes, just to cite a few. Nevertheless, it should be kept in mind that practical applications do not usually arise from where one expects them to come.

From a purely scientific viewpoint, the field of molecular machines is particularly challenging and motivating: the fabrication of dynamic molecular systems, with precisely designed dynamic properties, is still in its infancy and will certainly experience a rapid development during the next decades. Such a research area is highly multidisciplinary and requires a high level of competence in synthetic chemistry as well as in physical and materials sciences, which makes it an excellent school for young and ambitious scientists.

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