Highlight Review

Transition Metal-complexed Catenanes and Rotaxanes as Light-driven Molecular Machines Prototypes

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Abstract

In the course of the last decade, many dynamic molecular systems, for which the movements are controlled from the outside, have been elaborated. These compounds are generally referred to as "molecular machines." Our group has made and studied catenanes and rotaxanes since the early 80s. An important class of molecular machines is based on these interlocking or threaded ring compounds. Although a "molecular muscle" is briefly discussed in the present review article, we mostly focus on light-driven machines, consisting of ruthenium(II)-complexed rotaxanes or catenanes. The synthetic approach is based on the template effect of an octahedral ruthenium(II) centres. Two 1,10-phenanthroline ligands are incorporated in an axis or in a ring, affording the precursor to the rotaxane or the catenane, respectively. $Ru(diimine)_3{}^{2+}$ complexes display the universally used ^{3}MLCT (metal-to-ligand charge transfer) excited state and, another interesting excited state, the ^{3}LF (ligand field) state, which is strongly dissociative. In the past, the ^{3}LF state has mostly been considered as detrimental and thus, its reactivity has not been frequently utilised. By taking advantage of this latter state, it has been possible to propose a new family of molecular machines, which are set in motion by populating the dissociative ^{3}LF state, thus leading to ligand exchange in the coordination sphere of the ruthenium(II) centre.

◆ Introduction

Molecules are dynamic species in solution and even in the solid state. Processes such as nitrogen inversion in amines or rotation about a C–C bond in biphenyl derivatives have been studied for decades and are now in all the organic chemistry textbooks. Very different and much more recent is the elaboration and the study of compounds for which the motions can be triggered and controlled at will by sending an external signal to the molecular system. The molecules then behave like "molecular machines" or, at least, their prototypes. This field has experienced a spectacular development in the course of the last decade and books or special issues of chemistry journals have even been devoted to this new area of research.[1]

The field of catenanes and rotaxanes[2–4] is particularly important in relation to molecular machines. Promising systems have been proposed which are based on redox reactions involving, in particular, formation or dissociation of organic acceptor-donor complexes[5] or of transition metal complexes.[6] Protonation/deprotonation, leading to dissociation and/or formation of given subcomplexes within a multicomponent structure[7] is also an interesting possibility to induce a motion within a multicomponent molecule. Among the many examples of molecular machines reported in the course of the last decade, several examples of light-driven machines have been described.[8,9] Some of them contain a photoisomerizable group such as an azo benzene derivative. The light impulse converts the trans-isomer to the cis isomer, leading to a significant change of the geometry of the photochemically active group and thus strongly modifying its ability to interact with a given part of the molecular system. As a consequence, a rearrangement may occur.[9] Photoinduced electron transfer has also been used to set molecular systems in motion. Our group has been particularly interested in copper and, more recently, ruthenium(II)-containing interlocking or threaded ring systems.[10–13] The compounds can be set in motion using either an electrochemical signal, a chemical reaction or a photochemical process.

The present review article will be mostly focused on photochemically induced motions in ruthenium(II) catenanes and rotaxanes, although, in the first example which we will discuss the molecule is set in motion by performing a chemical reaction. We think that this first example is particularly illustrative of the general field of artificial molecular machines.

◆ Use of a Chemical Reaction to Induce the Contraction/Stretching Process of a Muscle-like Rotaxane Dimer[14]

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 represented thus 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 Figure 1. The motion is easy to visualize: both "strings" (mimicking the myosin-containing thick filament and the actin thin filament of the

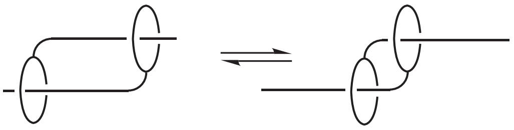

Figure 1. Gliding of the filaments in a rotaxane dimer: interconvertion of the stretched geometry and the contracted conformation.

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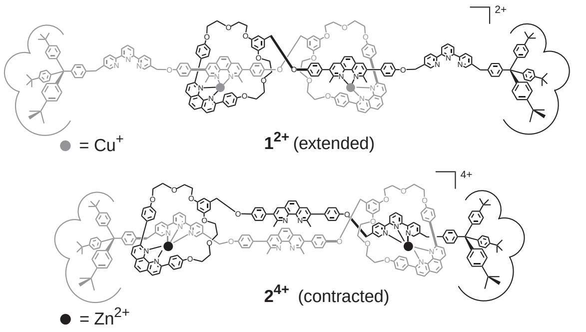

Figure 2. The two states of the muscle-like molecule.

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 Figure 2, each "filament" contains both a bidentate chelate (coordinated to copper(I) in compound $\mathbf{1}^{2+}$) and a tridentate chelate of the terpy 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 remetalated with $Zn(NO_3)_2$ affording quantitatively the 5-coordinate Zn^{2+} complex $\mathbf{2}^{4+}$ in the contracted situation (Figure 2). The reverse motion, leading back to the extended situation $\mathbf{1}^{2+}$, could be easily induced 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.

Use of Dissociative Excited States to Set Ru(II)-complexed Molecular Machines in Motion: Principle

Our group has recently described multicomponent ruthenium(II) complexes in which one part of the molecule can be set in motion photochemically.[15] Among the light-driven molecular machine prototypes which have been described in the course of the last 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.[16] 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 metal-to-ligand charge transfer (^{3}MLCT) state to result in expulsion of a given ligand. The principle of the whole process is represented in Figure 3.

It is thus essential that the ruthenium(II) complexes which 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. We will discuss the synthesis of a rotaxane and a catenane of this family and briefly describe the photochemical reactivity of these molecules. The complexes made and studied incorporate encumbering ligands, which will indeed facilitate the light-induced motions.

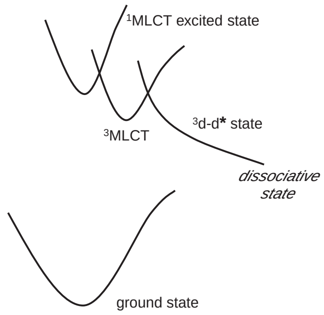

Figure 3. The ligand-field state ^{3}d–d* can be populated from the ^{3}MLCT state, provided the energy difference betweeen these two states is not too large: formation of this dissociative state leads to dissociation of a ligand.

Templated Synthesis of a Pseudo-rotaxane with a $[Ru(diimine)_3]^2$ Core[11] and Its Light-driven Unthreading Reaction

A rotaxane containing a ruthenium bis-phen complex (phen: 1,10-phenanthroline), acting as an axis, and a macrocycle incorporating a 2,2′-bipyridine (bipy) unit, threaded by the axis, has been synthesized. It was recently reported that a $[Ru(diimine)_2]^{2+}$ moiety can be inscribed in an axial compound by appropriate substitution of the diimine.[17] Subsequently, the $[Ru(diimine)_2]^{2+}$-containing axial fragment has also been incorporated in a pseudo-rotaxane and even in a complete rotaxane, the threaded ring being also coordinated to the ruthenium(II) center through a diimine chelate unit.

The synthetic strategy consists of a threading step (the axial component is threaded through the ring) followed by a stoppering reaction (a bulky substituent is attached at each end of the axis). The threading reaction was first tested on a model whose axis is end-functionalized by two unreactive chemical groups (ether functionalities; see Figure 4). Complex $\mathbf{3}$-$(PF_6)_2$ is a yellow solid that is formed quantitatively from its dichloro precursor (purple complex) by replacing the Cl^- ligands by CH_3CN in H_2O/CH_3CN. The macrocyclic compound **4**, which incorporates a 2,2′-bipyridine ligand substituted at its 6- and 6′-positions by alkyl groups, and a dimethyldi(*p*-alkoxyphenyl)methane fragment derived from "bisphenol A," has been obtained by reaction of the suitable dibromo precursor (6,6′-di[2-(2-bromoethoxy)ethoxypropyl]-2,2′-bipyridine) with the "bisphenol A" in 45% yield.

Compound **4** has a 35-membered ring, and CPK models indicate that its size should be sufficient to allow the threading reaction outlined in Figure 4, although the rotaxane-like molecule obtained should be tight, with contacts between the "bisphenol A" motif of the ring and the $–CH_2–CH_2–C_6H_4–CH_2–CH_2–$ fragment of the axial component. This steric hindrance may in part explain the poor yield of the reaction: $\mathbf{3}^{2+}$ and **4** react in ethylene glycol to afford a 20 to 25% yield of a mixture of complexes

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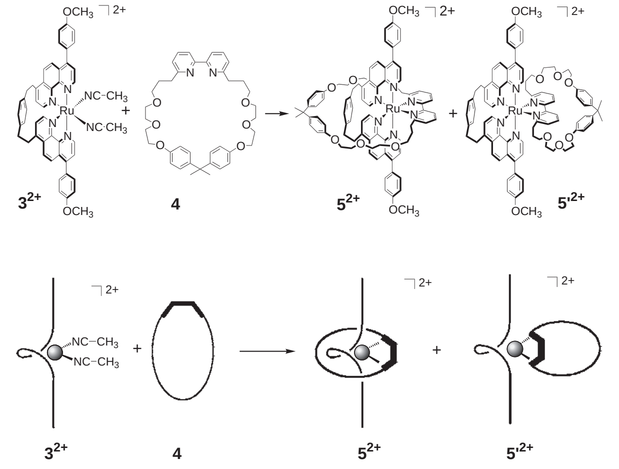

Figure 4. Synthesis of the pseudo-rotaxane $\mathbf{5}^{2+}$ and its exo-isomer $\mathbf{5}'^{2+}$.

containing $\mathbf{5}^{2+}$ and $\mathbf{5}'^{2+}$ (orange solid) after chromatography (Figure 4).

This mixture displays only one round-shaped spot on a thin layer chromatography, making the separation of these two complexes extremely difficult. By comparison, $\mathbf{3}^{2+}$ reacts with the acyclic ligand 6,6′-dimethyl-2,2′-bipyridine (6,6′-dmbp) to afford the corresponding complex in quantitative yield, under reaction conditions similar to those used for preparing $\mathbf{5}^{2+}$.

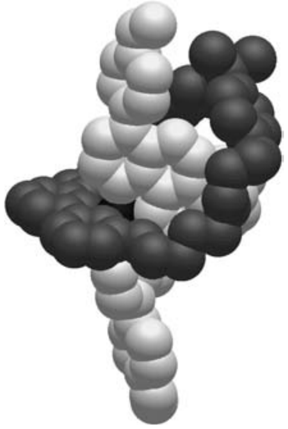

Figure 5. X-ray structure of the Ru(II)-complexed pseudorotaxane.

Single crystals of **5**-$(PF_6)_2$ could be obtained by slow diffusion of hexane in a solution of the complex in acetone, and an X-ray structure was obtained. As shown in Figure 5, $\mathbf{5}^{2+}$ is indeed a threaded species with a helical axis, the bis-phen ligand being wrapped around the metal center in a way similar to that recently observed with non-rotaxane like species.[17] The metal center is octahedrally coordinated, with little distortion. The Ru–N distances and N–Ru–N angles have the expected values (Ru–N distance: 2.055–2.068 Å for the phen ligands and Ru–N distance: 2.12–2.13 Å for the bipy part). The most striking feature of the structure is the distortion of the ring from planarity. Clearly, the ring is too small to accommodate "comfortably" the relatively thick axle and it can not run around the $–CH_2–CH_2–C_6H_4–CH_2–CH_2–$ part of the helical axis. The folded conformation of the macrocyclic component of $\mathbf{5}^{2+}$ results in a nonsymmetrical situation for which the "upper" and the "lower" parts of the rotaxane become nonequivalent in the solid state and in solution at low temperature, as evidenced by the ^{1}H NMR study. The very congested situation in $\mathbf{5}^{2+}$, as evidenced by the X-ray structure tends to explain why the preparative yield is poor. The presence of a certain proportion of the nonthreaded species (Figure 4) is also understood: the "unnatural" conformation of the ring in this species may be unfavorable but this destabilization energy is compensated by that introduced by the steric repulsion between the ring and the thread in the pseudorotaxane $\mathbf{5}^{2+}$. As expected, visible light irradiation of a solution of the $\mathbf{5}^{2+} + \mathbf{5}'^{2+}$ mixture in acetonitrile leads quantitatively to the dethreading products $\mathbf{3}^{2+}$ and **4** ($\lambda > 400$ nm). The photochemical reaction can easily be monitored by UV–vis spectroscopy. The mixture of isomeric complexes has an absorption spectrum characteristic of $[Ru(diimine)_3]^{2+}$ complexes, with a metal-to-ligand charge-transfer (MLCT) absorption band centered at 461 nm. Under irradiation, this band is gradually replaced by the MLCT band of $\mathbf{3}^{2+}$ ($\lambda_{max} = 404$ nm). Isosbestic points are observed at 355 and 424 nm as shown in Figure 6.

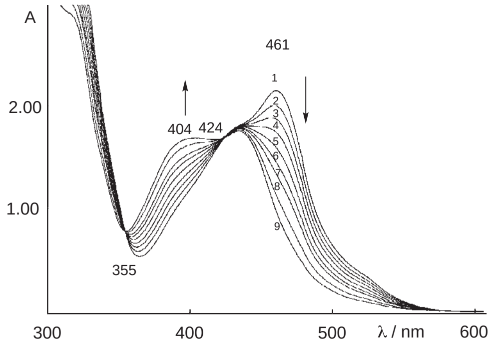

Figure 6. Electronic absorption spectra in CH_3CN of the mixture of $\mathbf{5}^{2+}$ and $\mathbf{5}'^{2+}$ before (1) and after different irradiation times (2: t = 20 s; 3: t = 40 s; 4: t = 60 s; 5: t = 90 s; 6: t = 120 s; 7: t = 150 s; 8: t = 210 s; 9: t = 300 s).

The synthesis of the full rotaxane, containing two large stoppers, was subsequently carried out. Nevertheless, the poor yield of threaded compound and our failure to separate the threaded complex from its non threaded isomer precluded any further study. Recent work has been performed[18] which shows that, by controlling in a better way the geometry of the ring, in particular by synthesizing a rigid analogue of **4**, it is possible to obtain an endo-complex (threaded structure) exclusively. These new complexes are obviously much more promising as light-driven molecular machines than the compounds derived from the small and flexible ring **4**.

◆ *Construction of a [2]Catenane Around a Ru(diimine)$_3^{2+}$ Complex Used as a Template*[13]

The design of the system and the synthetic strategy are depicted in Figure 7. The main point of the design is the observation that it should be possible to incorporate two bidentate chelates of the octahedron in a ring and subsequently to thread a fragment containing the third chelate through the ring. This second process would of course be driven by coordination to the central metal.

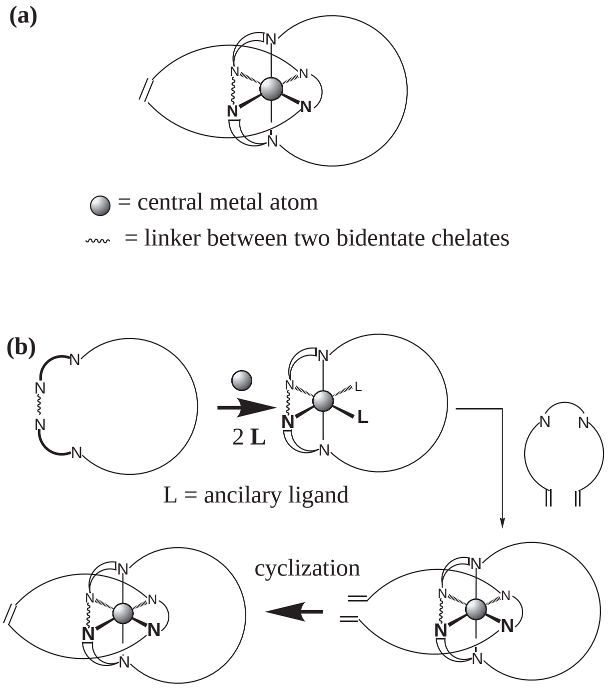

Figure 7. (a) Schematic representation of a transition metal-complexed [2]catenane containing two different rings. One of the macrocycles incorporates a bidentate chelate, whereas the other contains two bidentate coordinating fragments with a cis arrangement. (b) Synthetic strategy.

Tetradentate ligands consisting of two separate bidentate ligands connected by an appropriate spacer and leading to C_2-symmetric complexes have already been reported. A particular interesting example is that of von Zelewsky's chiragens,[19] consisting of two chiral bipy derivatives. Our group has also proposed a bis-phen molecule leading to a $Ru(phen)_3^{2+}$-derivative with a clearly identified axis bearing chemical functions.[17] The substitution positions on the phen nuclei attached to the functions to be used for further derivatization are different than those corresponding to the previous axis-containing complex, as shown in Figure 8. They seem to be appropriate to the formation of cyclic complexes.

The synthetic procedure starts with the preparation of a large ring incorporating two phen units. The choice of the ring was dictated by CPK models and by synthesis considerations. The precursors and the open-chain and cyclic compounds incorporating two phen fragments are represented on Figure 9.

6 was prepared in four steps from 3-bromo-8-amino-1,10-phenanthroline. It is a 50-membered ring which, on CPK models, looks adapted to the formation of octahedral bis-phen complexes, the two phen fragments being disposed cis to one another in the metal coordination sphere. Interestingly, the substitution positions of the *p*-alkoxyphenyl groups (8 and 8′ in **6**) are determining. By contrast, if *p*-anisyl groups are introduced para to the *N*-atoms of the phen nuclei (positions 7 and 7′), wrapping the corresponding ligand around an octahedron leads to a system with a clearly identified axis.[17] A key step is the coordination reaction, supposed to lead to the cyclic complex (Figure 8b). Several first-row transition metals were tested, leading to limited success. However, ruthenium(II) afforded the desired complex.

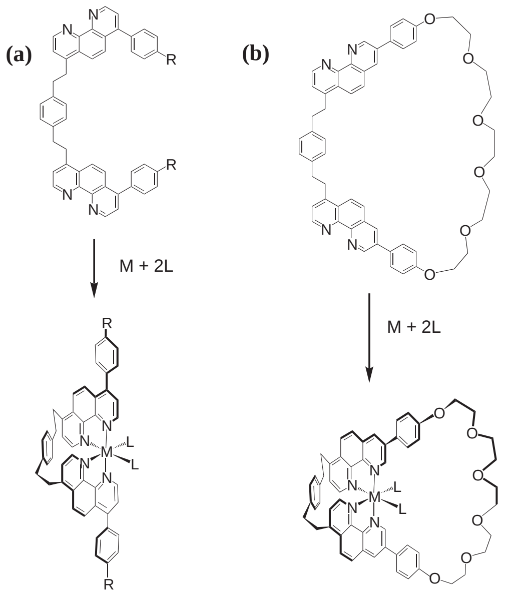

Figure 8. Formation of an axial (**a**) or a macrocyclic (**b**) complex. In both cases, connection of two positions para to the N atoms of the phen nuclei by the $–CH_2CH_2–C_6H_4–CH_2CH_2–$ bridge leads to a cis arrangement. Introduction of aromatic groups ($–C_6H_4–R$) on the other para positions leads to the axial complex (**a**), whereas the macrocyclic complex (**b**) can be obtained by utilizing the meta positions (C8) to attach the $–C_6H_4–R$ aromatic groups.

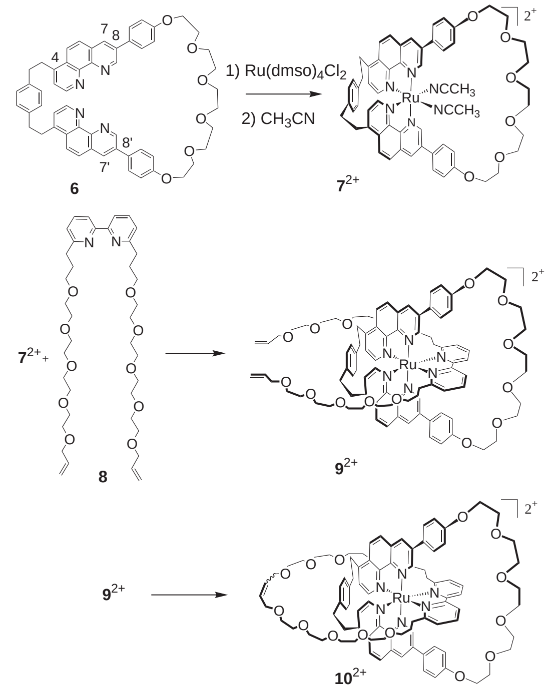

Figure 9. Synthesis of the ruthenium(II)-complexed [2]catenane $\mathbf{10}^{2+}$.

Complex $\mathbf{7}^{2+}$ was formed by reacting **6** and $Ru(DMSO)_4Cl_2$, followed by refluxing the dichloro intermediate complex in $CH_3CN–H_2O$. $\mathbf{7}^{2+}–(PF_6)_2$ was obtained as an orange solid in 21% yield, after anion exchange. $\mathbf{7}^{2+}$ is a rare example of a bis-phen or, more generally, a bis-bidentate octahedral complex with a cis-arrangement, inscribed in a ring. The next step was carried using **8** and the macrocyclic complex $\mathbf{7}^{2+}$. Threading of the "filament" **8** does take place under relatively harsh conditions (ethylene glycol: 140 °C) and the catenane precursor $\mathbf{9}^{2+}$ was obtained in good yield (56%). The final compound, catenane $\mathbf{10}^{2+}$, was prepared from $\mathbf{9}^{2+}$ in 68% yield by ring closing metathesis (RCM). The synthetic procedure used and the yield obtained were similar to those corresponding to the preparation of other transition-metal containing catenanes and knots using a related RCM-based approach.[20] $\mathbf{10}^{2+}$–$(PF_6)_2$ is a red-orange solid which has been fully characterized by various spectroscopic techniques. The ESMS and ^{1}H NMR spectra afford clear evidence for the structure of $\mathbf{10}^{2+}$.

Photoinduced Decoordination and Thermal Recoordination of a Ring in a Ruthenium(II)-containing [2]catenane[12]

The [2]catenanes $\mathbf{10}^{2+}$ was synthesized as described in the previous paragraph. The other [2]catenane of Figure 10, $\mathbf{11}^{2+}$, was prepared using a slightly different procedure. Compound $\mathbf{10}^{2+}$ consists of a 50-membered ring which incorporates two phen units and a 42-membered ring which contains the bipy chelate. Compound $\mathbf{11}^{2+}$ contains the same bipy-incorporating ring as $\mathbf{10}^{2+}$, but the other ring is a 63-membered ring. Clearly, from CPK model considerations, $\mathbf{11}^{2+}$ is more adapted than $\mathbf{10}^{2+}$ 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 motion and the thermal back reaction carried out with $\mathbf{10}^{2+}$ or $\mathbf{11}^{2+}$ are represented in Figure 10. They are both quantitative, as shown by UV–vis measurements and by ^{1}H NMR spectroscopy.

The photoproducts, [2]catenanes $\mathbf{10}'$ and $\mathbf{11}'$, 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 ($\mathbf{11}^{2+}$: $\lambda_{max} = 458$ nm) to purple ($\mathbf{11}'$: $\lambda_{max} = 561$ nm) and after a few minutes the reaction was complete. The recoordination reaction $\mathbf{11}' \rightarrow \mathbf{11}^{2+}$ was carried out by heating a solution of $\mathbf{11}'$. The quantum yield for the photochemical reaction $\mathbf{11}^{2+} \rightarrow \mathbf{11}'$ at 25 °C and $\lambda = 470$ nm (±50 nm) can be very roughly estimated as 0.014 ± 0.005. One of the weak points of the present system is certainly the limited control over the shape of the photoproduct since the decoordinated ring can occupy several positions. It is hoped that, in the future, an additional tuneable interaction between the two rings of the present catenanes, $\mathbf{10}'$ or $\mathbf{11}'$ 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.

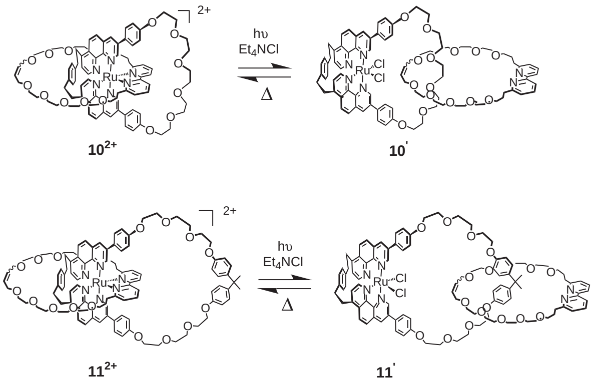

Figure 10. Catenanes $\mathbf{10}^{2+}$ or $\mathbf{11}^{2+}$ undergo a complete rearrangement by visible light irradiation: the bipy-containing ring is efficiently decoordinated in the presence of Cl^-. By heating the photo-products $\mathbf{10}'$ or $\mathbf{11}'$, the starting complexes $\mathbf{10}^{2+}$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

Conclusion and Prospective

The most important motivations of the researchers involved in the field of artificial molecular machines and motors, to many groups including ours, is certainly the synthetic challenge that the elaboration of such systems represents. It is indeed very challenging to reproduce some of the simplest functions of the natural biological motors (motor proteins, DNA polymerase, bacterial flagella, etc.) using synthetic molecular systems. It must nevertheless be kept in mind that the presently accessible molecular machines and motors are extremely primitive compared to the beautiful and exceedingly complex molecular machines of nature.

As far as practical applications are concerned, several possibilities can be explored, although technological applications are probably not for tomorrow. Information storage and processing at the molecular level is for the moment the most popular field of applications since the spectacular reports of Heath, Stoddart, and their co-workers.[21] Other ambitious and futuristic practical outcomes could be considered such as the fabrication of "micro-robots" or even "nanorobots" able to perform various functions: transport molecules or ions through a membrane, sort different molecules, store energy, just to cite a few. In medicinal chemistry, it is conceivable that such devices carry a given drug to a specific target where it is needed, open or close a gate or a valve which controls delivery of a drug from a micro-device, act as a nano-syringe able to inject a given molecule inside a cell, among the many functions that nano-mechanical devices should be able to fulfil in the future.

More specifically, **light-driven** machines are especially attractive to construct nanoscopic devices. The use of a photonic signal will allow ultra fast communication with the molecular system. In addition, interfacing of a molecule with light does not seem to be a problem, contrary to electrochemically-driven systems which require, most of the time, electrodes, either at the macroscopic level or at the nanoscopic one if single molecules are to be used.

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