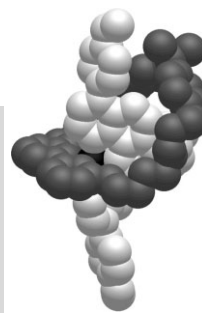


DOI: 10.1002/adma.200502394

Transition-Metal-Complexed Molecular Machine Prototypes**

By Sylvestre Bonnet, Jean-Paul Collin,* Masatoshi Koizumi, Pierre Mobian, and Jean-Pierre Sauvage*



In the course of the last decade, many dynamic molecular systems, whose movements are controlled externally, have been elaborated. These compounds are generally referred to as “molecular machines”. Transition-metal-containing catenanes and rotaxanes are ideally suited to build such systems. In the present article, we will discuss a few examples of molecular machines elaborated and studied in Strasbourg. In the first section, we will discuss an electrochemically driven system consisting of a fast-moving pirouetting rotaxane. The second section will be devoted to a linear rotaxane dimer whose behavior is reminiscent of muscle movement, in the sense that it can stretch and contract. In the rest of this article, the focus will be mostly on light-driven machines consisting of ruthenium(II)-complexed rotaxanes, catenanes, and scorpionates. In the case of rotaxanes and catenanes, the synthetic approach is based on the template effect of an octahedral ruthenium(II) center. Two polydentate ligands are incorporated in an axis or in a ring, affording the precursor to the rotaxane or the catenane, respectively. $Ru(diimine)_3^{2+}$ and $Ru(terpy)(phen)(L)^{2+}$ (terpy: terpyridine; phen: 1,10-phenanthroline) complexes display the universally used 3MLCT (metal-to-ligand charge transfer) excited state and another interesting excited state, the 3LF (ligand field) state, which is strongly dissociative. 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 3LF state, thus leading to ligand exchange in the coordination sphere of the ruthenium(II) center.

1. Introduction

Molecules are dynamic species in solution and even in the solid state. Processes such as the chair/boat equilibrium of cyclohexane, the nitrogen inversion in amines, and the rotation about a C–C bond in biphenyl derivatives have been studied for decades and now appear in organic chemistry textbooks. Very different and much more recent is the elaboration and the study of compounds whose motions can be triggered and controlled at will by sending an external signal to the molecu-

lar 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, with books and special issues of chemistry journals being devoted to this new area of research.^[1]

Rotaxanes and catenanes^[2–4] are particularly important in relation to molecular machines. Promising systems have been proposed that 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 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 azobenzene derivative. The light impulse converts the trans isomer to the cis isomer, leading to a significant change in 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] Pho-

[*] Dr. J.-P. Collin, Dr. J.-P. Sauvage, Dr. S. Bonnet, Dr. M. Koizumi, Dr. P. Mobian
Laboratoire de Chimie Organo-Minérale, UMR 7513 du CNRS
Institut Le Bel, Université Louis Pasteur
4 rue Blaise Pascal, 67000 Strasbourg Cedex (France)
E-mail: jpcollin@chimie.u-strasbg.fr; sauvage@chimie.u-strasbg.fr

[**] We thank all the very talented and enthusiastic researchers who participated in the work discussed in the present progress report. Their names appear in the references. We also thank the CNRS and the European Commission for their constant financial support. S. B. acknowledges the Région Alsace for financial support.

toinduced 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.

2. Results

2.1. A Fast-Moving Electrochemically Driven Machine Based on a Pirouetting Copper-Complexed Rotaxane

The rate of motion in artificial molecular machines and motors is an important factor. Depending on the nature of the

movement, the time required for motion can range from microseconds, as in the case of organic rotaxanes acting as light-driven molecular shuttles,^[8d] to seconds or even minutes in other systems involving threading–unthreading reactions^[8f,g] or metal-centered redox processes based on the Cu^{II}/Cu^I couple.^[6]

In order to increase the rate of motion, a new rotaxane, in which the metal center is made as accessible as possible, was prepared; the ligand set around the copper center was thus of little sterical hindrance 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, **1**₄⁺ and **1**₅²⁺, are depicted in Figure 1^[14] (the subscripts 4 and 5 indicate the coordination number of the copper center). The molecular axis contains a “thin” 2,2′-



Sylvestre Bonnet was born in 1976 in Chartres. His undergraduate studies were in Physical Chemistry at the Ecole Normale Supérieure of Lyon, and he graduated in Transition Metal Chemistry and Molecular Engineering from the University Louis Pasteur in Strasbourg. His Master's Degree and Ph.D., which were conducted under the supervision of Dr. Jean-Pierre Sauvage and Dr. Jean-Paul Collin, were both devoted to molecular machines. Since his graduation in 2005, he has held a postdoctoral position in the laboratory of Prof. Gerard van Koten at the University of Utrecht.



Masatoshi Koizumi was born in Nagano, Japan, in 1973. He completed his M.Sc. degree in 1999 and Ph.D. in 2002 at Nagoya University working on asymmetric hydrogenation under the supervision of Prof. R. Noyori. He then worked as a postdoctoral fellow (JSPS) in the field of molecular machines with Dr. Jean-Pierre Sauvage at Université Louis Pasteur in Strasbourg until 2004. He is currently an ERATO (JST) researcher in the group of Prof. S. Kobayashi at the University of Tokyo.



Pierre Mobian was born in 1976 in Strasbourg and studied Chemistry at the Université Louis Pasteur. 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 Strasbourg in 1999, where he obtained his Ph.D. in 2003 working on the field of light-driven molecular machines. He was a postdoc at the University of Geneva working with Jerome Lacour on the resolution of organic cations. He is now a postdoctoral fellow in the group of Dr. Jean-Pierre Sauvage.

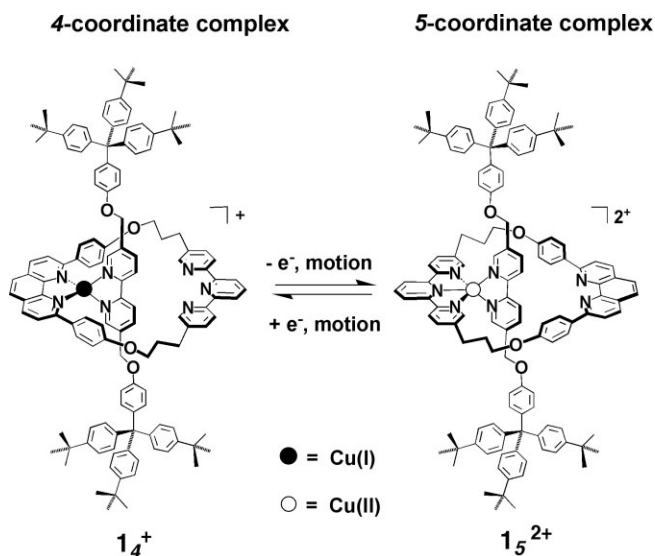


Figure 1. Electrochemically induced pirouetting of the ring in rotaxane 1^{4+} ; the bidentate chelate and the tridentate fragment are alternatively coordinated to the copper center. Adapted with permission from [14]. Copyright 2004, the Royal Society of Chemistry.

bipyridine (bipy) motif, which is less bulky than a 1,10-phenanthroline (phen) 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 the α -position to the nitrogen atoms. 1_4^{4+} rearranges to the five-coordinate species 1_5^{2+} after oxidation and vice versa. The electrochemically driven motions were studied by cyclic voltammetry (CV). The lower limit for the rate constant, k , of the process can be estimated to be 500 s^{-1} or $\tau < 2 \text{ ms}$ (where $\tau = k^{-1}$).



The rearrangement rate of the four-coordinate Cu^{II} complex is lower than that of the monovalent complex. It is, nevertheless, several orders of magnitude larger than in related catenanes or rotaxanes with more encumbering ligands:



This first example shows that subtle structural factors can have a very significant influence on the general behavior (rate of movement, in particular) of $(\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}})$ -based molecular machines. Further modifications will certainly lead to new systems with even shorter response times.

2.2. Use of a Chemical Reaction to Induce the Contraction/Stretching Process of a Musclelike Rotaxane Dimer

Linear machines and motors are essential in many biological processes such as, in particular, contraction and stretching of skeletal muscles. With respect to “artificial muscles”, there-

fore, one-dimensional molecular assemblies that are able to undergo stretching and contraction 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.^[15] The system is based on a symmetrical doubly threaded topology, as represented in Figure 2. 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 each another but stay together as a result of the rotaxane nature of the system.

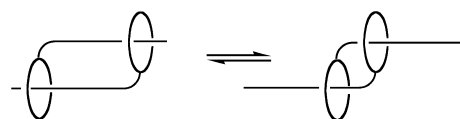


Figure 2. Gliding of the filaments in a rotaxane dimer: interconversion between the stretched and contracted conformations. Reproduced from [15a].

The copper-complexed rotaxane dimer 2^{2+} was synthesized (this required more than 20 steps starting from commercially available compounds). As shown in Figure 3, each “filament” contains both a bidentate chelate (coordinated to copper(I) in compound 2^{2+}) and a tridentate chelate of the terpyridine (terpy) type, which is free in the copper(I) complex 2^{2+} . The rotaxane dimer was set in motion by exchanging the complexed metal centers. The free ligand, obtained in quantitative yield by reacting the four-coordinate copper(I) complex 2^{2+} (stretched geometry) with an excess of KCN, was subsequently remetalated with $\text{Zn}(\text{NO}_3)_2$, affording quantitatively the five-coordinate Zn^{2+} complex, 3^{4+} , in the contracted conformation (Fig. 3). The reverse motion, leading back to the extended conformation 2^{2+} , could be easily induced upon addition of excess $\text{Cu}(\text{CH}_3\text{CN})_4^{+}$. From Corey–Pauling–Koltun (CPK) model estimations, the length of the organic backbone changes from 85 to 65 Å in moving from the contracted to the extended conformation.

2.3. 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.^[16] Among the light-driven molecular-machine prototypes that 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 $\text{Ru}(\text{diimine})_3^{2+}$ complexes.^[17] 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

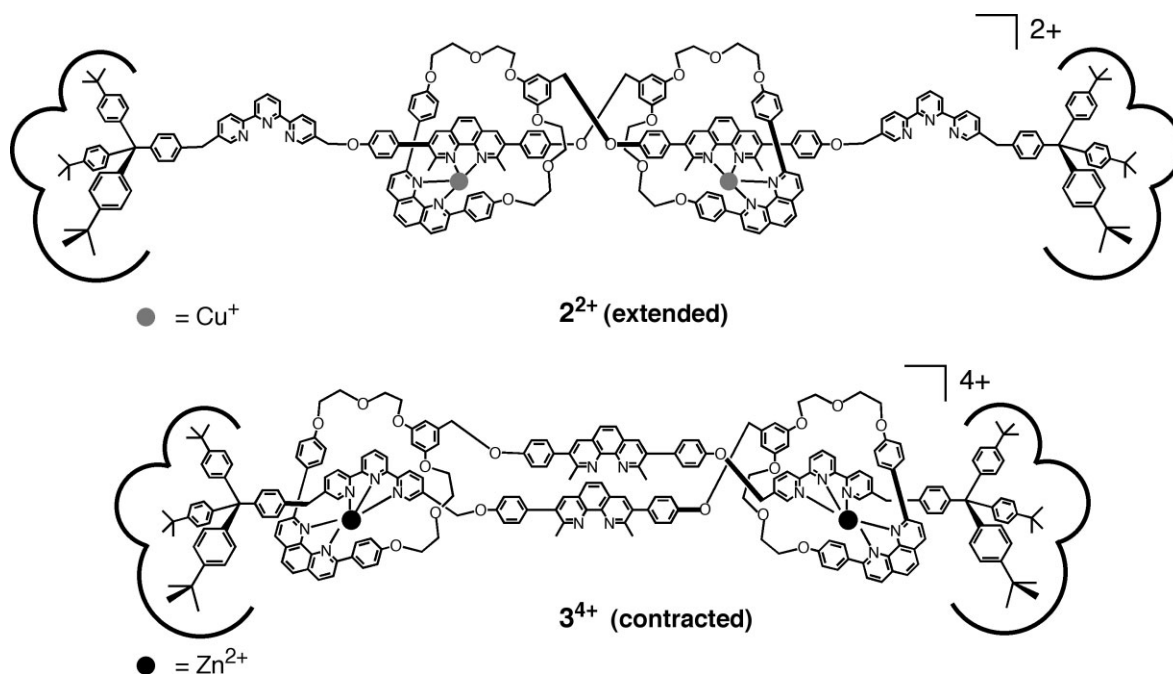


Figure 3. The two states of the musclelike molecule. Reproduced from [15a].

these systems, the light-driven motions are based on the formation of dissociative excited states. Complexes of the $[\text{Ru}(\text{diimine})_3]^{2+}$ 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 ($^3\text{d-d}^*$ state) can be efficiently populated from the metal-to-ligand charge transfer ($^3\text{MLCT}$) state to result in expulsion of a given ligand. The principle of the whole process is represented in Figure 4.

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

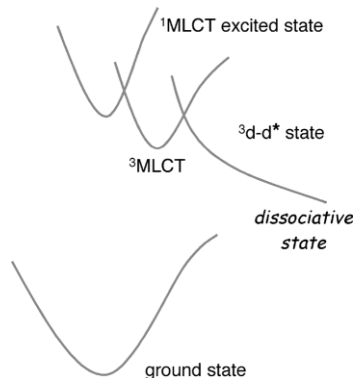


Figure 4. The ligand-field state $^3\text{d-d}^*$ can be thermally populated from the photoinduced $^3\text{MLCT}$ state, provided the energy difference between these two states is not too large: formation of this dissociative state leads to dissociation of a ligand. Reproduced from [12].

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.

2.4. Templated Synthesis of a Pseudorotaxane with a $[\text{Ru}(\text{diimine})_3]^{2+}$ Core and its Light-Driven Unthreading Reaction

A rotaxane containing a ruthenium bis-phen complex acting as an axis and a macrocycle incorporating a bipy unit threaded by the axis has been synthesized. It was recently reported that a $[\text{Ru}(\text{diimine})_2]^{2+}$ moiety can be inscribed in an axial compound by appropriate substitution of the diimine.^[18] Subsequently, the $[\text{Ru}(\text{diimine})_2]^{2+}$ -containing axial fragment has also been incorporated in a pseudorotaxane^[11] and even in a complete rotaxane,^[19] 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 to each end of the axis). The threading reaction was first tested on a model whose axis was end-functionalized by two unreactive chemical groups (ether functionalities; see Fig. 5). Complex **4**-(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 $\text{H}_2\text{O}/\text{CH}_3\text{CN}$. The macrocyclic compound **5**, which incorporates a bipy ligand substituted at its 6- and 6'-positions

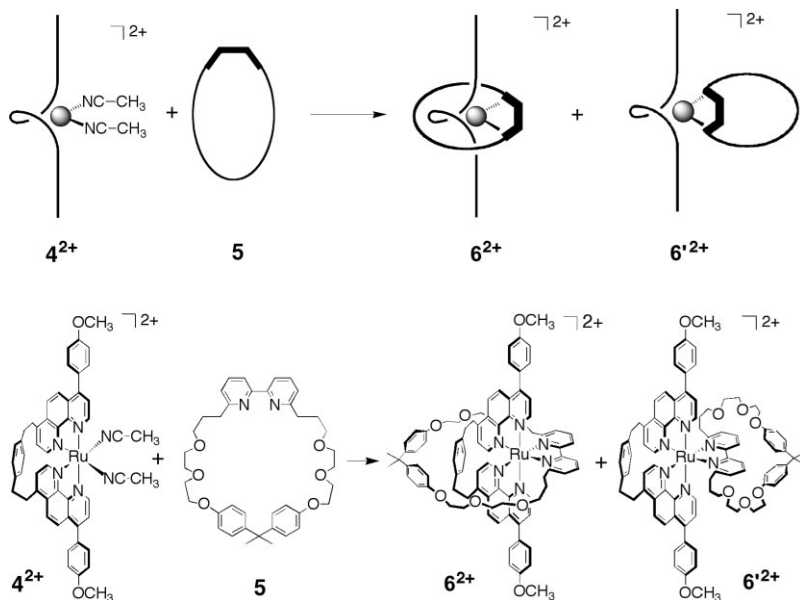


Figure 5. Synthesis of the pseudorotaxane 6^{2+} and its exo-isomer $6'^{2+}$. Reproduced from [11b].

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 “bis-phenol A” in a 45 % yield. Compound **5** has a 35-membered ring, and CPK models indicate that its size should be sufficient to allow the threading reaction outlined in Figure 5, although the rotaxanelike molecule obtained should be tight, with contacts between the “bisphenol A” motif of the ring and the $-\text{CH}_2-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2-\text{CH}_2-$ fragment of the axial component. This steric hindrance may in part explain the poor yield of the reaction: 4^{2+} and **5** react in ethylene glycol (140 °C, 4 h; stoichiometric; concentration of the reactants: 0.01 mol L^{-1}) to afford a 20–25 % yield of a mixture of complexes containing 6^{2+} and $6'^{2+}$ (orange solid) after chromatography (Fig. 5). This mixture displays only one circular spot in thin-layer chromatography, making the separation of these two complexes extremely difficult. By comparison, 4^{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 6^{2+} .

Single crystals of $6-(\text{PF}_6)_2$ could be obtained by slow diffusion of hexane in a solution of the complex in acetone, and an X-ray crystal structure was obtained. As shown in Figure 6, 6^{2+} is indeed a threaded species with a helical axis, the bisphen ligand being wrapped around the metal center in a way similar to that recently observed in non-rotaxanelike 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 2.12–2.13 Å for the bipy ligands). The most striking feature of the structure is the deviation of the ring from planarity. Clearly, the ring is too small to accommodate “com-

fortably” the relatively thick axle and it can not run around the $-\text{CH}_2-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2-\text{CH}_2-$ part of the helical axis. The folded conformation of the macrocyclic component of 6^{2+} results in a non-symmetrical situation for which the “upper” and the “lower” parts of the rotaxane become non-equivalent in the solid state and in solution at low temperature, as evidenced by an ^1H NMR study. The very congested situation in 6^{2+} , as evidenced by the X-ray crystal structure, tends to explain why the preparative yield is poor. The presence of a certain proportion of the nonthreaded species (Fig. 5) 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 6^{2+} . As expected, visible-light irradiation of a solution of the $6^{2+} + 6'^{2+}$ mixture in acetonitrile leads quantitatively to the dethreading products 4^{2+} and **5** (wavelength, $\lambda > 400 \text{ nm}$). The photochemical reaction can easily be monitored by UV-vis spectroscopy. The mixture of isomeric complexes has an absorption spectrum characteristic of $[\text{Ru}(\text{diimine})_3]^{2+}$ complexes, with an MLCT absorption band centered at 461 nm. Upon irradiation, this band is gradually replaced by the MLCT band of 4^{2+} ($\lambda_{\text{max}} = 404 \text{ nm}$). Isosbestic points are observed at 355 and 424 nm, as shown in Figure 7.

The synthesis of the full rotaxane, containing two large stoppers, was subsequently carried out. Nevertheless, the poor yield of the threaded compound and our failure to separate the threaded complex from its nonthreaded isomer precluded any further study. Recent work has been performed^[19] which shows that, by controlling the geometry of the ring in a better way (in particular by synthesizing a rigid analogue of **5**) it is

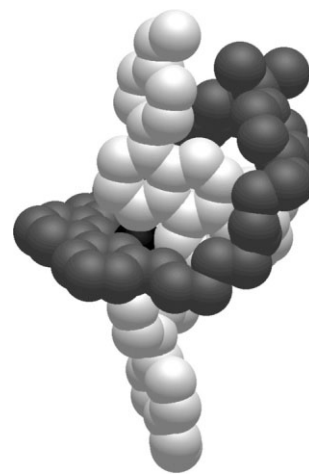


Figure 6. X-ray structure of the Ru^{II} -complexed pseudorotaxane 6^{2+} . Reproduced from [11b].

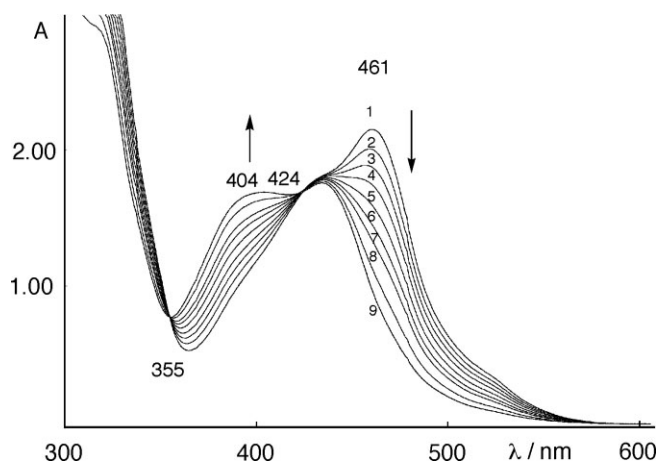


Figure 7. Electronic absorption spectra in CH_3CN of the mixture of 6^{2+} and $6'^{2+}$ before (1) and after different irradiation times (t) (2: $t=20$ s; 3: $t=40$ s; 4: $t=60$ s; 5: $t=90$ s; 6: $t=120$ s; 7: $t=150$ s; 8: $t=210$ s; 9: $t=300$ s). Reproduced from [11b].

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 **5**.

2.5. Construction of a [2]Catenane Around a $\text{Ru}(\text{diimine})_3^{2+}$ Complex Used as a Template

The design of the system and the synthetic strategy are depicted in Figure 8.^[13] 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.

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 particularly interesting example is that of von Zelewsky and co-workers' chiragens,^[20] consisting of two chiral bipy derivatives. Our group has also proposed a bis-phen molecule leading to a $\text{Ru}(\text{phen})_3^{2+}$ derivative with a clearly identified axis bearing chemical functions.^[18] The substitution positions on the phen nuclei attached to the functions to be used for further derivatization are different from those corresponding to the previous axis-contain-

ing complex, as shown in Figure 9. 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 presented in Figure 10.

7 was prepared from 3-bromo-8-amino-1,10-phenanthroline in four steps. It is a 50-membered ring which, from the CPK models, seems to be adapted to the formation of octahedral bis-phen complexes, with the two phen fragments being arranged in a cis configuration relative to each other in the metal coordination sphere. Interestingly, the substitution positions of the *p*-alkoxyphenyl groups (8 and 8' in **7**) are determining for positioning the *p*-anisyl groups in the right direction. By contrast, if *p*-anisyl groups are introduced in a position 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, which is supposed to lead to the cyclic complex (Fig. 8b). Several first-row transition metals were tested, leading to limited success. However, ruthenium(II) afforded the desired complex.

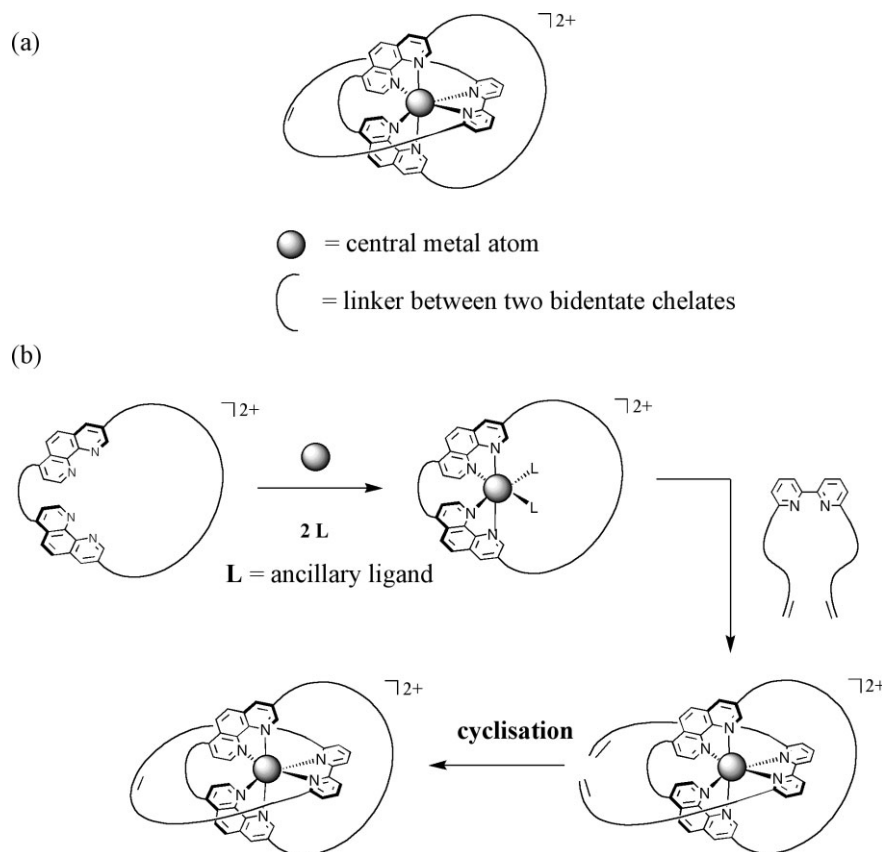


Figure 8. a) Schematic representation of a transition-metal-complexed [2]catenane containing two different rings. One of the macrocycles incorporates a bidentate chelate, whereas the other contains two bidentate coordinating fragments with a cis arrangement. b) Synthetic strategy. Reproduced with permission from [13b]. Copyright 2003, the American Chemical Society.

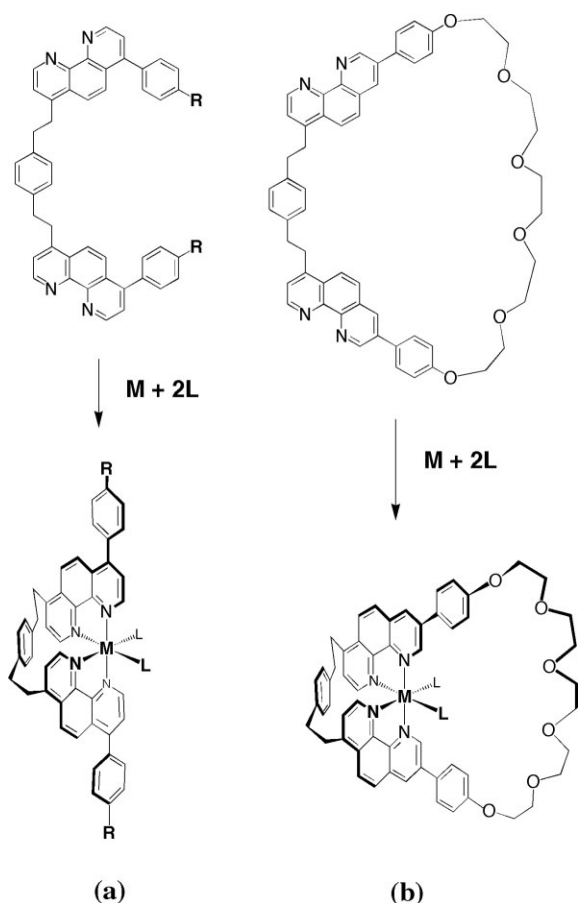


Figure 9. Formation of an axial (a) and a macrocyclic (b) complex. In both cases, connection of two para positions to N atoms of the phen nuclei by a $-\text{CH}_2\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2\text{CH}_2-$ bridge leads to a cis arrangement. Introduction of aromatic groups ($-\text{C}_6\text{H}_4-\text{R}$) 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 $-\text{C}_6\text{H}_4-\text{R}$ aromatic groups. Reproduced with permission from [13b]. Copyright 2003, the American Chemical Society.

Complex 8^{2+} was formed by reacting **7** and $\text{Ru}(\text{DMSO})_4\text{Cl}_2$, (DMSO: dimethyl sulfoxide) followed by refluxing the dichloro intermediate complex in $\text{CH}_3\text{CN}\cdot\text{H}_2\text{O}$. 8^{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 out using **9** and the macrocyclic complex 8^{2+} . Threading of the “filament” **9** does take place under relatively harsh conditions (ethylene glycol, 140°C) and the catenane precursor 10^{2+} was obtained in good yield (56 %). The final compound, catenane 11^{2+} , was prepared from 10^{2+} in a 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.^[21] 11^{2+} is a red-orange solid which has been fully characterized by various spectroscopic techniques. The electrospray mass spectrometry

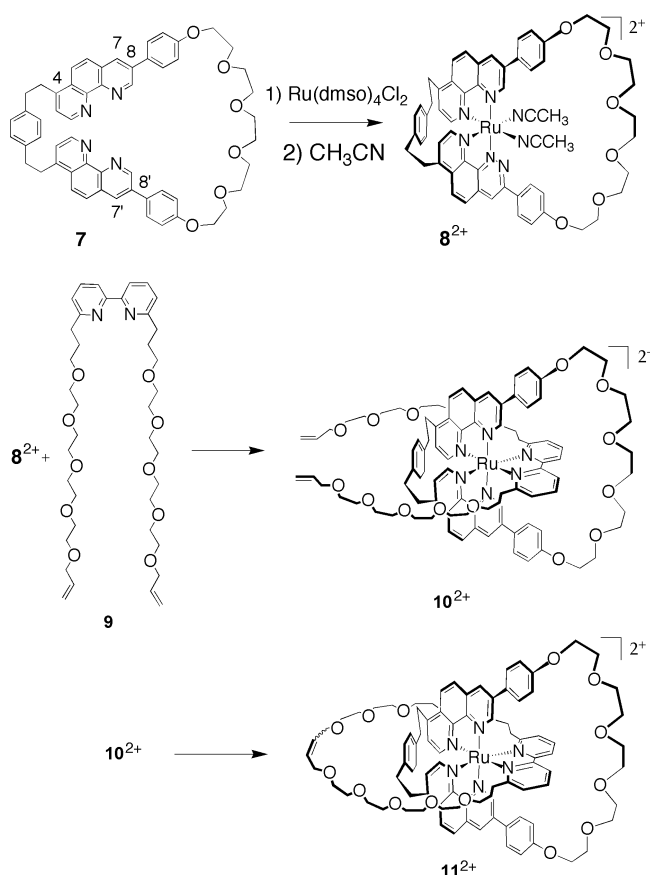


Figure 10. Sequence of reactions producing the ruthenium(II)-complexed [2]catenane 11^{2+} ; dmsO: dimethyl sulfoxide. Reproduced with permission from [13b]. Copyright 2003, the American Chemical Society.

(ES-MS) and ^1H NMR spectroscopy provide clear evidence for the structure of 11^{2+} .

2.6. Photoinduced Decoordination and Thermal Reoordination of a Ring in a Ruthenium(II)-Containing [2]Catenane

The [2]catenane 11^{2+} was synthesized as described in the previous paragraph. The other [2]catenane shown in Figure 11,^[12] 12^{2+} , was prepared using a slightly different procedure. Compound 11^{2+} consists of a 50-membered ring that incorporates two phen units and a 42-membered ring that contains the bipy chelate. Compound 12^{2+} contains the same bipy-incorporating ring as 11^{2+} , but the other ring is a 63-membered ring. Clearly, from CPK model considerations, 12^{2+} is more adapted than 11^{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 11^{2+} or 12^{2+} are represented in Figure 11. They are both quantitative, as shown by UV-vis measurements and by ^1H NMR spectroscopy.

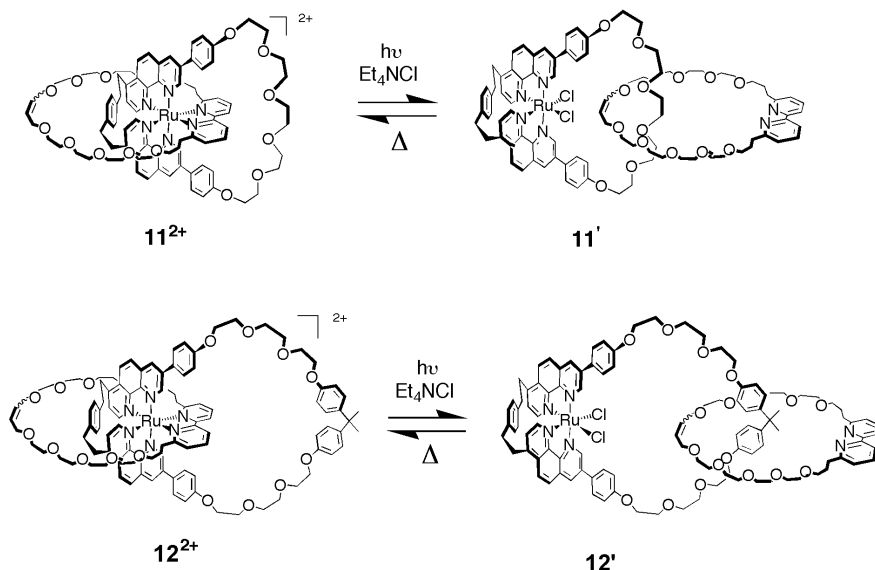


Figure 11. Catenanes 11^{2+} or 12^{2+} undergo a complete rearrangement by visible-light irradiation: the bipy-containing ring is efficiently decomplexed in the presence of Cl^- . By heating the photoproducts $11'$ or $12'$, the starting complexes 11^{2+} or 12^{2+} are quantitatively regenerated. Reproduced from [12].

The photoproducts, [2]catenanes $11'$ and $12'$, contain two disconnected rings since the photochemical reaction leads to decomplexation of the bipy chelate from the ruthenium(II) center. In a typical reaction, a degassed CH_2Cl_2 solution of 12^{2+} and $\text{NEt}_4^+\text{Cl}^-$ was irradiated with visible light at room temperature. The color of the solution rapidly changed from red (12^{2+} : $\lambda_{\text{max}} = 458 \text{ nm}$) to purple ($12'$: $\lambda_{\text{max}} = 561 \text{ nm}$) and after a few minutes the reaction was complete. The recoordination reaction $12' \rightarrow 12^{2+}$ was carried out by heating a solution of $12'$. The quantum yield for the photochemical reaction $12^{2+} \rightarrow 12'$ at 25°C and $\lambda = 470 \text{ nm}$ ($\pm 50 \text{ nm}$) can be very roughly estimated to be 0.014 ± 0.005 . One of the weak points of the present system is certainly the limited control had over the shape of the photoproduct, since the decomplexed ring can occupy several positions. It is hoped that, in the future, an additional tunable interaction between the two rings of the present catenanes, $11'$ and $12'$, will allow better control over the geometry of the whole system. A two-color machine will be elaborated, for which both motions will be driven by photonic signals operating at different wavelengths.

2.7. Use of the $\text{Ru}(\text{terpy})(\text{phen})(\text{L})^{2+}$ Core Instead of the $\text{Ru}(\text{diimine})_3^{2+}$ Core

In the $\text{Ru}(\text{diimine})_3^{2+}$ -based systems described above, the ruthenium core acts both as a templating moiety and as a component of the photochemically active central complex responsible for inducing the molecular motion. The ligand to be photoexpelled is a hindered chelate of the dmbp-type (dbmp: 6,6'-dimethyl-2,2'-bipyridine) inscribed in a ring. However, all attempts to use leaving bidentate chelates other

than dmbp turned out to be disappointing in terms of quantum yield and efficiency. Another way of varying these photochemical systems is to radically change the photochemical core and use a $\text{Ru}(\text{terpy})(\text{phen})(\text{L})^{2+}$ moiety, where L is a monodentate ligand. Visible-light irradiation of these complexes leads to the selective expulsion of the monodentate ligand and its replacement by a solvent molecule (see Fig. 12).^[22] In $\text{Ru}(\text{terpy})(\text{phen})(\text{L})^{2+}$ complexes, the monodentate nature of the leaving ligand L and the less-crowded coordination sphere around the ruthenium center compared to $\text{Ru}(\text{diimine})_3^{2+}$ complexes led us to think that, in future light-driven molecular machines, the thermal back-coordination step would be easier using the former core compared to what was obtained using the latter. The syntheses of complexes of the type $\text{Ru}(\text{terpy})(\text{phen})(\text{L})^{2+}$ have been described for a great variety of li-

gands L (chloride, water, acetonitrile, benzonitrile derivatives, pyridines substituted in 3,4 and/or 5 positions, sulfoxides, and thioethers).^[22,23] The absorption maxima of these complexes vary with the nature of the monodentate ligands, from ca. 430 nm for sulfoxides to ca. 460–470 nm for nitriles and thioethers, ca. 490 nm for pyridines, 505 nm for water, and 515 nm for Cl^- . Controlling the irradiation wavelength will thus enable the selective photoexpulsion of one type of ligand in a mixture of complexes with different monodentate ligands.

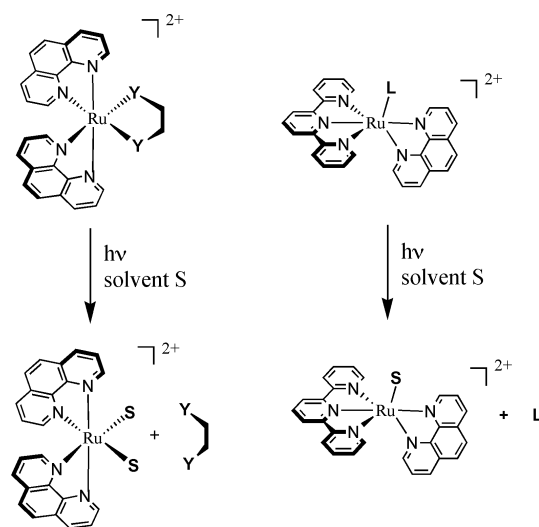


Figure 12. In $\text{Ru}(\text{phen})_2(\text{L})^{2+}$ complexes (left), the most-hindered chelate L is photoexpelled and replaced by two monodentate solvent molecules. In $\text{Ru}(\text{terpy})(\text{phen})(\text{L})^{2+}$ complexes (right), the monodentate ligand L is selectively photoexpelled and replaced by a solvent molecule.

A particularly promising feature of the Ru(terpy)-(phen)(L)²⁺ series, with respect to future molecular machines and motors, is related to the pronounced effect of steric factors on the photochemical reactivity of the complexes.^[24] When the bulkiness of the spectator phenanthroline was increased, the steric congestion of the coordination sphere of the ruthenium complex also increased. This congestion was shown by quantitative and comparative distance and angle measurements on four X-ray crystal structures (see Fig. 13a). This increased congestion was qualitatively correlated to the enhanced photoreactivities of these complexes. More specifically, exchanging phenanthroline with 2,9-dimethylphenanthroline (dmp) increased, by one to two orders of magnitude, the quantum yield of the photosubstitution reaction of L by pyridine with L = dimethylsulfide or 2,6-dimethoxybenzonitrile (see Fig. 13b). In the most congested case, Ru(terpy*)(dmp)(CH₃SCCH₃)²⁺ (terpy* = 4'-(3,5-ditertibutyl)phenyl-2,2',6',2''-terpyridine), the photosubstitution quantum yield was shown to be $\phi = 0.36$ at room temperature in pyridine, which is an extremely high value in ruthenium(II) photochemistry. Control of the bulkiness of the spectator chelates leading to the control of the congestion of the complex and, hence, to the efficiency of ligand photoexpulsion, is a specific feature of the Ru(terpy)(phen)(L)²⁺ core.

As a first application of this new Ru(terpy)(phen)(L)²⁺ core, a prototype of a photocontrolled molecular machine based on a scorpionate complex was proposed.^[25] In complex **13**²⁺ the terpy moiety was covalently attached to a

benzonitrile ligand by a flexible polyether chain. As shown by the X-ray crystal structure (see Fig. 14a), this terminal ligand is bound to the ruthenium atom as the sixth ligand of the coordination sphere. When irradiated by white light at room temperature in a water/acetone mixture, the benzonitrile moiety is selectively and quantitatively photoexpelled and replaced by a water molecule to give the new complex **14**²⁺ (Fig. 14b). Since water is a very weak ligand for the Ru(terpy)-(phen)(L)²⁺ core, the back-coordination of the benzonitrile takes place within a day at room temperature or in two hours under refluxing in acetone, yielding the starting metallamacrocyclic **13**²⁺. These thermal conditions are very mild compared to the back-coordination of the rings in the pseudotaxane or model compounds of the Ru(phen)₂ family; they are slightly milder than the conditions reported for the back-coordination in catenane **12**²⁺ (2 h at 80 °C in diethylene glycol). This scorpionate molecule is the first example of a photo-reactive molecule based on a Ru(terpy)(phen)(L)²⁺ complex

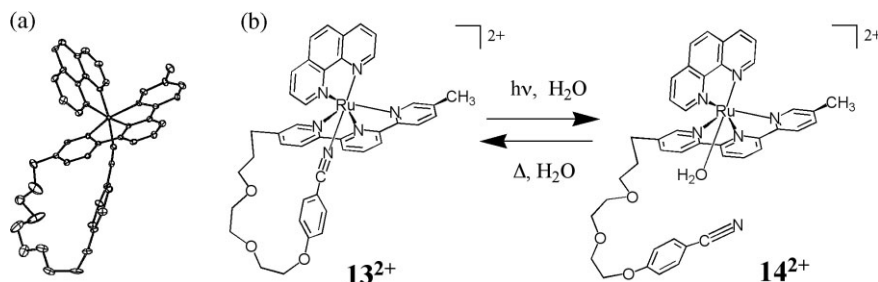


Figure 14. a) X-ray crystal structure of the scorpionate complex **13**²⁺ built on the Ru(terpy)(phen)²⁺ core. b) Photoinduced decooordination of the benzonitrile tail in acetone/water and recoordination by heating in neat acetone. Adapted with permission from [25]. Copyright 2003, the Royal Society of Chemistry.

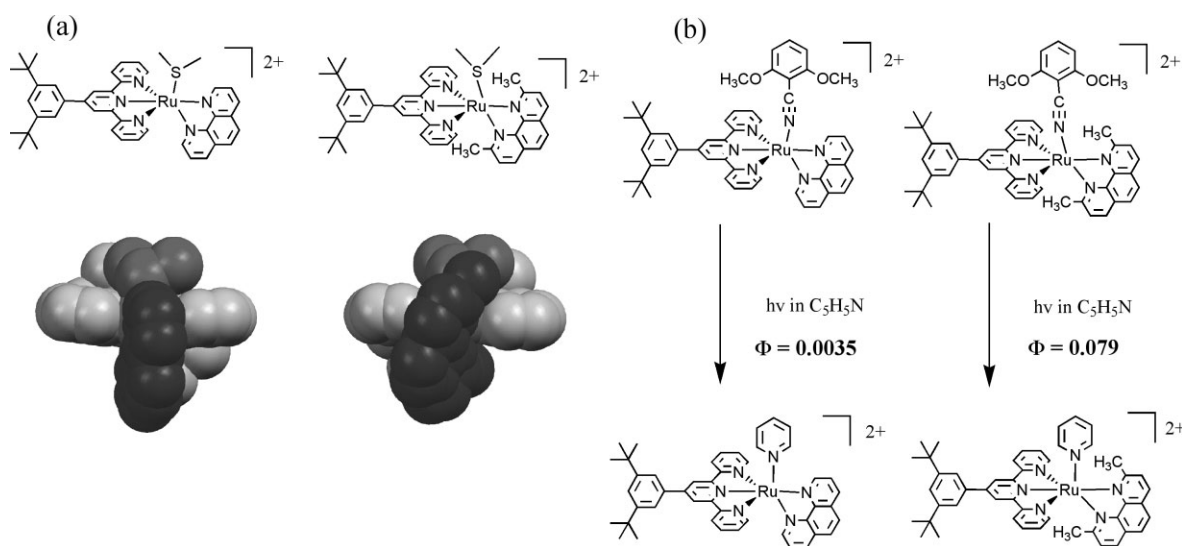


Figure 13. a) Plan view of Ru(terpy*)(phen)(dms)²⁺ and Ru(terpy*)(dmp)(dms)²⁺ complexes showing the very distorted X-ray crystal structure of the former compared to its unhindered derivative (dms = dimethylsulfide; terpy* = 4'-(3,5-ditertibutyl)phenyl-2,2',6',2''-terpyridine; dmp = 2,9-dimethylphenanthroline). b) Higher photoreactivity of Ru(terpy*)(dmp)(MeOBN)²⁺ compared to Ru(terpy*)(phen)(MeOBN)²⁺ (MeOBN = 2,6-dimethoxybenzonitrile). ϕ : photosubstitution quantum yield. Adapted with permission from [24]. Copyright 2004, the American Chemical Society.

that shows a large-scale motion at the molecular level (opening and closing of a ruthena-macrocycle).

Considering the tunable photoreactivity of the Ru(terpy)-(phen) core and the great variety of monodentate ligands that can be coordinated to it, we were looking for a strategy towards a molecular-ring analogue to 8^{2+} but including the Ru(terpy)(phen) core instead of Ru(phen)₂. Indeed, in 8^{2+} , the position of the two acetonitrile ligands *inside* the macrocyclic cavity enabled us to design a templated synthesis of catenanes (see above). We needed similar geometric properties in order to use the Ru(terpy)(phen) core in comparable molecular assemblies. Moreover, the use of a *para*-phenylene bridge in 8^{2+} enabled the avoidance of isomerization of the Ru(phen)₂ coordination pattern during the photoexpulsion of the hindered chelate.^[12] In the case of a Ru(terpy)(phen)(L)²⁺ complex, the symmetry is inherently different, which led us to design AMphen (8-anisyl-2-mesityl-1,10-phenanthroline), a dissymmetric phenanthroline chelate with a large hindering mesityl group in the 2-position. Based on this ligand, we recently published the synthesis of the Ru(terpy)(phen) core-including macrocycle, 15^{2+} , by a synthesis-on-the-complex strategy.^[26] Because of the presence of the mesityl group, this macrocycle exists in two isomeric forms (see Fig. 15). In the so-called "thermal isomer", 15_{th}^{2+} , the pyridine ligand lies inside the cavity defined by the macrocycle and on the same side as the anisyl group. On the contrary, in the "photochemical isomer", 15_{photo}^{2+} , the pyridine ligand lies outside the macrocycle and on the same side as the mesityl group. Interconversion between these two forms was shown to be possible: irradiation of 15_{th}^{2+} in pyridine yields quantitatively 15_{photo}^{2+} , whereas heating 15_{photo}^{2+} in the dark in DMSO at 140 °C for two hours, followed by two hours of reflux in pyridine yields 15_{th}^{2+} with a good overall yield (85 %, see Fig. 15). In these two reactions, the phenanthroline moiety rotates by an angle of 90° around the ruthenium center, which induces a major reorganization of the flexible polymethylene chain used to close the molecular ring.

As far as we are aware, macrocycle 15_{th}^{2+} is the first macrocyclic species that includes a Ru(terpy)(phen)(L)²⁺ complex.

Because of the intracyclic position of the monodentate ligand L in this isomer, this molecule allows us to envision that catenanes or rotaxanes can be constructed on Ru(terpy)-(phen)(L)²⁺ compounds. Considering the potential variety of monodentate ligands that can be coordinated and the mildness of the thermal coordination conditions, the Ru(terpy)-(phen)(L)²⁺ family appears to be a highly promising photoactive core that can be used for developing future light-driven molecular machines.

3. Conclusion and Prospects

The most important motivation for researchers and groups (including ours) involved in the field of artificial molecular machines and motors is certainly the synthetic challenge that the production of such systems represents. It is indeed very challenging to reproduce some of the simplest functions of 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 found in Nature. It must also be stressed that the study of molecular machines as single molecules will also represent another very ambitious task. Until now, artificial systems have been almost exclusively investigated as collections of molecules in solution or in films.

As far as practical applications are concerned, several possibilities can be explored, although technological applications are probably not foreseeable in the immediate future. Information storage and processing at the molecular level is, for the moment, the most popular field of application, ever since the spectacular reports of Heath, Stoddart and co-workers.^[27] Other ambitious and futuristic practical outcomes could be considered, such as the fabrication of "microrobots" or even "nanorobots" able to perform various functions: transport molecules or ions through a membrane, sort different molecules, and store energy, to cite just a few. In medicinal chemistry, it is conceivable that such devices can carry a given drug to a specific target where it is needed, open or close a gate or valve that controls delivery of a drug from a microdevice, and act as a nanosyringe that is able to inject a given molecule into a cell, which are all among the many functions that nanomechanical devices should be able to perform in the future.

Received: November 8, 2005
Final version: January 31, 2006
Published online: April 12, 2005

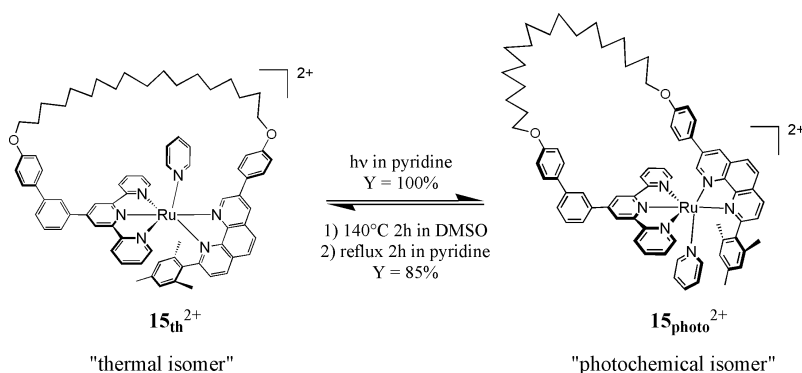


Figure 15. Major reorganization of a flexible (CH₂)₁₈ chain by photoinduced rotation of the phen bidentate chelate in complex 15_{th}^{2+} . Reverse motion is obtained by heating 15_{photo}^{2+} at 140 °C in DMSO. Adapted with permission from [26]. Copyright 2005, the Royal Society of Chemistry.

- [1] a) V. Balzani, M. Venturi, A. Credi, *Molecular Devices and Machines*, Wiley-VCH, Weinheim, Germany **2003**. b) J.-P. Sauvage, *Molecular Machines and Motors*, Springer Series on Structure & Bonding, Vol. 99, Springer, Berlin, Heidelberg **2001**. c) V. Balzani, A. Credi, F. M. Raymo, J. F. Stoddart, *An-*

- gew. Chem. Int. Ed. **2000**, 39, 3348. d) V. Balzani, A. Credi, M. Venturi, *Pure Appl. Chem.* **2003**, 75, 541. e) Special issue on "Molecular Machines", *Acc. Chem. Res.* **2001**, 34, 341. f) B. L. Feringa, *Molecular Switches*, Wiley-VCH, Weinheim, Germany **2001**. g) L. Fabbri, M. Licchelli, P. Pallavicini, *Acc. Chem. Res.* **1999**, 32, 846. h) T. R. Kelly, H. de Silva, R. A. Silva, *Nature* **1999**, 401, 150. i) N. Koumura, R. W. J. Zijlstra, R. A. van Delden, N. Harada, B. L. Feringa, *Nature* **1999**, 401, 152. j) D. A. Leigh, J. K. Y. Wong, F. Dehez, F. Zerbetto, *Nature* **2003**, 424, 174. k) M. C. Jimenez-Molero, C. Dietrich-Buchecker, J. P. Sauvage, *Chem. Commun.* **2003**, 1613. l) E. Katz, O. Lioubashevsky, I. Willner, *J. Am. Chem. Soc.* **2004**, 126, 15520. m) A. N. Shipway, I. Willner, *Acc. Chem. Res.* **2001**, 34, 421. n) A. Harada, *Acc. Chem. Res.* **2001**, 34, 456.
- [2] For early work, see: a) G. Schill, *Catenanes, Rotaxanes and Knots*, Academic, New York **1971**. b) *Molecular Catenanes, Rotaxanes and Knots* (Eds: J.-P. Sauvage, C. Dietrich-Buchecker), Wiley-VCH, Weinheim, Germany **1999**. c) F. Vögtle, T. Dünwald, T. Schmidt, *Acc. Chem. Res.* **1996**, 29, 451. d) M. Fujita, *Acc. Chem. Res.* **1999**, 32, 53. e) Special issue, *New J. Chem.* **1993**, 17. f) T. Hoshimo, M. Miyauchi, Y. Kawaguchi, H. Yamaguchi, A. Harada, *J. Am. Chem. Soc.* **2000**, 122, 9876. g) Y. Kawaguchi, A. Harada, *Org. Lett.* **2000**, 2, 1353. h) A. Bogdan, M. O. Vysotsky, T. Ikai, Y. Okamoto, V. Boehmer, *Chem. Eur. J.* **2004**, 10, 3324.
- [3] a) C. A. Stanier, M. J. O'Connell, W. Clegg, H. L. Anderson, *Chem. Commun.* **2001**, 493. b) C. A. Stanier, S. J. Alderman, T. D. W. Claridge, H. L. Anderson, *Angew. Chem. Int. Ed.* **2002**, 41, 1769. c) J. A. Wisner, P. D. Beer, M. G. B. Drew, M. R. Sambrook, *J. Am. Chem. Soc.* **2002**, 124, 12469. d) K. Chichak, M. C. Walsh, N. R. Branda, *Chem. Commun.* **2000**, 847. e) A. Breault, C. A. Hunter, P. C. Mayers, *Tetrahedron* **1999**, 55, 5265. f) H. Dürr, S. Bossmann, *Acc. Chem. Res.* **2001**, 34, 905. g) H. Iwamoto, K. Itoh, H. Nagamiya, Y. Fukazawa, *Tetrahedron Lett.* **2003**, 44, 5773. h) D. Fitzmaurice, S. N. Rao, J. A. Preece, J. F. Stoddart, S. Wenger, N. Zacheroni, *Angew. Chem. Int. Ed.* **1999**, 38, 1147. i) H. W. Gibson, N. Yamaguchi, L. Hamilton, J. W. Jones, *J. Am. Chem. Soc.* **2002**, 124, 4653. j) P. Samori, F. Jäckel, Ö. Ünsal, A. Godt, J. P. Rabé, *ChemPhysChem* **2001**, 2, 461. k) P. Hodge, P. Monvisade, G. J. Owen, F. Heatley, Y. Pang, *New J. Chem.* **2000**, 24, 703. l) S. Y. Chang, J. S. Choi, K. S. Jeong, *Chem. Eur. J.* **2001**, 7, 2687. m) T. Fujimoto, A. Nakamura, Y. Inoue, Y. Sakata, T. Kaneda, *Tetrahedron Lett.* **2001**, 42, 7987. n) K. Kim, *Chem. Soc. Rev.* **2002**, 31, 96. o) K. M. Park, S. Y. Kim, J. Heo, D. Whang, S. Sakamoto, K. Yamaguchi, K. Kim, *J. Am. Chem. Soc.* **2002**, 124, 2140. p) B. Korybut-Daszkiewicz, A. Wieckowska, R. Bilewicz, S. Domagala, K. Wozniak, *J. Am. Chem. Soc.* **2001**, 123, 9356. q) L. Chen, X. Zhao, Y. Chen, C. X. Zhao, X. K. Jiang, Z. T. Li, *J. Org. Chem.* **2003**, 68, 2704. r) G. J. E. Davidson, S. J. Loeb, *Angew. Chem. Int. Ed.* **2003**, 42, 74. s) R. G. E. Coumans, J. A. A. W. Elemans, P. Thordarson, R. J. M. Nolte, A. E. Rowan, *Angew. Chem. Int. Ed.* **2003**, 42, 650. t) A. Arduini, R. Ferdani, A. Pochini, A. Secchi, F. Ugozzoli, *Angew. Chem. Int. Ed.* **2000**, 39, 3453. u) C. P. McArdle, J. J. Vittal, R. J. Puddephatt, *Angew. Chem. Int. Ed.* **2000**, 39, 3819. v) K. A. Udachin, L. D. Wilson, J. A. Ripmeester, *J. Am. Chem. Soc.* **2000**, 122, 12375. w) M. J. Gunter, N. Bampas, K. D. Johnstone, J. K. M. Sanders, *New J. Chem.* **2001**, 25, 166. x) P. Ghosh, O. Mermagen, C. A. Schalley, *Chem. Commun.* **2002**, 2628. y) A. Andrievsky, F. Ahuis, J. L. Sessler, F. Vögtle, D. Gudat, M. Moini, *J. Am. Chem. Soc.* **1998**, 120, 9712. z) A. Bellaissaoui, S. Shimada, A. Ohishi, N. Tamaoki, *Tetrahedron Lett.* **2003**, 44, 2307.
- [4] a) R. Shukla, M. J. Deetz, B. D. Smith, *Chem. Commun.* **2000**, 2397. b) I. Smukste, D. B. Smith, *J. Org. Chem.* **2003**, 68, 2547. c) D. L. Simone, T. M. Swager, *J. Am. Chem. Soc.* **2000**, 122, 9300. d) M. J. MacLachlan, A. Rose, T. S. Swager, *J. Am. Chem. Soc.* **2000**, 122, 9180. e) N. Watanabe, T. Yagi, N. Kihara, T. Takata, *Chem. Commun.* **2002**, 2720. f) N. Watanabe, N. Kihara, Y. Furusho, T. Takata, Y. Araki, O. Ito, *Angew. Chem. Int. Ed.* **2003**, 42, 681. g) I. Willner, V. Pardo-Yissar, E. Katz, K. T. Ranjit, *J. Electroanal. Chem.* **2001**, 497, 172.
- [5] R. A. Bissell, E. Córdova, A. E. Kaifer, J. F. Stoddart, *Nature* **1994**, 369, 133.
- [6] a) A. Livoreil, C. O. Dietrich-Buchecker, J.-P. Sauvage, *J. Am. Chem. Soc.* **1994**, 116, 9399. b) J.-P. Collin, P. Gaviña, J.-P. Sauvage, *Chem. Commun.* **1996**, 2005. c) L. Raehm, J.-M. Kern, J.-P. Sauvage, *Chem. Eur. J.* **1999**, 5, 3310. d) J.-P. Sauvage, *Acc. Chem. Res.* **1998**, 31, 611.
- [7] J. D. Badjic, V. Balzani, A. Credi, S. Silvi, J. F. Stoddart, *Science* **2004**, 303, 1845.
- [8] a) R. Ballardini, V. Balzani, M. T. Gandolfi, L. Prodi, M. Venturi, D. Philp, H. G. Ricketts, J. F. Stoddart, *Angew. Chem. Int. Ed. Engl.* **1993**, 32, 1301. b) A. Livoreil, J.-P. Sauvage, N. Armaroli, V. Balzani, L. Flamigni, B. Ventura, *J. Am. Chem. Soc.* **1997**, 119, 12114. c) N. Armaroli, V. Balzani, J.-P. Collin, P. Gaviña, J.-P. Sauvage, B. Ventura, *J. Am. Chem. Soc.* **1999**, 121, 4397. d) A. M. Brouwer, C. Frocht, F. G. Gatti, D. A. Leigh, L. Mottier, F. Paolucci, S. Roffia, G. W. H. Worpel, *Science* **2001**, 291, 2124. e) P. R. Ashton, R. Ballardini, V. Balzani, A. Credi, K. R. Dress, E. Ishow, C. J. Kleverlaan, O. Kocian, J. A. Preece, N. Spencer, J. F. Stoddart, M. Venturi, S. Wenger, *Chem. Eur. J.* **2000**, 6, 3558. f) P. R. Ashton, R. Ballardini, V. Balzani, I. Baxter, A. Credi, M. C. T. Fyfe, M. T. Gandolfi, M. Gómez-López, M.-V. Martínez-Díaz, A. Piersanti, N. Spencer, J. F. Stoddart, M. Venturi, A. J. P. White, D. J. Williams, *J. Am. Chem. Soc.* **1996**, 118, 11932. g) V. Balzani, A. Credi, G. Mattersteig, O. A. Matthews, F. M. Raymo, J. F. Stoddart, M. Venturi, A. J. P. White, D. J. Williams, *J. Org. Chem.* **2000**, 65, 1924.
- [9] a) H. Murakami, A. Kawabuchi, K. Kotoo, M. Kunitake, N. Nakashima, *J. Am. Chem. Soc.* **1997**, 119, 7605. b) V. Balzani, A. Credi, F. Marchioni, J. F. Stoddart, *Chem. Commun.* **2001**, 1860.
- [10] a) C. O. Dietrich-Buchecker, J.-P. Sauvage, J.-P. Kintzinger, *Tetrahedron Lett.* **1983**, 24, 5095. b) C. O. Dietrich-Buchecker, J.-P. Sauvage, J.-M. Kern, *J. Am. Chem. Soc.* **1984**, 106, 3043. c) C. O. Dietrich-Buchecker, J.-P. Sauvage, *Tetrahedron* **1990**, 46, 503. d) J.-C. Chambron, C. O. Dietrich-Buchecker, J.-P. Sauvage, in *Comprehensive Supramolecular Chemistry* (Eds: J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle, J.-M. Lehn, J.-P. Sauvage, M. W. Hosseini), Vol. 9, Pergamon, Oxford, UK **1996**, p. 43. e) C. O. Dietrich-Buchecker, J.-P. Sauvage, *Chem. Rev.* **1987**, 87, 795.
- [11] a) J. C. Chambron, J. P. Collin, V. Heitz, D. Jouvenot, J. M. Kern, P. Mobian, D. Pomeranc, J. P. Sauvage, *Eur. J. Org. Chem.* **2004**, 1627. b) D. Pomeranc, D. Jouvenot, J.-C. Chambron, J.-P. Collin, V. Heitz, J. P. Sauvage, *Chem. Eur. J.* **2003**, 9, 4247.
- [12] P. Mobian, J. M. Kern, J. P. Sauvage, *Angew. Chem. Int. Ed.* **2004**, 43, 2392.
- [13] a) P. Mobian, J. M. Kern, J. P. Sauvage, *Helv. Chim. Acta* **2003**, 86, 4195. b) P. Mobian, J. M. Kern, J. P. Sauvage, *J. Am. Chem. Soc.* **2003**, 125, 2016.
- [14] I. Poleschak, J. M. Kern, J.-P. Sauvage, *Chem. Commun.* **2004**, 474.
- [15] a) C. Jiménez, C. Dietrich-Buchecker, J.-P. Sauvage, *Angew. Chem. Int. Ed.* **2000**, 39, 3284. b) C. Jiménez, C. Dietrich-Buchecker, J.-P. Sauvage, *Chem. Eur. J.* **2002**, 8, 1456.
- [16] a) J. P. Collin, A.-C. Laemmel, J.-P. Sauvage, *New J. Chem.* **2001**, 25, 22. b) A.-C. Laemmel, *Ph.D. Thesis*, Louis Pasteur University, Strasbourg, France **2000**.
- [17] a) M. Adelt, M. Devenney, T. J. Meyer, D. W. Thompson, J. A. Treadway, *Inorg. Chem.* **1998**, 37, 2616. b) J. Van Houten, J. Watts, *Inorg. Chem.* **1978**, 17, 3381. c) H. F. Suen, S. W. Wilson, M. Pomerantz, J. L. Walsch, *Inorg. Chem.* **1989**, 28, 786. d) D. V. Pinnick, B. Durham, *Inorg. Chem.* **1984**, 23, 1440. e) M. Gleria, F. Minto, G. Beggiato, P. Bortolus, *J. Chem. Soc. Chem. Commun.* **1978**, 285. f) B. Durham, J. V. Caspar, J. K. Nagle, T. J. Meyer, *J. Am. Chem. Soc.* **1982**, 104, 4803. g) S. Tachiyashiki, K. Mizumachi, *Coord. Chem. Rev.* **1994**, 132, 113.

- [18] a) D. Pomeranc, J.-C. Chambron, V. Heitz, J.-P. Sauvage, *C. R. Acad. Sci.* **2001**, *4*, 197. b) D. Pomeranc, V. Heitz, J.-C. Chambron, J.-P. Sauvage, *J. Am. Chem. Soc.* **2001**, *123*, 12215.
- [19] D. Jouvenot, M. Koizumi, J.-P. Collin, J.-P. Sauvage, *Eur. J. Inorg. Chem.* **2005**, 1850.
- [20] P. Hayoz, A. von Zelewsky, H. Stoeckli-Evans, *J. Am. Chem. Soc.* **1993**, *115*, 5111.
- [21] a) C. O. Dietrich-Buchecker, G. Rapenne, J.-P. Sauvage, *Coord. Chem. Rev.* **1999**, *185–186*, 167. b) G. Rapenne, C. O. Dietrich-Buchecker, J.-P. Sauvage, *J. Am. Chem. Soc.* **1999**, *121*, 994.
- [22] S. Bonnet, J.-P. Collin, J.-P. Sauvage, E. Schofield, *Dalton Trans.* **2003**, 4654.
- [23] a) M. J. Root, E. Deutsch, *Inorg. Chem.* **1985**, *24*, 1464. b) C. R. Hecker, P. E. Fanwick, D. R. McMillin, *Inorg. Chem.* **1991**, *30*, 659. c) J. J. Rack, J. R. Winkler, H. B. Gray, *J. Am. Chem. Soc.* **2001**, *123*, 2432.
- [24] S. Bonnet, J.-P. Collin, J.-P. Sauvage, E. Schofield, *Inorg. Chem.* **2004**, *43*, 8346.
- [25] E. R. Schofield, J.-P. Collin, N. Gruber, J.-P. Sauvage, *Chem. Commun.* **2003**, 188.
- [26] S. Bonnet, J.-P. Collin, J.-P. Sauvage, *Chem. Commun.* **2005**, 3195.
- [27] C. P. Collier, G. Mattersteig, E. W. Wong, Y. Luo, K. Beverly, J. Sampaio, F. M. Raymo, J. F. Stoddart, J. R. Heath, *Science* **2000**, *289*, 1172.