Ruthenium-based light-driven molecular machine prototypes: synthesis and properties

Sylvestre Bonnet and Jean-Paul Collin*

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In the past years, many dynamic systems often referred to as "molecular machines" have been elaborated. They are generally set in motion by external stimuli like chemical, electrochemical, or photochemical reactions. Light irradiation seems particularly promising since the input signal can be switched on and off fast and readily on a very small place. In this *tutorial review*, we will highlight recent advances in the design and synthesis of various ruthenium(II) complexed rotaxanes, catenanes, scorpionates or macrocycles. In these compounds, one part of the system is set in motion by photochemically expelling a given chelate. We will discuss the behaviour of various topologically non-trivial systems like catenanes and rotaxanes as well as acyclic and macrocyclic models.

Introduction

Inducing molecular motions in a controlled fashion under the action of an external signal, either to mimic some of the functions of biological motors, or in relation to artificial molecular switches, machines, and devices, is particularly challenging. As far as synthetic systems are concerned, catenanes and rotaxanes occupy a special position[1–4] although non-interlocked systems like scorpionates have also been investigated.[5,6] In many systems, the movements have been triggered by an electrochemical signal.[7,8] In this case, an electroactive component is reduced or oxidized to lead to a new and unstable species whose relaxation to a thermodynamically more stable situation implies a motion. A few molecular machines have also been described which operate under the action of a chemical signal (pH change,[6,9] metal exchange,[10] or a series of organic reactions[11]).

In particular, light irradiation has also been reported to produce molecular motions, either alone or in conjunction with a redox chemical reaction.[5,8,12–18] Pure photonic stimuli are particularly promising as the system in motion is not altered by the addition of chemicals; however, only a few examples have been reported so far. Most of them contain a photoisomerizable group, such as an azobenzene or alkene function. The light pulse 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. Notably, the rotary motor proposed by Feringa *et al.* is a remarkable example since the rotational motion is realized by a sequence of photochemical and thermal steps, without consuming any chemical reagent.[13] Recent optimization of this system led to a decreased temperature for the thermal step, so that the rotation takes places continuously and in a unidirectional way under light irradiation at room temperature.[13,19]

Our group has proposed another approach to light-driven machines, based on multicomponent ruthenium(II)

Laboratoire de Chimie Organo-Minérale, LC 3, UMR 7177 du CNRS, Université Louis Pasteur, Faculté de Chimie, 4 rue Blaise Pascal, 67070 Strasbourg Cedex, France. E-mail: jpcollin@chimie.u-strasbg.fr; Fax: +33 (0)3 90 24 13 68; Tel: 33 (0)3 90 24 13 58


Sylvestre Bonnet

Sylvestre Bonnet received his Master's Degree from the Université Louis Pasteur in 2002, where he also did his PhD in the group of Jean-Pierre Sauvage. After graduating in 2005 he moved to Utrecht University where he worked as a postdoctoral fellow in the group of Prof. Gerard van Koten and Prof. Bert Klein Gebbink. In 2007 he moved to Leiden University, where he is currently working as a postdoctoral fellow in the group of Prof. Jan Reedijk.


Jean-Paul Collin

Jean-Paul Collin was born in 1945 in Metz. After his PhD in electrochemistry with Prof. J.-P. Schwing at Strasbourg University, he did postdoctoral work with Prof. J.-M. Lehn on water photolysis. He is now a CNRS research director. He joined J.-P. Sauvage's group in 1983, and his present research interests concern photoinduced charge separation in multicomponent molecular systems and molecular machines.

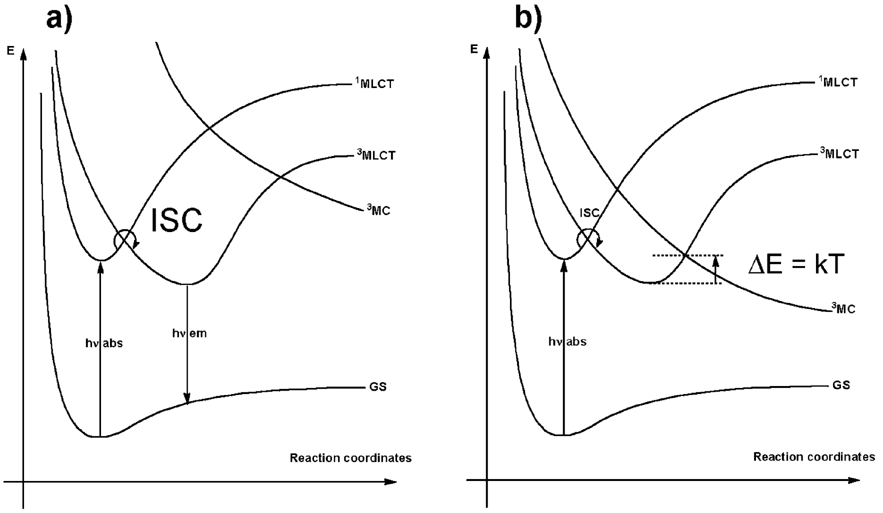


Fig. 1 (a) Large ^{3}MLCT–^{3}MC energy gap: fluorescence may occur; (b) small ^{3}MLCT–^{3}MC energy gap: thermal population of the ^{3}MC leads to a strongly dissociative state.

complexes.[20] Polypyridyl ruthenium(II) complexes have been used extensively in light-induced electron and energy transfer processes,[21] but photochemical ligand exchange has rather been considered as a detrimental reaction until now. In our systems however, such ligand photosubstitution reactions have been used in order to set the molecule into motion.[5,12,15] Such a process requires population of a dissociative excited state from the triplet metal-to-ligand charge transfer (^{3}MLCT) excited state. Most ruthenium(II) polypyridyl complexes display intense absorption in the visible region due to ^{1}MLCT excited states. The fate of the ^{3}MLCT obtained after intersystem crossing depends on the magnitude of the ligand field of the complexes. This magnitude can be controlled by the steric and electronic properties of the chelates. In undistorted complexes like $Ru(phen)_3^{2+}$, fluorescence or non-radiative decay may occur.[22] If the distortion of the coordination octahedron is sufficient to lower the ligand field, which can be realized by using one or several sterically hindering ligands, a strongly dissociative metal-centered (MC) state can be efficiently populated from the ^{3}MLCT state to result in expulsion of a given ligand. The principle of the whole process based on well-established ruthenium(II) photochemistry is represented in Fig. 1.[22–24]

Polypyridyl ruthenium(II) complexes can be classified into four main classes, depending on the denticity of their ligands. The complexes that have more than one monodentate ligand are geometrically too complex to lead to pre-organized multicomponent architectures like rotaxanes and catenanes; they may, however, show rich ligand photoexpulsion reactions.[23] On the contrary, complexes of the type $Ru(terpy)_2^{2+}$ are simple on the geometrical point of view but the terdentate nature of the two chelates makes them non-reactive towards ligand photoexpulsion. In this review, we will focus on the two other families of ruthenium(II) polypyridyl complexes leading to light-driven molecular machine prototypes: the $Ru(phen)_2(L)^{2+}$ family, where phen = 1,10-phenanthroline and L is a hindered diimine bidentate chelate; and the Ru(terpy)(N–N)(L)$^{2+}$ family, where terpy is a derivative of 2,2′:6′,2″-terpyridine, N–N is a bidentate diimine chelate like 1,10-phenanthroline or 2,2′-bipyridine, and L is a monodentate ligand (Fig. 2).

Construction of multicomponent architectures based on the $Ru(phen)_2$ core

In $Ru(diimine)_3^{2+}$ compounds, one part of the system is set in motion by photochemically expelling the most hindered chelate, the reverse motion being performed simply by heating the product of the photochemical reaction so as to regenerate the original state. We will discuss the synthesis of a rotaxane and a catenane of this family and briefly describe how it was possible to set into motion these molecules using light as the only source of energy.

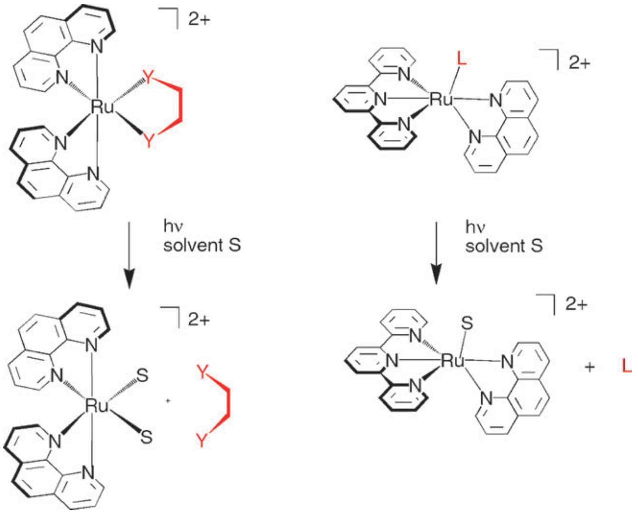


Fig. 2 The two main classes of photoreactive ruthenium(II) polypyridyl complexes: in $Ru(phen)_2(L)^{2+}$, the hindered bidentate chelate L is photoexpelled by light irradiation (left); in the Ru(terpy)(phen)(L)$^{2+}$ series, photoexpulsion occurs selectively on the monodentate ligand (right). Reproduced with permission from ref. 3. Copyright 2006 Wiley-VCH.

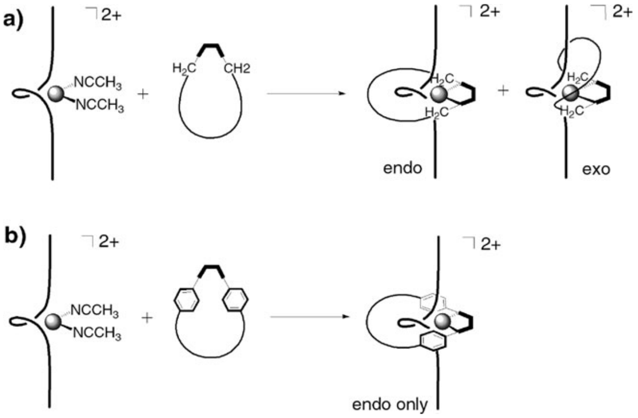


Fig. 3 Threading of a macrocycle on a Ru(phen)$_2$-containing helical axis; (a) when the ring is built with a flexible dmbipy chelate, both *endo*- and *exo*-coordination occur; (b) replacing dmbipy with the more rigid dpbipy chelate leads to *endo*-coordination only. Adapted with permission from ref. 25. Copyright 2003 Wiley-VCH.

Synthesis of a rotaxane including a Ru(diimine)$_3$$^{2+}$ moiety

We have recently reported the synthesis of [2]-rotaxanes constructed around a Ru(diimine)$_3$$^{2+}$ core.[15,25] It was shown that a Ru(phen)$_2$ moiety could be incorporated in an axial compound by appropriate substitution of the phenanthrolines, *i.e.* in the *para* position to one nitrogen atom of each chelate. Threading of a ring on such an axis, followed by stoppering of the pseudo-rotaxane (bulky substituents were attached at each end of the axis), led to the full rotaxane. The first ring used was a derivative of 6,6′-dimethyl-2,2′-bipyridine (dmbipy), and in the course of the threading reaction we noticed that both *exo*- and *endo*-coordination to the ruthenium(II) centre of the rod-like fragment took place (Fig. 3a).[25] These isomers could not be separated by chromatography, neither before nor after the stoppering reaction. In order to circumvent this synthetic difficulty, the dmbipy motif was replaced by a 6,6′-diphenyl-2,2′-bipyridine chelate (dpbipy), which provided much better geometrical control of the system.[15] According to CPK models, *exo* coordination of a dpbipy-incorporating ring is virtually impossible, except with very large rings. This approach turned out to be successful and the desired rotaxane was prepared in good yield, without formation of *exo*-coordinated species (Fig. 3b and 4).

The threading reaction was tested with both ends of the helical rod-shaped fragment bearing inert –OCH$_3$ groups leading to pseudorotaxane **3**$^{2+}$. As depicted in Fig. 4, the starting ruthenium(II) complex **1**$^{2+}$ and ring **2** were reacted under relatively harsh conditions to afford the threaded complex **3**$^{2+}$ in good yield (91%). **1**$^{2+}$ was a ruthenium(II) complex containing a helical bis(phenanthroline) organic fragment.[25] Compound **2** was a 37-membered ring whose synthesis has recently been described.[15] The presence of a dpbipy chelate and a bis-phenol A unit (bis-phenol A = 1,1′-bis(*p*-hydroxyphenyl)-1″,1‴-dimethylmethane) ensures some rigidity to the ring, which prevents swinging of the bis-phenol A fragment "behind" the bipy chelate. As expected, **3**$^{2+}$ is the *endo*-coordinated compound, with no contamination of the *exo*-isomer as shown in solution by 2D NMR ROESY experiments.

The complete rotaxane was prepared from **2** and **4**$^{2+}$, the phenolic analogue of **1**$^{2+}$, whose synthesis had previously been reported.[25] The reaction is presented in Fig. 5.

The "threading" step of **4**$^{2+}$ through ring **2** afforded the pre-rotaxane **5**$^{2+}$ in 82% yield. It was carried out in ethylene glycol at 140 °C. The "stoppering" reaction was performed using large tetraarylmethane derivatives based on those reported by Gibson *et al.*[26] This derivative **6** was reacted with **5**$^{2+}$ in DMF, at 60 °C, in the presence of a large excess of K$_2$CO$_3$ under argon. After work-up and chromatography the full rotaxane **7**$^{2+}$ was obtained as a red solid in 56% yield.

Synthesis of a catenane including a Ru(diimine)$_3$$^{2+}$ fragment

As already mentioned, the bis(phenanthroline) ligand shown in Fig. 4 and 5 was well adapted to the formation of a clearly identified axis after complexation to ruthenium(II), thus allowing the formation of the photoactive rotaxane **7**$^{2+}$. In a similar manner, another phenylene-bridged bis(phenanthroline) bearing anisyl groups in the *meta* position to the nitrogen atoms (instead of the *para* position) was designed and synthesized.[27] This geometry enabled the synthesis of macrocycles incorporating the Ru(phen)$_2$ moiety (Fig. 6). This macrocycle was used as a templating element in order to incorporate the Ru(diimine)$_3$$^{2+}$ core in a catenane.

First, a new bis(phenanthroline) macrocycle was built. Macrocycle **8** (Fig. 6), a 59-membered ring, appeared well-

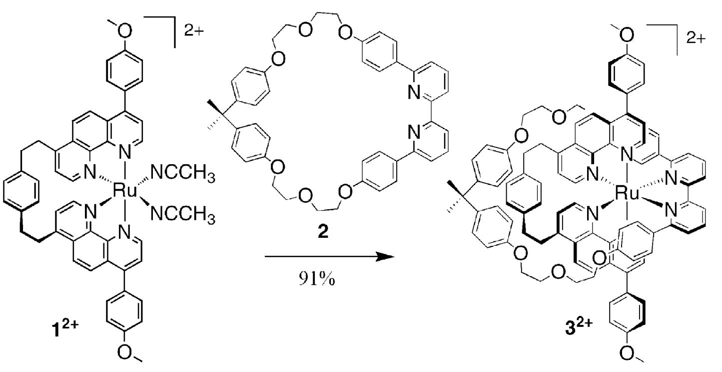


Fig. 4 Synthesis of a pseudo-rotaxane incorporating the Ru(phen)$_2$ core. Adapted with permission from ref. 15. Copyright 2005 Wiley-VCH.

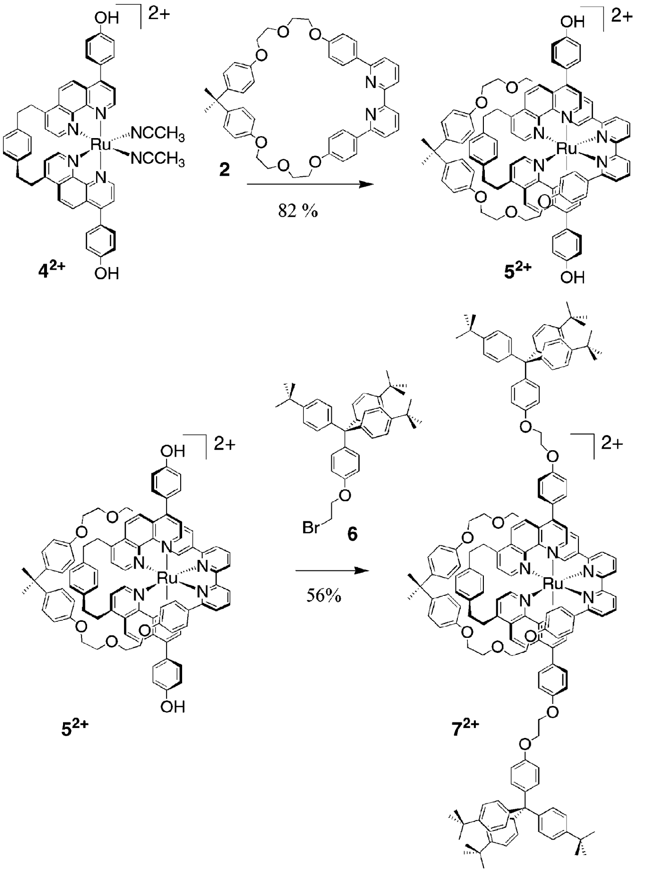


Fig. 5 Synthesis of a Ru(phen)$_2$-incorporating rotaxane. Reproduced with permission from ref. 15. Copyright 2005 Wiley-VCH.

adapted to the formation of octahedral bis-phenanthroline complexes by CPK modeling, with the two phen fragments being disposed *cis* to one another in the metal coordination sphere.[27] Insertion of the metal centre into the macrocycle cavity was achieved by reacting macrocycle **8** and RuCl$_2$(DMSO)$_4$ in refluxing 1,2-dichloroethane under high-dilution conditions. The intermediate dichloro complex was not isolated; instead the crude reaction mixture was heated under reflux in CH$_3$CN–H$_2$O to replace the auxiliary chloro ligands by CH$_3$CN. The "threading step" was carried out using the 2,2′-bipyridine derivative **10** bearing two terminal olefins (see Fig. 7). The threading reaction took place under relatively harsh conditions (ethylene glycol, 140 °C) and the catenane precursor **11**$^{2+}$ was obtained in a surprisingly good yield of 46%. The final catenane **12**$^{2+}$ was prepared by ring-closing metathesis (RCM): a CH$_2$Cl$_2$ solution of complex **11**$^{2+}$ and [RuCl$_2$CHPh(PCy$_3$)$_2$] was stirred under argon for three days. The final catenane was isolated in 76% yield. This preparative yield was in the same range as those obtained for making other transition metal-containing catenanes and knots by means of a similar RCM-based approach.[28]

This strategy led to the formation of a Ru(diimine)$_3$$^{2+}$-incorporating catenane formed from two different rings: the smaller 42-membered ring incorporates a 6,6′-bipyridine fragment, whereas the other 59-membered ring contains the two phenanthrolines of the octahedral metal complex. This catenane was with no doubt the first example of an interlocking ring system built on a tris-bidentate chelate transition-metal complex used as template.

Photoreactivity of the Ru(diimine)$_3$$^{2+}$-based systems

The light-induced motion and the thermal back reaction carried out with catenane **12**$^{2+}$ are represented in Fig. 8.

Catenane **12′** contains two disconnected rings as the photochemical reaction leads to decomplexation of the bipy chelate from the ruthenium(II) center.[20] It must be stressed that the drawing of the decoordinated form **12′** is only indicative and does not imply that the geometry of the molecule is as shown. The photochemical reaction **12**$^{2+}$ → **12′** (in the presence of chloride ions) as well as the thermal backward reaction were monitored by UV-Vis measurements. In a typical reaction, a degassed 10^{-4} M solution of **12**$^{2+}$ in CH$_2$Cl$_2$ containing a tenfold excess of Et$_4$NCl was irradiated at room temperature using a 250 W halogen lamp ($\lambda > 400$ nm). The colour of the solution rapidly changed from red (**12**$^{2+}$: $\lambda_{\max} = 458$ nm) to purple (**12′**: $\lambda_{\max} = 561$ nm), and after a few minutes the reaction was complete. A clean isosbestic point at 484 nm was observed, which indicates that the conversion **12**$^{2+}$ → **12′** was selective. The recoordination reaction **12′** → **12**$^{2+}$ was carried out efficiently by heating a solution of **12′** in ethylene glycol either at 140 °C for 15 minutes or at 80 °C for 2 h. Both the photochemical decoordination of the ring and its thermal recomplexation were quantitative.

The photochemical behaviour of pseudo-rotaxane **3**$^{2+}$ was studied in a similar way. By irradiating a solution of **3**$^{2+}$ in 1,2-dichloroethane using a band-pass filter centered around 470 nm and in the presence of a large excess of chloride ions, a clean photochemical reaction took place. The reaction is schematically represented in Fig. 9.

The photoinduced "unthreading" reaction was monitored with UV-Vis spectroscopy. The series of visible spectra showed

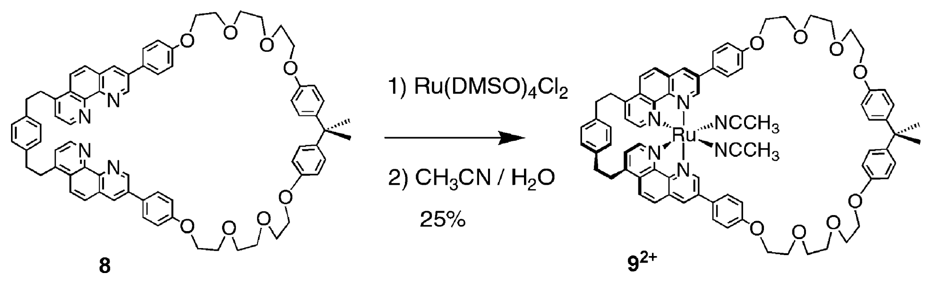


Fig. 6 A phenylene-bridged ligand with anisyl groups in the *meta* position leads to a macrocycle incorporating the Ru(phen)$_2$ moiety. Adapted with permission from ref. 27. Copyright 2003, the American Chemical Society.

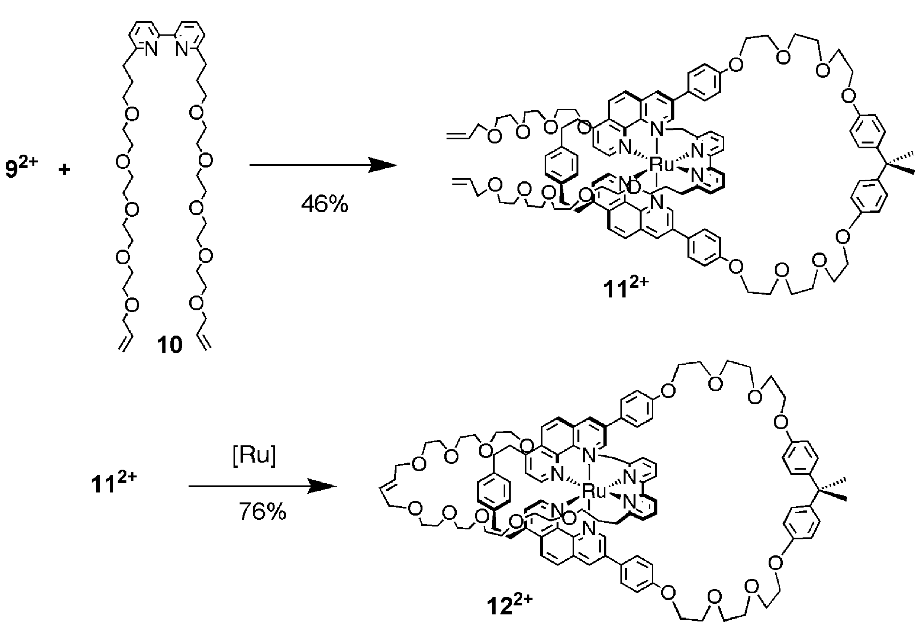


Fig. 7 Synthesis of a Ru(diimine)$_2$-incorporating catenane. Adapted with permission from ref. 27. Copyright 2003, the American Chemical Society.

a clear isosbestic point at 485 nm, which indicated that the photochemical reaction was selective and virtually quantitative. From a band centered at 465 nm, typical of a Ru(diimine)$_3{}^{2+}$ complex, a new spectrum was obtained upon irradiation, which corresponded to a RuCl$_2$(diimine)$_2$ complex ($\lambda_{\max}$ = 562 nm). As expected, the MLCT band for the photochemical product was strongly bathochromically shifted from that of the tris-diimine complex. The selectivity of the unthreading reaction was confirmed from ^{1}H NMR spectroscopy and thin-layer chromatography. At the end of the reaction, **13** was the only photochemical product detected and the starting complex $\mathbf{3}^{2+}$ had completely disappeared.

Similar experiments have been performed with the stoppered rotaxane. The reaction is represented in a schematic fashion in Fig. 10.

Photochemical decoordination of the ring in $\mathbf{7}^{2+}$ was also selective and clean. Here again, by analogy with $\mathbf{3}^{2+}$, an isosbestic point was observed at 486 nm. Thin-layer chromatography turned out to be particularly useful to monitor the reaction. It showed that $\mathbf{7}^{2+}$ was gradually converted to a single purple complex **14** under irradiation (470 nm). Importantly, traces of the free ring **2** could not be detected, demonstrating that both forms of the rotaxane, $\mathbf{7}^{2+}$ and **14**, do not undergo unthreading, even to a minor extent. The thermal recoordination reaction of **14**, to lead back to $\mathbf{7}^{2+}$, was also studied. Unfortunately, experimental data indicated that this reaction was neither clean nor selective, contrary to the case of the related catenane ($\mathbf{12}' \rightarrow \mathbf{12}^{2+}$) or to the case of the threading reaction of $\mathbf{1}^{2+}$ through **2**.

In summary, Ru(diimine)$_2$-incorporating catenanes and rotaxanes have been synthesized by the templating approach. They represent a new kind of light-driven machine, with a photonic signal being used to set one of the rings in motion by disconnecting it from the ring incorporating the metal centre. In the case of the catenane, simple heating regenerates the starting complex, with both reactions (decoordination and recoordination) being quantitative. Photoinduced expulsion is as efficient for the rotaxane as for the catenane, but for unknown reasons the thermal back-coordination step does not occur satisfactorily in the latter. Unexpected photochemical processes leading to cyclometallated complexes cannot be totally excluded. In addition, the extreme sensitivity of multi-component molecules to mechanical stress and steric hindrance is probably one source of this difference in reactivity. Such sensitivity to the exact mechanical properties of the ring–ring or ring–axis assemblies may be exemplified by the

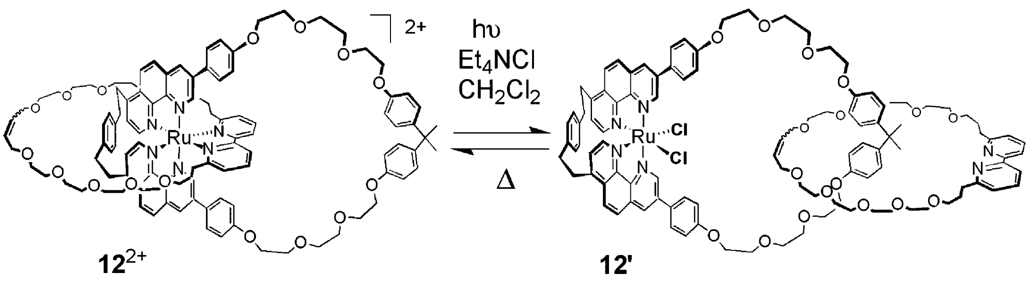
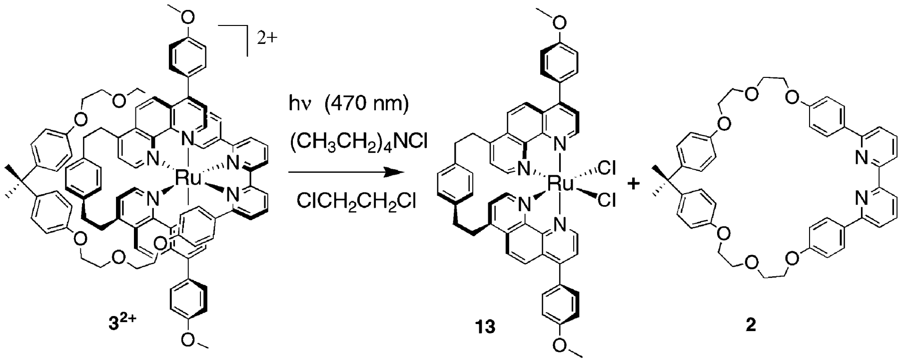
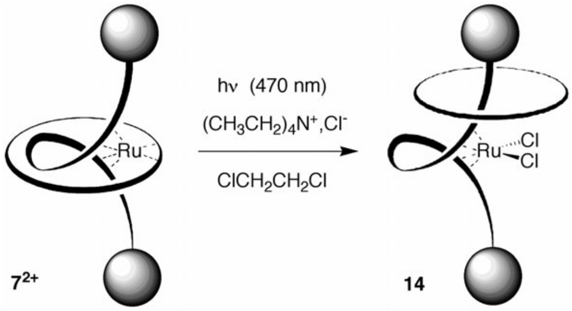


Fig. 8 Catenane $\mathbf{12}^{2+}$ undergoes a complete rearrangement by visible light irradiation. The bpy-containing ring is decoordinated in the presence of Cl$^-$. By heating **12′**, the starting complex $\mathbf{12}^{2+}$ is regenerated. Adapted with permission from ref. 12. Copyright 2004 Wiley-VCH.



3^{2+} **13** **2**

Fig. 9 Photoinduced de-threading of a Ru(diimine)$_3^{2+}$-incorporating pseudo-rotaxane. Reproduced with permission from ref. 15. Copyright 2005 Wiley-VCH.



7^{2+} **14**

Fig. 10 De-threading experiment in a Ru(diimine)$_3^{2+}$-containing rotaxane. Reproduced with permission from ref. 15. Copyright 2005 Wiley-VCH.

photoreactivity difference between catenane $\mathbf{12}^{2+}$ and a similar molecule made with a smaller Ru(phen)$_2$-containing ring (50 atoms instead of 59):[12] under similar irradiation conditions, the reaction half-time of the photochemical de-coordination of the dmbipy-containing ring increased from 38 to 1400 seconds when the size of the ring was decreased. In conclusion, the exact mechanical features of the ring and the axis of the rotaxane need probably to be finely tuned in order to obtain the same behaviour as the catenane.

Model studies towards multi-site molecular machines

In the catenane described above, the ring that is photochemically de-coordinated includes "only" one hindered bidentate chelate. As a result, the motion that is obtained enables the molecule to be compared to a two-state system: the ring is coordinated, or not. Bistable molecular systems and switches may have great applications in the near future,[2] but the ability to switch reversibly by light only from one A state to another B state represents still a greater challenge. The application of polypyridyl ruthenium(II) complexes to molecular switches would require the inclusion of two different ligands in the ring that can be photoexpelled. If possible, coordination of either one or the other ligand to the Ru(phen)$_2$ core would give complexes with different light-absorption properties, so that selective irradiation of one or the other coordination isomer could be done (Fig. 11).

Preliminary studies have been undertaken in this direction. A new series of bidentate chelates were designed and synthesized.[29,30] The first example concerns the dCN$_n$ ligands which incorporate two benzonitrile moieties linked together by a polyethylene glycol –O(CH$_2$)$_n$O– (n = 2, 3 or 4) bridge. These ligands were shown to coordinate efficiently to the Ru(phen)$_2$ core (Fig. 12a). Their corresponding complexes $\mathbf{15}^{2+}$, $\mathbf{16}^{2+}$ and $\mathbf{17}^{2+}$ displayed ^{1}MLCT absorption bands in the near-UV region (380–400 nm), whereas the Ru(phen)$_2$(dmbipy)$^{2+}$ complex absorbs at 465 nm. As in the case of the dmbipy chelate, dCN$_n$ ligands were shown to be quantitatively and selectively photoexpelled by light irradiation in acetonitrile. Thermal back-coordination of the dCN$_n$ ligands from the intermediate Ru(phen)$_2$(CH$_3$CN)$_2^{2+}$ complex is also quantitative. Chelate exchange experiments were undertaken in non-coordinating solvents like acetone or ethoxyethoxyethanol: when Ru(phen)$_2$(dmbipy)$^{2+}$ was irradiated in the presence of a ten-fold excess of dCN$_n$, chelate-to-chelate exchange reaction occurred, which led selectively and quantitatively to Ru(phen)$_2$(dCN$_n$)$^{2+}$ and free dmbipy (Fig. 12b). The dmbipy hindering chelate was thermally back-coordinated to the Ru(phen)$_2$ core by heating the mixture in the dark. This thermal chelate exchange reaction was also quantitative.

Such results were encouraging as the integration of dCN$_n$ ligands in macrocyclic rings could be envisaged. In a catenane

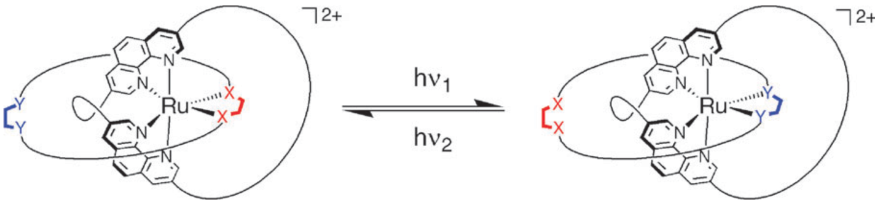


Fig. 11 Switching process based on ruthenium(II) polypyridyl catenanes. Selective irradiation is required for full photochemical control.

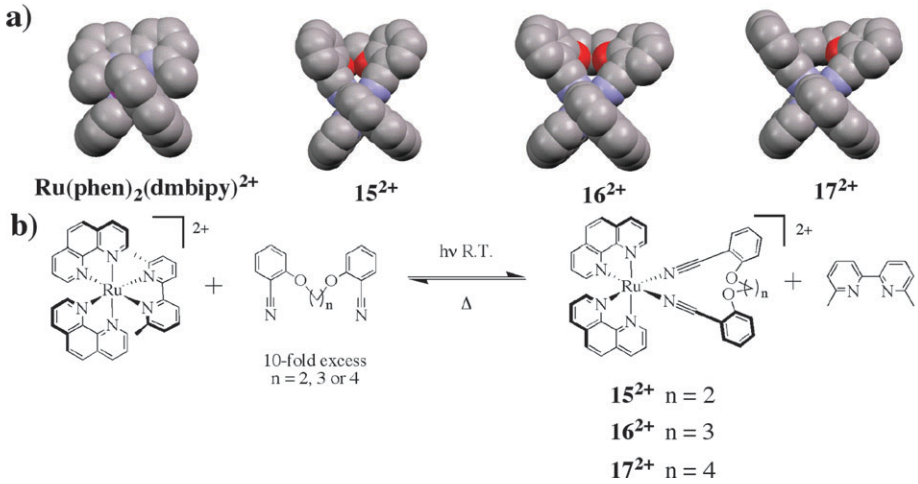


Fig. 12 (a) X-Ray structures of complexes (from left to right) Ru(phen)$_2$(dmbipy)$^{2+}$, $\mathbf{15}^{2+}$, $\mathbf{16}^{2+}$ and $\mathbf{17}^{2+}$; (b) chelate-to-chelate exchange experiment: the dmbipy hindered chelate is photochemically replaced by dCN$_n$ and thermally recovered as the most stable species. Both photochemical and thermal reactions are quantitative.

where one ring would incorporate both one dmbipy and one dCN$_n$ chelate, selective irradiation would lead to a flip-flop motion of the ring. Alternatively, white-light irradiation could be combined with thermal conditions to control the motion of the ring independently of the solvent or, ultimately, in the solid-state.

The second example concerns the potential of bis-thioether ligands BTE$_n$, which have the general formula R–S–(CH$_2$)$_n$–S–R (where R = aryl and n = 2, 3). From the various studies carried out on ruthenium(II)–thioether complexes, it is concluded that the thioether ligand is, as expected, a weak σ-donor but a relatively powerful π-acceptor. It was thus expected that, compared to a diimine chelate, a bis-thioether would be more readily decomplexed. The chemical reaction affording bis-thioether complexes Ru(phen)$_2$(BTE$_n$)$^{2+}$ with two simple bis-thioether ligands (BTE$_2$ and BTE$_3$, defined by R = C_6H_5) is represented in Fig. 13.

The starting complex, Ru(phen)$_2$(CH$_3$CN)$_2$$^{2+}$ was reacted with a slight excess of a given bis-thioether in ethylene glycol (2 h at 140 °C), to afford the desired complex $\mathbf{18}^{2+}$ (n = 2) or $\mathbf{19}^{2+}$ (n = 3) in good yield. These two new complexes were characterized by ^{1}H NMR spectroscopy, electrospray mass spectrometry and X-ray studies. It is noteworthy that only one diastereomer was formed in each case: the *Λ* configuration of the Ru(II) centre corresponds to the *R* configuration of each chiral sulfur atom and *vice versa*. This complexation selectivity reflects the high stability of the isomer formed.

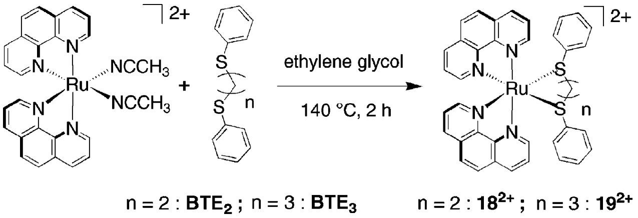


Fig. 13 Synthesis of the bis-thioether complexes Ru(phen)$_2$(BTE$_n$)$^{2+}$: $\mathbf{18}^{2+}$ (n = 2) and $\mathbf{19}^{2+}$ (n = 3). Reproduced with permission from ref. 30. Copyright 2007, Elsevier.

In order to prepare a rotaxane precursor consisting of a wheel threaded by a Ru(phen)$_2$ building block, a bis-thioether motif was also incorporated in a macrocycle. It was hoped that the Ru(phen)$_2$ fragment would form an *endo* complex with the ring, and thus be located in the macrocyclic cavity after complexation. Unfortunately, as discussed later, the complexation mode turned out to be different and an *exo* S-bonded ruthenium(II) complex was obtained. The X-ray structure of the ring, incorporating both a dpbipy unit and an –S(CH$_2$)$_3$S– fragment is represented in Fig. 14.

By analogy with the coordination chemistry of the simple bis-thioethers (Fig. 13) it was expected that the macrocyclic ligand and a ruthenium(II) complex such as [Ru(phen)$_2$-(CH$_3$CN)$_2$]$^{2+}$ would react by heating these reagents in a hydroxylated solvent to afford the desired product. Indeed, by heating [Ru(phen)$_2$(CH$_3$CN)$_2$]$^{2+}$ and the macrocycle in ethylene glycol (115 °C), the expected Ru(II) complex $\mathbf{20}^{2+}$ was obtained in a nearly quantitative yield (Fig. 15). 2D COSY and ROESY NMR experiments raised no ambiguity related to the location of the Ru(phen)$_2$ fragment with respect to the ring. The complex is *exo*, the –S(CH$_2$)$_3$S– bidentate chelate being oriented towards the outside of the macrocycle. This situation is of course very unfavourable with regard to the

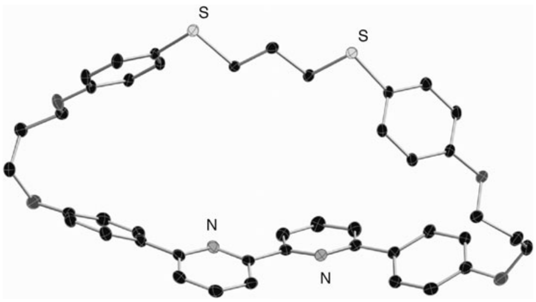


Fig. 14 View of the crystal structure of the macrocycle incorporating both a dpbipy and a bis-thioether unit. Solvent molecules and H atoms are omitted for clarity. Ellipsoids are scaled to enclose 50% of the electronic density. Reproduced with permission from ref. 30. Copyright 2007, Elsevier.

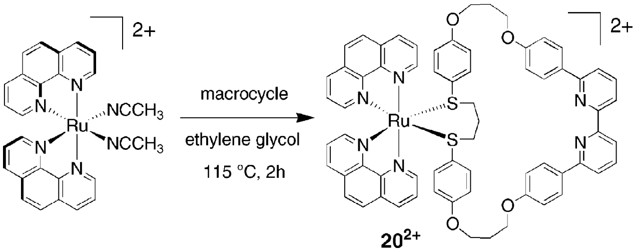


Fig. 15 Synthesis of ruthenium complex $\mathbf{20}^{2+}$. Reproduced with permission from ref. 30. Copyright 2007, Elsevier.

hypothetical formation of future threaded structures supposed to lead to rotaxanes.

Photoreactivity of the bis-thioether ruthenium complexes 18^{2+}, 19^{2+} and 20^{2+}

Under light irradiation (Xe lamp, $\lambda > 340$ nm), the expected ligand exchange takes place as represented in Fig. 16.

The photoinduced ligand substitution was monitored by UV-Vis spectroscopy. The photochemical expulsion of the bis-thioether ligand BTE$_2$ takes place very selectively and efficiently. Clear isosbestic points are observed at 438 nm and 445 nm for $\mathbf{18}^{2+}$ and $\mathbf{19}^{2+}$, respectively. Such photochemical reactions have also been observed in acetonitrile. Monitoring the reaction by ^{1}H NMR spectroscopy confirmed the selective formation of Ru(phen)$_2$(CH$_3$CN)$_2$$^{2+}$, with a complete release of the bis-thioether ligand in less than one hour. For $\mathbf{20}^{2+}$, the photochemical reaction is very similar to that of $\mathbf{18}^{2+}$ and $\mathbf{19}^{2+}$.

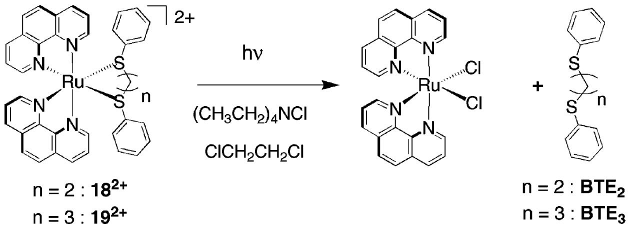


Fig. 16 Light-induced expulsion of the bis-thioether chelate of $\mathbf{18}^{2+}$ and $\mathbf{19}^{2+}$. Reproduced with permission from ref. 30. Copyright 2007, Elsevier.

Use of the Ru(terpy)(phen)(L)$^{2+}$ core

In the Ru(diimine)$_3$$^{2+}$-based systems described above, the ruthenium core acted both as a templating moiety and as a component of the photochemically active central complex responsible for the molecular motion. The ligand to be photo-expelled was a hindered chelate of the 6,6′-dimethylbipyridine (dmbp) type incorporated in a ring. However, most attempts to use different leaving bidentate chelates (like bis-thioether or dCN$_n$) turned out either to be disappointing in terms of quantum yield, or to lead to coordinating geometries that are unfavourable towards inclusion of the ruthenium complex in a molecular ring.[30] Another way of varying such photoreactive systems was to radically change the photochemical core and use a Ru(terpy)(phen)(L)$^{2+}$ moiety, where L is a monodentate ligand (Fig. 2). Visible light irradiation of such complexes leads indeed to selective expulsion of the monodentate ligand and its replacement by a solvent molecule.[24] In Ru(terpy)(phen)(L)$^{2+}$ complexes, the monodentate nature of the leaving ligand L and the less crowded coordination sphere around the ruthenium centre compared to Ru(diimine)$_3$$^{2+}$ complexes inclined us to think that, in future light-driven molecular machines, thermal back-coordination would be easier with the former core than with the latter. The syntheses of complexes of the type Ru(terpy)(phen)(L)$^{2+}$ have been described with a great variety of ligands L (water, acetonitrile, benzonitrile derivatives, pyridines substituted in the 3, 4 and/or 5 position, sulfoxides and thioethers).[31,32] The absorption maxima of these complexes vary with the nature of the monodentate ligands, from ~430 nm for sulfoxides to ~460–470 nm for nitriles and thioethers, ~490 nm for pyridines and 505 nm for water. Controlling the irradiation wavelength would thus enable selective photoexpulsion of one type of ligand in a mixture of complexes with different coordinated monodentate ligands L (see above).[33]

A particularly promising feature of the Ru(terpy)(phen)(L)$^{2+}$ series, in relation to future molecular machines

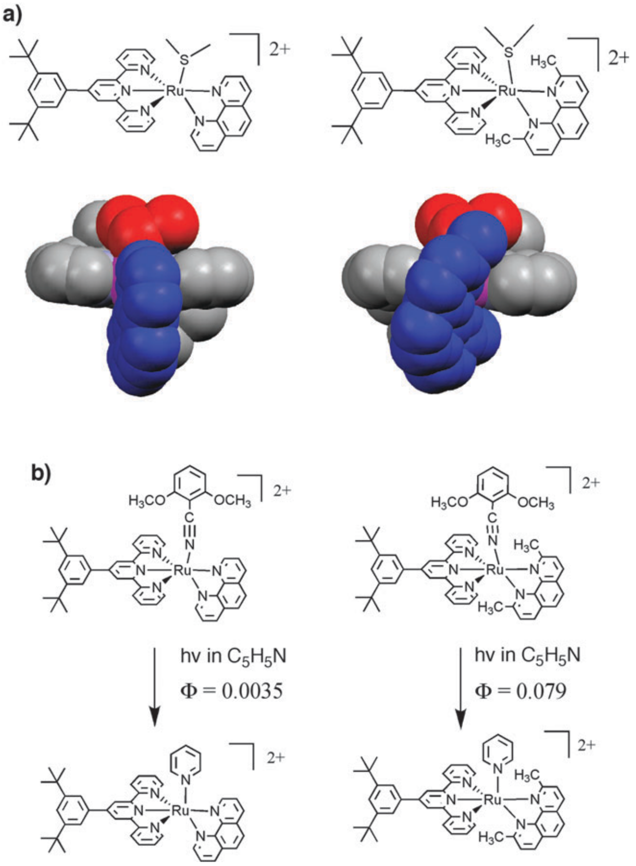


Fig. 17 (a) Increased steric congestion in Ru(dtbp-terpy)(dmp)(dms)$^{2+}$ compared to Ru(dtbp-terpy)(phen)(dms)$^{2+}$ shown by front views of the X-ray structures of both complexes; (b) increased photosubstitution quantum yield with the hindered dmp spectator chelate compared to its unhindered analogue phen. Quantum yield values are given at room temperature in neat pyridine. Adapted with permission from ref. 31. Copyright 2004, the American Chemical Society.

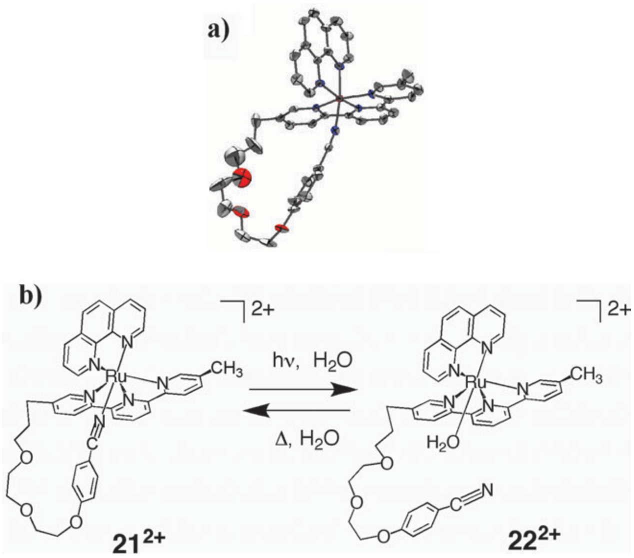


Fig. 18 (a) X-Ray structure of the scorpionate complex **21**$^{2+}$; (b) photoinduced decoordination of the benzonitrile tail in acetone–water and re-coordination by heating in neat acetone.

and motors, is related to the pronounced effect of steric factors on the photochemical reactivity of the complexes.[32] When the bulkiness of the spectator phenanthroline moiety was increased, the steric congestion of the coordination sphere of the ruthenium complex also increased. This congestion was shown by comparison of selected distances and angles in the X-ray crystal structures of hindered and unhindered complexes (Fig. 17a). Such increased structural congestion was qualitatively correlated to an enhanced photoreactivity (Fig. 17b). More specifically, changing 1,10-phenanthroline (phen) for 2,9-dimethyl-1,10-phenanthroline (dmp) increased by one to two orders of magnitude the quantum yield of the photosubstitution reaction of L by pyridine with L = dimethyl sulfide or 2,6-dimethoxybenzonitrile. In the most congested case (Ru(dtbp-terpy)(dmp)(CH_3SCH_3)$^{2+}$) (dtbp-terpy = 4′-(3,5-di-*tert*-butyl)phenyl-2,2′:6′,2″-terpyridine), the photosubstitution quantum yield was shown to be ϕ = 0.36 at room temperature in pyridine, which is an extremely high value in ruthenium(II) photochemistry. The control of the bulkiness of the spectator chelates, leading to 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. This new property, added to the potential variety in monodentate ligands L and to the expected mildness of thermal back-coordination conditions, makes the Ru(terpy)-(phen)(L)$^{2+}$ family a highly promising photoactive core for elaborating future light-driven molecular machines.

As a first application of this new core, a prototype of a photocontrolled molecular machine based on a scorpionate complex of the type Ru(terpy)(phen)(L)$^{2+}$ has been proposed.[5] In complex **21**$^{2+}$, the terpyridine moiety was covalently attached to a benzonitrile ligand by a flexible polyether chain. As shown by an X-ray crystal structure (Fig. 18a), this terminal ligand was bound to the ruthenium atom as the sixth ligand on the coordination sphere of the metal. When irradiated by white light at room temperature in a water–acetone mixture, the benzonitrile moiety was selectively and quantitatively photoexpelled and replaced by a water molecule to give the new complex **22**$^{2+}$ (Fig. 18b). Water being a very weak ligand for the Ru(terpy)(phen)(L)$^{2+}$ core, back-coordination of the benzonitrile ligand takes place within a day at room temperature, or within two hours in refluxing acetone, to yield the starting metallamacrocycle **21**$^{2+}$. These thermal conditions are very mild compared to the back-coordination of the rings in the pseudo-rotaxane or model compounds of the Ru(phen)$_3$$^{2+}$ family; it is 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 photoreactive molecule based on a Ru(terpy)-(phen)(L)$^{2+}$ complex showing large-scale motion at the molecular level (opening and closing of a metallamacrocycle).

Building a Ru(terpy)(phen)(L)$^{2+}$-incorporating macrocycle

Considering the tunable photoreactivity of the Ru(terpy)-(phen) core and the great variety of monodentate ligands that can be coordinated to it, our group was looking for a strategy towards a molecular ring analogue to **9**$^{2+}$ but including the Ru(terpy)(phen) core instead of Ru(phen)$_2$. In the latter case, the use of a *para*-phenylene bridge enabled avoidance of the isomerisation of the Ru(phen)$_2$ coordination pattern during photoexpulsion of the hindered chelate.[27] In the former case, the different symmetry of the complex and the will to avoid time-consuming synthesis of a terpy-phen bridged ligand led into the design of a dissymmetric phenanthroline chelate bearing a hindering mesityl group in the *ortho*-position to one nitrogen atom of the chelate (Fig. 19). The hope was that isomer **b** of Fig. 19 would be avoided. The templated synthesis of rotaxane or catenanes including a Ru(terpy)(phen)(L)$^{2+}$ unit would indeed require that the monodentate ligand L be inside the macrocyclic cavity like in isomer **a** of Fig. 19; in isomer **b** the coordination site for the monodentate ligand is located outside the macrocyclic cavity, which would prevent the formation of pre-rotaxanes or pre-catenanes. The synthesis of macrocycle **23**$^{2+}$ (Fig. 20) by a synthesis-on-the-complex strategy has recently been published.[34] During the synthesis, a coordinated pyridine ligand avoided any interference of the Ru(terpy)(phen)(L)$^{2+}$ moiety with the organic reactions. A Grubbs catalyzed olefin metathesis reaction was the key point for the macrocyclisation step.

The use of a mesityl group in position 2 of the phenanthroline chelate led to unexpected results, as white light irradiation

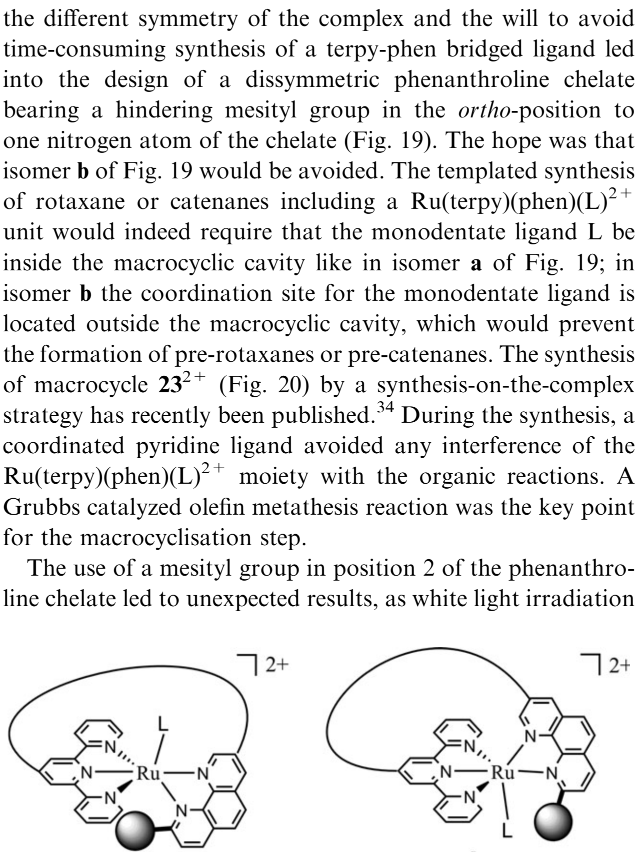


Fig. 19 How to include a Ru(terpy)(phen) in a macrocycle (isomer **a**). Isomer **b** may be avoided by using a hindering group in the 2 position of the phenanthroline unit.

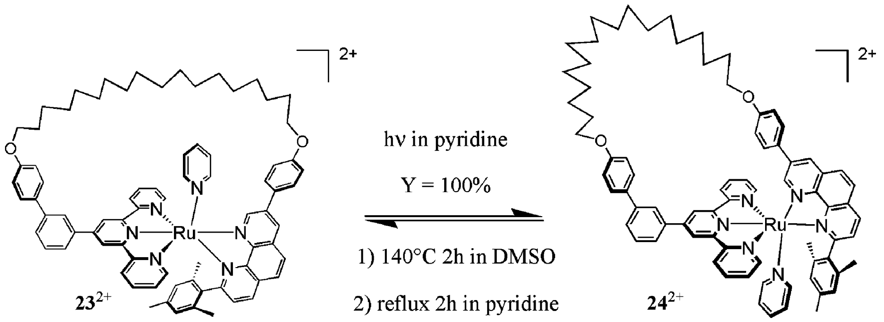


Fig. 20 Major reorganization of a flexible $(CH_2)_{18}$ chain by photoinduced rotation of the phen bidentate chelate. Reverse motion is obtained by heating in DMSO.

of macrocycle $\mathbf{23}^{2+}$ ("thermal" isomer) in pyridine led quantitatively to its coordination isomer $\mathbf{24}^{2+}$ ("photochemical" isomer). In such a photochemical process, the phenanthroline moiety rotated 90° compared to the terpyridine chelate, which induced a major reorganization of the flexible polymethylene chain used to close the macrocycle. Reverse rotation of the phenanthroline was achieved only by heating photochemical isomer $\mathbf{24}^{2+}$ at 140 °C in DMSO for 2 h, followed by thermal ligand exchange in pyridine to recover $\mathbf{23}^{2+}$. The whole process is summarized in Fig. 20.

Such a $Ru(terpy)(phen)(L)^{2+}$ incorporating macrocycle allowed to envision that catenanes or rotaxanes could be constructed on $Ru(terpy)(phen)(L)^{2+}$ compounds. Studies are ongoing to thread monodentate ligand-bearing molecular strings into macrocycle $\mathbf{23}^{2+}$. The work already carried out on molecular machines incorporating the $Ru(diimine)_3{}^{2+}$ moiety will be extended to the new $Ru(terpy)(phen)(L)^{2+}$ photoreactive and templating centre.

Conclusion

The most important motivations of the researchers involved in the field of artificial molecular machines 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. The modern tools available in synthetic chemistry, either from the organic viewpoint or concerning the preparation of transition metal complexes, allow preparation of more and more sophisticated molecular systems. In the present review, we have shown that the combination of the two types of expertise, namely synthesis and photochemistry, permits tackling of problems related to controlled dynamic systems. In the course of the past decades, the archetype $Ru(bpy)_3{}^{2+}$ has been at the origin of an extremely active field of research aimed at converting light energy into chemical energy. It has also been used more recently by a few groups to fabricate light-driven molecular machines. $Ru(diimine)_3{}^{2+}$-type complexes could lead to photochemically labile complexes, able to undergo controlled ligand substitution under light irradiation, provided the three diimine chelates have been substituted in the proper way. Such systems, once incorporated in rotaxanes, catenanes or scorpionates, represent promising light-driven molecular machine prototypes. It must nevertheless be kept in mind that the presently accessible molecular machine prototypes are extremely primitive compared to the beautiful and exceedingly complex molecular machines of 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, but the studies of surfaces and interfaces by new spectroscopic techniques will certainly permit new development for this emerging field in the near future.

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