Artificial molecular-level machines with $[\mathrm{Ru(bpy)}_3]^{2+}$ as a "light-fueled motor"

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ABSTRACT. A molecular-level machine is an assembly of a discrete number of molecular components (that is, a supramolecular structure) designed to perform mechanical-like movements (output) as a consequence of appropriate external stimuli (input). Like macroscopic machines, molecular-level machines are characterized by (i) the kind of energy input supplied to make them work, (ii) the kind of movement performed by their components, (iii) the way in which their operation can be controlled and monitored, (iv) the possibility to repeat the operation at will and establish a cyclic process, (v) the time scale needed to complete a cycle of operation, and (vi) the function performed. The most convenient way to supply energy to an artificial molecular-level machine is through a photochemical reaction. $[\mathrm{Ru(bpy)}_3]^{2+}$ (bpy=2,2'-bipyridine) can be used as a photosensitizer to power mechanical movements in machines based on pseudorotaxanes, rotaxanes and catenanes. Besides being used as an external photosensitizer, $[\mathrm{Ru(bpy)}_3]^{2+}$ can be incorporated in one of the machine components as a "light-fueled" motor. Three types of photochemically driven piston/cylinder systems and a photocontrollable molecular abacus are described. Other kinds of more sophisticated molecular-level machines based on rotaxanes and catenanes are proposed. The extension of the concept of machine to the molecular level is important not only for the sake of basic research, but also for the growth of nanoscience and the development of nanotechnology.

1. INTRODUCTION

From the chemical literature of the last 20 years, it is clear that $[\mathrm{Ru(bpy)}_3]^{2+}$ (bpy=2,2'-bipyridine) is one of the best studied and most used compounds. The reason is that this metal complex exhibits a unique combination of chemical, photochemical, photophysical and electrochemical properties (Figure 1) [1]. On choosing the right counter ion, $[\mathrm{Ru(bpy)}_3]^{2+}$ can be dissolved in a variety of solvents, from dichloromethane to water. It is thermodynamically stable and kinetically inert, and shows very intense ligand centered absorption bands in the UV spectral region and a broad and intense metal-to-ligand charge-transfer (MLCT) band in the visible region with maximum at 450 nm (Figure 2). Its lowest excited state, a formally triplet ^{3}MLCT, is reached with unitary efficiency from the upper lying excited states, is relatively long lived (1.1 μs in deaerated acetonitrile solution at 298 K, 5 μs in rigid matrix at 77 K), and exhibits a moderately intense emission around 600 nm (Φ = 0.07 in deaerated acetonitrile at 298 K). $[\mathrm{Ru(bpy)}_3]^{2+}$ has also very interesting electrochemical properties [2]. In acetonitrile solution at room temperature, it shows a metal-centered oxidation process (Figure 3, left) and three distinct ligand-centered reduction processes (in DMF, at 219 K six reduction

processes are observed, Figure 3 [2](c). In its ^{3}MLCT excited state, $[\mathrm{Ru(bpy)}_3]^{2+}$ is both a good reductant and a good oxidant (Figure 1). Several hundreds of Ru-polypyridine complexes have been synthesized and characterized since it has been found that the redox and excited state properties can be tuned by changing the ligands or ligand substituents [1]. Because of such outstanding properties, $[\mathrm{Ru(bpy)}_3]^{2+}$ as well as other complexes of the Ru-polypyridine family have extensively been used as luminescent, chemiluminescent, and electrochemiluminescent sensors [3], as donor or acceptor species in bimolecular energy- and electron-transfer processes, and as photo- and electroactive building blocks in a variety of supramolecular species [4] (including dendrimers [5]). Particularly worth mentioning is the use of $[\mathrm{Ru(bpy)}_3]^{2+}$ as an electron-transfer photosensitizer in the attempt to achieve photochemical [6] or photoelectrochemical conversion [7] of solar energy.

In this paper we would like to present a novel application of the photoinduced electron-transfer processes of $[\mathrm{Ru(bpy)}_3]^{2+}$, namely the use of this compound as a "light-fueled motor" capable of powering mechanical movements in artificial molecular-level machines [8].

2. ARTIFICIAL MOLECULAR-LEVEL MACHINES

It has long been known that our body can be viewed as a very complex ensemble of molecular-level machines that power our motions, repair dam-

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$(^1MLCT)[Ru(bpy)_3]^{2+}$

$\lambda_{max} = 450\,nm$
$\varepsilon_{max} = 15000\,M^{-1}cm^{-1}$

$\Phi_{isc} = 1$

$E^{\circ\circ} = 2.12\,eV$
$\tau \cong 1\,\mu s$
$\Phi_{em} = 0.07$

$(^3MLCT)[Ru(bpy)_3]^{2+}$

$-0.79\,V$

hv'

$+0.83\,V$

hv

$\lambda_{max} = 610\,nm$

$+1.33\,V$

$-1.29\,V$

$[Ru(bpy)_3]^{3+}$

Ru^{2+}
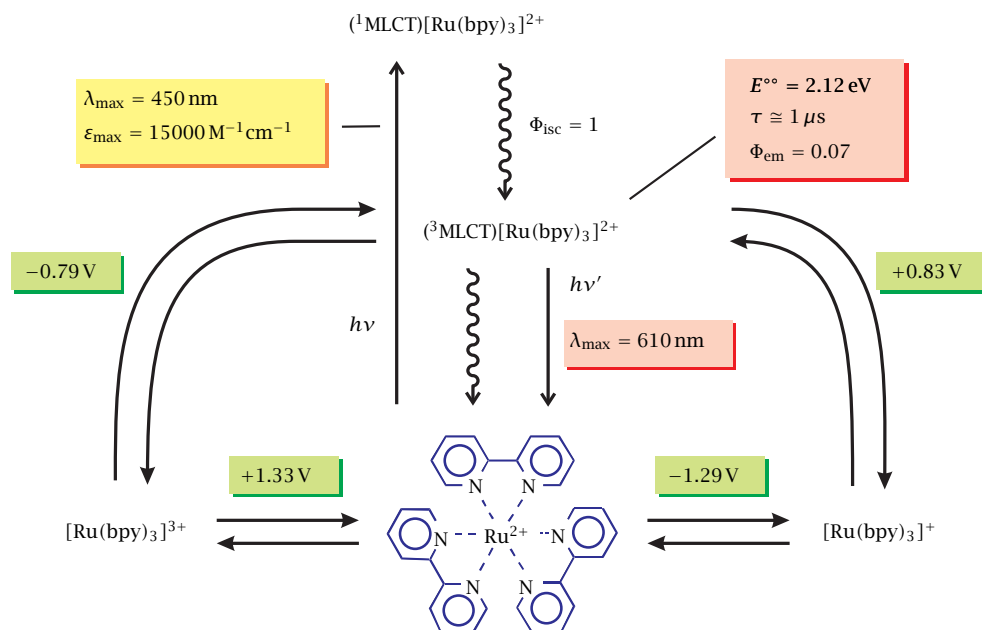
$[Ru(bpy)_3]^{+}$

Figure 1. *Schematic representation of some important properties of* $[Ru(bpy)_3]^{2+}$ *in deaerated acetonitrile solution at 298 K. The potential values are referred to SCE.*
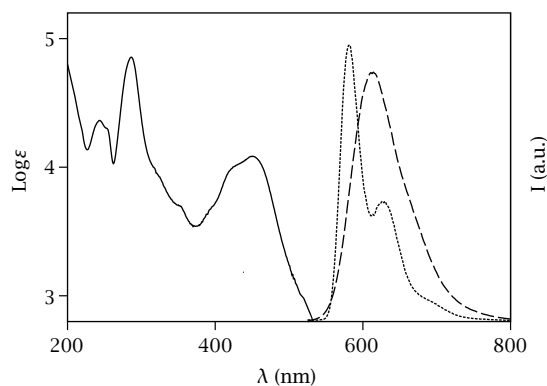
Figure 2. *Absorption (298 K, solid line) and emission (298 K, dashed line; 77 K, dotted line) spectra of* $[Ru(bpy)_3]^{2+}$ *in acetonitrile solution.*
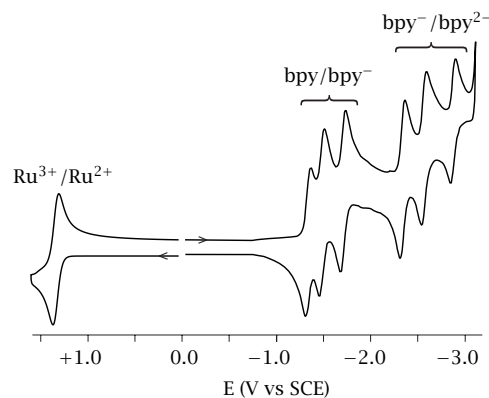
Figure 3. *Cyclic voltammetric behaviour of* $[Ru(bpy)_3]^{2+}$. *Oxidation:* CH_3CN, *298 K; reduction: DMF, 219 K.*

age, and orchestrate our inner worlds of sense, emotion, and thought [9]. The idea of constructing artificial molecular-level machines, however, is quite recent. This topic was briefly discussed for the first time by Richard P. Feynman [10], Nobel Laureate in Physics, in his famous address *There is plenty of room at the bottom* to the American Physical Society in 1959, and only in the last few years systematic studies have been performed in this field [11].

A *molecular-level machine* can be defined as an assembly of a discrete number of molecular components (that is, a *supramolecular* structure) designed to per-

form mechanical-like movements (output) as a consequence of appropriate external stimuli (input). The extension of the concept of machine to the molecular level is important not only for the sake of basic research, but also for the growth of nanoscience and the development of nanotechnology. The miniaturization of components for the construction of useful devices, which is an essential feature of modern technology, is currently pursued by the large-downward (top-down) approach. This approach, however, which leads physicists and engineers to manipulate progressively smaller pieces of matter, has its intrinsic limitations. An alternative and promising strategy is offered by the small-upward

(bottom-up) approach. Chemists, by the nature of their discipline, are already at the bottom, since they are able to manipulate molecules (i.e., the smallest entities with distinct shapes and properties) and are therefore in the ideal position to develop bottom-up strategies for the construction of nanoscale machines.

3. CHARACTERISTICS OF MOLECULAR-LEVEL MACHINES

Molecular-level machines operate via electronic and nuclear rearrangements, i.e., through some kind of chemical reaction. Like macroscopic machines, they are characterized by (i) the kind of energy input supplied to make them work, (ii) the kind of movement performed by their components, (iii) the way in which their operation can be controlled and monitored, (iv) the possibility to repeat the operation at will and establish a cyclic process, (v) the time scale needed to complete a cycle of operation, and (vi) the function performed.

Before discussing in detail the fundamental problem of the energy supply to make artificial molecular-machine work [point (i)], we will briefly comment on the other requirements. The motions performed by these machines [point (ii)] imply substantial changes in the relative positions of the components parts as a consequence of rotations around covalent bonds or the making and breaking of intercomponent noncovalent bonds. In order to control and monitor the machine operation [point (iii)], the motions of the component parts should cause readeable changes in some properties of the system; any kind of chemical or physical techniques can be useful, particularly the various types of spectroscopies. Since a machine has to work by repeating cycles [point (iv)], an important requirement is that any chemical reaction taking place in the machine has to be reversible. The operation time scale [point (v)] can range from less than picoseconds to hours, depending on the nature of the components and the type of rearrangements involved. Finally, the functions that can be performed by exploiting the movements of the components in artificial molecular-level machines [point (vi)] are various and, to a large extent, still unpredictable.

4. ENERGY SUPPLY

The most obvious way to supply energy to a chemical system is through an exergonic chemical reaction. In his address to the American Physical Society, R. P. Feynman observed [10]: *"An internal combustion engine of molecular size is impossible. Other chemical reactions, liberating energy when cold, can be used instead"*. This is exactly what happens in our body, where the chemical energy supplied by food is used in long series of slightly exergonic reactions to power the biological machines that sustain life.

If a molecular-level machine has to work by inputs of chemical energy, it will need addition of fresh reactants ("fuel") at any step of its working cycle, with the concomitant formation of waste products [12]. Accumulation of waste products, however, will compromise the operation of the machine unless they are removed from the system, as it happens in our body as well as in macroscopic internal combustion engines. The need to remove waste products introduces noticeable limitations in the design and construction of artificial molecular-level machines based on "chemical fuel" inputs.

Chemical fuel, however, is not the only means by which energy can be supplied to make artificial molecular machines work. Nature shows that in green plants the energy needed to sustain the machinery of life is supplied by sunlight. Photochemical energy inputs can indeed cause the occurrence of *endergonic* chemical reactions, which can make a machine work without formation of waste products. Currently there is an increasing interest in the development of photon-powered molecular-level machines, taking advantage of the recent, outstanding progress made by supramolecular photochemistry [13].

Photochemical inputs offer other advantages compared to chemical inputs. For example, they can be switched on and off easily and rapidly. It should also be noted that lasers provide the opportunity of working in very small space and very short time domains.

A further advantage offered by the use of photochemical techniques is that photons, besides supplying the energy needed to make a machine work, can also be useful to "read" the state of the system and thus to control and monitor the operation of the machine [14].

Needless to say, the operation of a molecular machine is accompanied by partial conversion of free energy into heat, regardless of the nature of the energy input.

In this paper we will review our work on photochemically-driven molecular-level machines developed in collaboration with the group of Professor J. F. Stoddart and investigated in our laboratory. A comprehensive review on artificial molecular-level machines has recently appeared [11](d).

5. PSEUDOROTAXANES, ROTAXANES, AND CATENANES

Since the molecular-level machines discussed in this paper are based on pseudorotaxanes, rotaxanes, and catenanes, we will briefly recall some relevant features of these multicomponent systems.

Rationale and efficient synthetic approaches for the preparation of pseudorotaxanes, rotaxanes and catenanes are available [15]. The strategies chosen by Stoddart and coworkers (Figure 4) [16] are based on
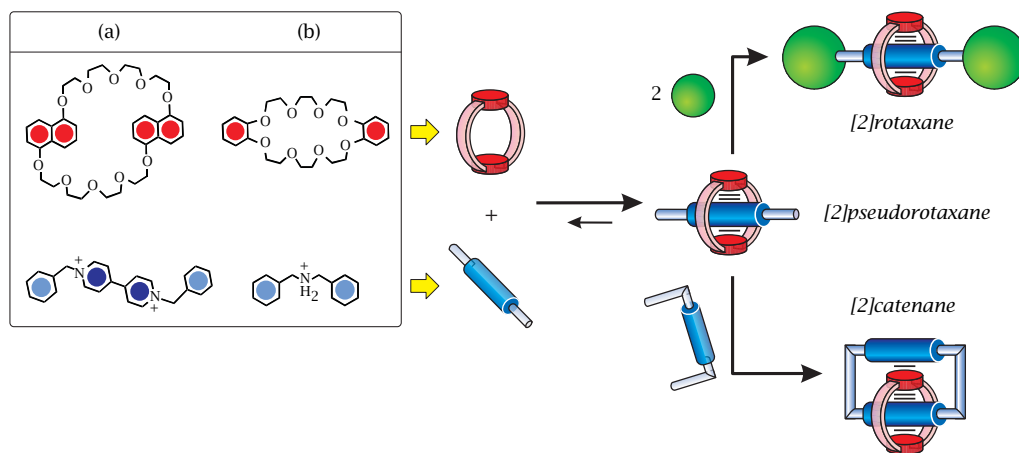
Figure 4. *Pictorial representation of the self-assembly of pseudorotaxanes based on (a) charge-transfer and* $C - H \cdots O$ *hydrogen-bonding interactions and (b)* $NH_2^+ \cdots O$ *hydrogen-bonding interactions. Routes towards the syntheses of rotaxanes and catenanes are also schematized.*

(i) charge-transfer and $C - H \cdots O$ hydrogen-bonding interactions between an electron-acceptor (e.g., 1,1'-dibenzyl-4,4'-bipyridinium dication) and an electron-donor (e.g., 1,5-dinaphtho[38]crown-10), and/or (ii) hydrogen bonding interactions between secondary ammonium functions (e.g., dibenzylammonium ion) and a suitable crown ether (e.g., dibenzo[24]crown-8). The charge-transfer (CT) interaction between electron-donor and electron-acceptor units introduces low energy CT excited states which are responsible not only for the presence of broad and weak absorption bands in the visible region, but also for the quenching of the potentially luminescent excited states localized on the molecular components. Figure 5(a) shows a schematic energy-level diagram for catenane $\mathbf{2}^{4+}$ and its separated components cyclobis(paraquat-*p*-phenylene) ($\mathbf{1}^{4+}$) and 1,5-dinaphtho[38]crown-10 (**3**). It should be noted that, when engaged in CT interactions, the electron-donor and electron-acceptor units become more difficult to oxidize and to reduce, respectively (Figure 5(b)). Furthermore, units which are topologically equivalent and not interacting in an isolated component may not be so when the component is engaged in non-symmetric interactions with another component. In pseudorotaxanes, rotaxanes, and catenanes based on CT interactions, mechanical movements can be promoted by destroying such interactions, i.e., by reducing the electron-acceptor unit(s) or oxidizing the electron-donor one(s). This result can be achieved by chemical, electrochemical, or photochemical reactions. In most cases, the CT interaction can be restored by an opposite redox process, which thus promotes a reverse mechanical movement leading back to the original structure.

Contrary to what happens in the case of CT interactions, hydrogen-bonding interactions between secondary ammonium centers and suitable crown ethers do not introduce low lying energy levels. Therefore, even if the absorption bands of the molecular components of pseudorotaxanes, rotaxanes and catenanes based on this kind of interaction are often perturbed compared with the corresponding absorption bands of the isolated molecular components, no new band is present in the visible region. As far as luminescence is concerned, in the supramolecular architecture each component maintains its potentially luminescent levels, but intercomponent photoinduced energy- and electron-transfer processes can occur. The electrochemical properties of the separated components are more or less modified when the components are assembled. In these compounds, mechanical movements can be caused by acid/base chemical inputs that create/destroy the hydrogen bonding interaction which is responsible for assembly and spatial organization. The easiest way to produce an acid/base input is, of course, the addition of suitable chemical species, but photochemical and electrochemical inputs can also be used in principle.

The simplest machine-like behaviour that can be obtained by redox and/or acid/base inputs in pseudorotaxanes, rotaxanes, and catenanes are schematized in Figure 6.

6. LIGHT AS ENERGY SUPPLY IN MOLECULAR-LEVEL MACHINES BASED ON CT INTERACTIONS

As mentioned above, systems stabilized by electron donor-acceptor interactions exhibit CT bands in their absorption spectra. Light excitation of the CT bands leads formally to the transfer of an electron from the
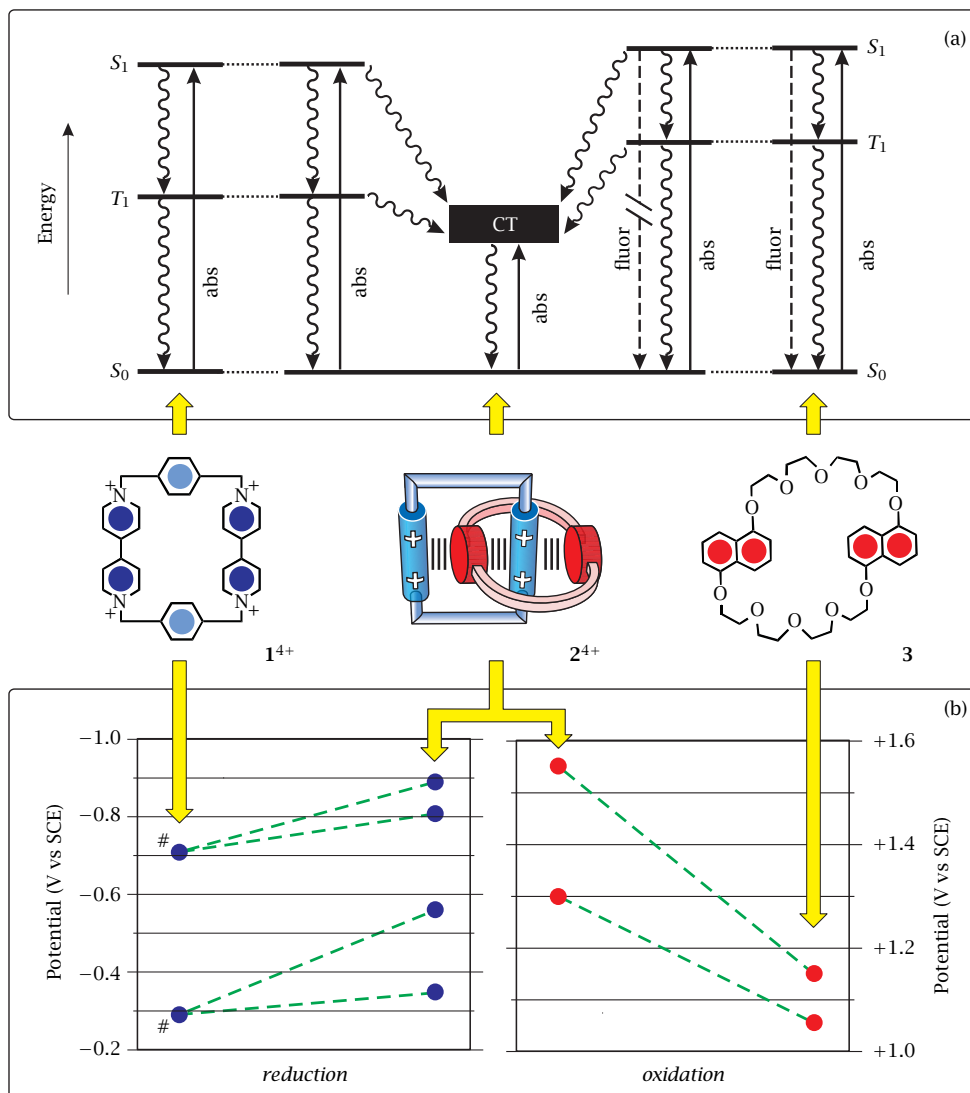
Figure 5. *(a) Schematic energy-level diagram for catenane 2^{4+} and its separated components. The wavy lines indicate nonradiative decay paths of the electronic excited states. (b) Correlations between potential values obtained for catenane 2^{4+} and its separated components. Processes marked with # involve two electrons (*CH_3CN*, 298 K).*

donor to the acceptor component and is therefore expected to destabilize the structure based on CT interaction. For example, in the pseudorotaxane formed by the tetracationic cyclophane 1^{4+} and a thread-like species containing a 1,5-dioxynaphthalene unit (Figure 7) [17], light excitation causes destabilization of the pseudorotaxane structure. However, no de-threading of the two components can be observed because of the occurrence of a very fast (picosecond time scale) back electron-transfer process that deactivates the CT excited state and restores the ground state CT interaction [18]. In other words, the destabilization time scale is much shorter than the time required by the extensive nuclear movements needed for the dethreading process (or, more gen-

erally, for changing the supramolecular structure of pseudorotaxanes, rotaxanes and catenanes). Therefore, the possibility of causing a machine-like movement by direct light excitation of CT-based systems is precluded.

In order to cause extensive light-driven nuclear motions, a longer lasting (as a limiting case, a permanent) destabilization of the CT interaction must be produced. This result can be obtained by introducing into the system a photosensitizer capable of causing a long lived (or permanent) reduction of the acceptor or oxidation of the donor involved in the CT interactions. We have found that $[Ru(bpy)_3]^{2+}$, because of its outstanding excited state and redox properties, can indeed play this role, as described in the next sections.
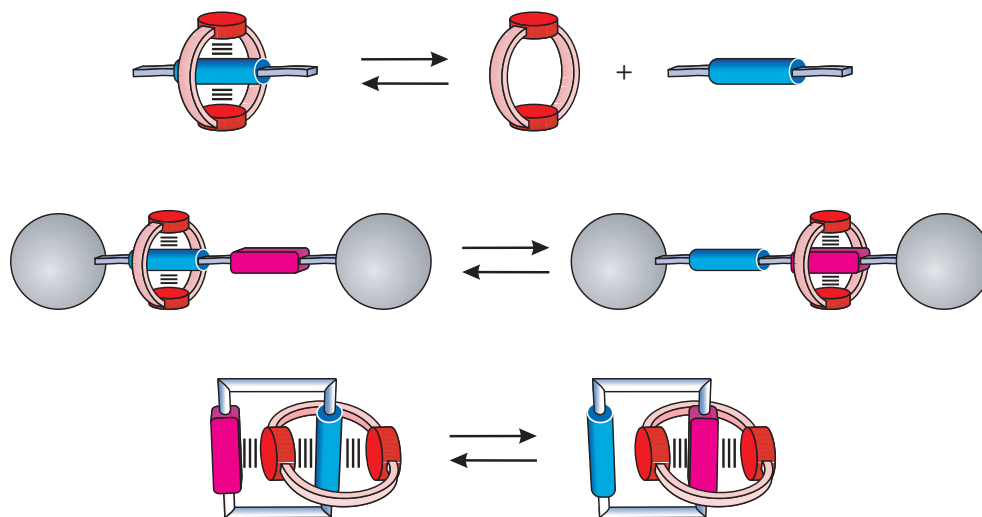
Figure 6. *Machine-like movements that can be obtained by redox and/or acid/base inputs in pseudorotaxanes, rotaxanes, and catenanes.*
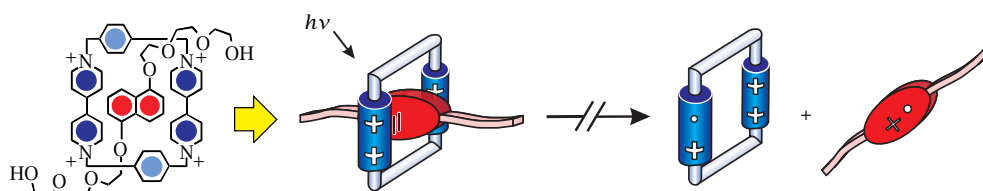

Figure 7. *A pseudorotaxane based on CT interaction between the tetracationic cyclophane $\mathbf{1}^{4+}$ and a thread like species containing a $1,5$-dioxynaphthalene unit. Direct light excitation does not cause dethreading.*

7. $[\mathrm{Ru(bpy)}_3]^{2+}$ AS A "LIGHT-FUELED MOTOR" IN PSEUDOROTAXANES

Dethreading/rethreading of the wire and ring components of a pseudorotaxane reminds the movement of a piston in a cylinder. This mechanical movement has been successfully performed by light inputs using $[\mathrm{Ru(bpy)}_3]^{2+}$ as a photosensitizer in three different systems.

7.1. Intermolecular photosensitization. The first attempt to induce dethreading of a pseudorotaxane by light excitation was performed by using $[\mathrm{Ru(bpy)}_3]^{2+}$ as an external electron-transfer photosensitizer and triethanolamine as a sacrificial reductant (Figure 8(a)) [17]. In deaerated solution, irradiation with visible light of $[\mathrm{Ru(bpy)}_3]^{2+}$ causes the permanent reduction of one of the bipyridinium units of the ring since the back electron-transfer reaction is prevented by the reaction of $[\mathrm{Ru(bpy)}_3]^{3+}$ with triethanolamine. Once the ring has received an electron, the interaction responsible for the pseudorotaxane structure is partly destroyed and therefore the wire dethreads from the reduced ring. If oxygen is allowed to enter the irradiated solution,

oxidation of the reduced bipyridinium unit restores the interaction and causes rethreading. The threading, dethreading, and rethreading processes can be easily monitored by absorption and fluorescence spectroscopy [17].

7.2. Intramolecular photosensitization. Second generation photochemically driven piston/cylinder systems have then been designed, in which the pseudorotaxane structure incorporates $[\mathrm{Ru(bpy)}_3]^{2+}$ as a "light-fueled motor" in the wire (Figure 8(b)) [20] or in the macrocyclic ring (Figure 8(c)) [21]. In deaerated solution excitation of $[\mathrm{Ru(bpy)}_3]^{2+}$ with visible light in the presence of a sacrificial donor causes, in both cases, permanent reduction of the electron-acceptor unit and, as a consequence, dethreading takes place. Rethreading can again be obtained by allowing oxygen to enter the solution, as evidenced by changes in the spectroscopic properties (absorption and emission) of the system. Many dethreading/rethreading cycles can be performed on the same solution without any appreciable loss of signal until most of the reductant scavenger is consumed.
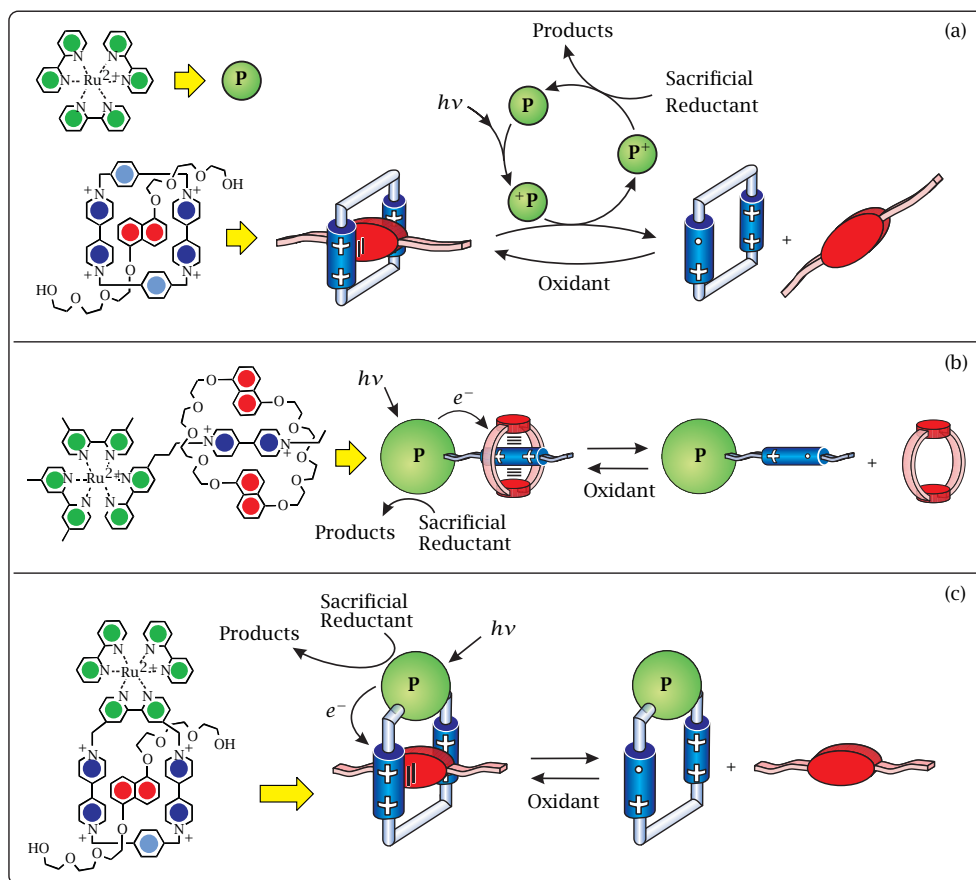
Figure 8. *Light-driven dethreading of pseudorotaxanes by excitation of a photosensitizer (a) as an external reactant; (b) as a stopper in the wire-type component; (c) as a component of the macrocyclic ring. Rethreading is obtained by adding an external oxidant such as oxygen.*

It should be pointed out that in the above described systems light excitation drives only the dethreading movement, and that waste chemical species are produced in the forms of the products of the sacrificial electron donor (triethanolamine) and acceptor (dioxygen). Recently, we have studied a system (Figure 9) [22], based on azobenzene isomerization, where dethreading/rethreading is exclusively governed by light energy without generation of any waste product.

8.   [Ru(bpy)$_3$]$^{2+}$ AS A "LIGHT-FUELED MOTOR" IN ROTAXANES

8.1. A photocontrollable molecular abacus.   In order to achieve photoinduced ring switching in rotaxanes containing two different recognition sites in the dumbbell-shaped component, the thoroughly designed compound **4**$^{6+}$ shown in Figure 10 was synthesized [23]. This compound is made of the electron-donor macrocycle **R** and a dumbbell-shaped component which contains (i) [Ru(bpy)$_3$]$^{2+}$ (**P**) as one of its stoppers, (ii) a 4,4'-bipyridinium unit (**A$_1$**) and a 3,3'-dimethyl-4,4'-bipyridinium unit (**A$_2$**) as electron accepting stations, (iii) a *p*-terphenyl-type ring system as a rigid spacer (**S**), and (iv) a tetraarylmethane group as the second stopper (**T**). The structure of rotaxane **4**$^{6+}$ was characterized by mass spectrometry and NMR spectroscopy, which also established, along with cyclic voltammetry, that the stable translational isomer is the one in which the **R** component encircles the **A$_1$** unit, in keeping with the fact that this station is a better electron acceptor than the other one. The electrochemical, photophysical and photochemical (under continuous and pulsed excitation) properties of the rotaxane, its dumbbell-shaped component, and some model compounds have then been investigated and two strategies have been devised in order to obtain the photoinduced abacus-like movement of the **R** macrocycle between the two stations **A$_1$** and **A$_2$**: one was based on processes involving only the rotaxane components (intramolecular mechanism), while
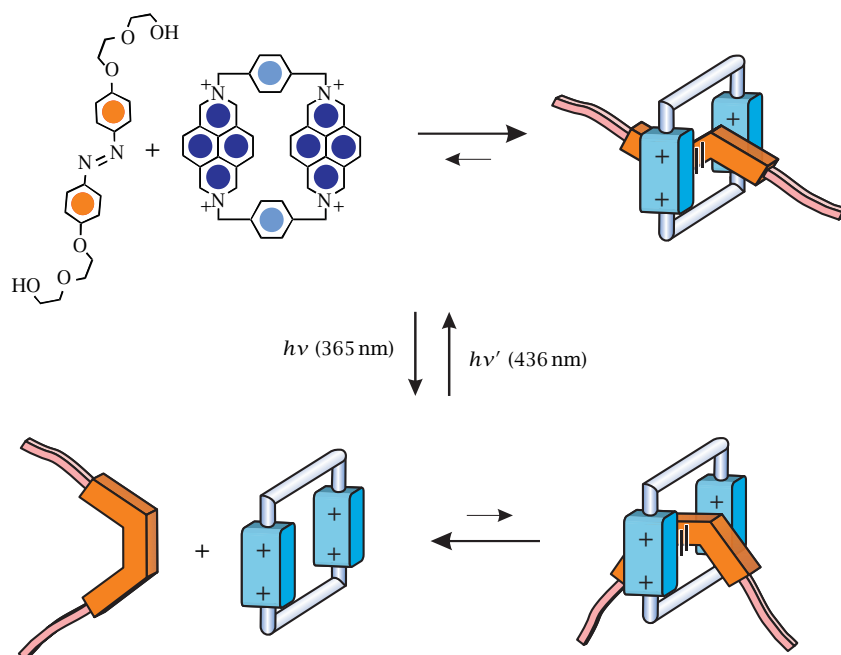
Figure 9. *Dethreading/rethreading of a pseudorotaxane as a consequence of the photoinduced cis-trans isomerization of the thread-like component.*

the other one required the help of external reactants (sacrificial mechanism).

The intramolecular mechanism, illustrated in the left part of Figure 10, is based on the following four operations [23]:

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

(b) *Ring displacement:* the ring moves from the reduced station A_1^- to A_2 (Step 4), a step that has to compete with the back electron-transfer process from A_1^- (still encircled by **R**) to the oxidized photoactive unit P^+ (Step 5). This is the most difficult requirement to meet in the intramolecular mechanism.

(c) *Electronic reset:* a back electron-transfer process from the "free" reduced station A_1^- to P^+ (Step 6) restores the electron-acceptor power to the A_1 station.

(d) *Nuclear reset:* as a consequence of the electronic reset, back movement of the ring from A_2 to A_1 takes place (Step 7).

The results obtained [23] seem to indicate that electronic reset of the system after light excitation (Step 5; $k = 2.4 \times 10^5 \, s^{-1}$) is faster than the ring displacement (Step 4). We are now trying to modify the system in the attempt to further decrease the rate of the back

electron-transfer reaction (Step 5) so as to achieve the displacement of the ring (Step 4) before the occurrence of the electronic reset. It is worthwhile noticing that in a system which behaves according to the intramolecular mechanism shown in Figure 10 (left) each light input causes the occurrence of a forward and back ring movement (i.e., a full cycle) without generation of any waste product. In some way, it can be considered as a "four-stroke" cyclic linear motor powered by light.

The alternative, less demanding mechanism is based on the use of external sacrificial reactants (a reductant like triethanolamine and an oxidant like dioxygen) that operate as illustrated in the right part of Figure 10:

(a) *Destabilization of the stable translational isomer*, as in the previous mechanism.

(b') *Ring displacement after scavenging of the oxidized photoactive unit:* since the solution contains a suitable sacrificial reductant, a fast reaction of such species with P^+ (Step 8) competes successfully with the back electron-tranfer reaction (Step 5); therefore, the originally occupied station remains in its reduced state A_1^-, and the displacement of the ring **R** to A_2 (Step 4), even if it is slow, does take place.

(c') *Electronic reset:* after an appropriate time, restoration of the electron-acceptor power of the A_1 station is obtained by oxidizing A_1^- with a suitable oxidant, such as O_2 (Step 9).

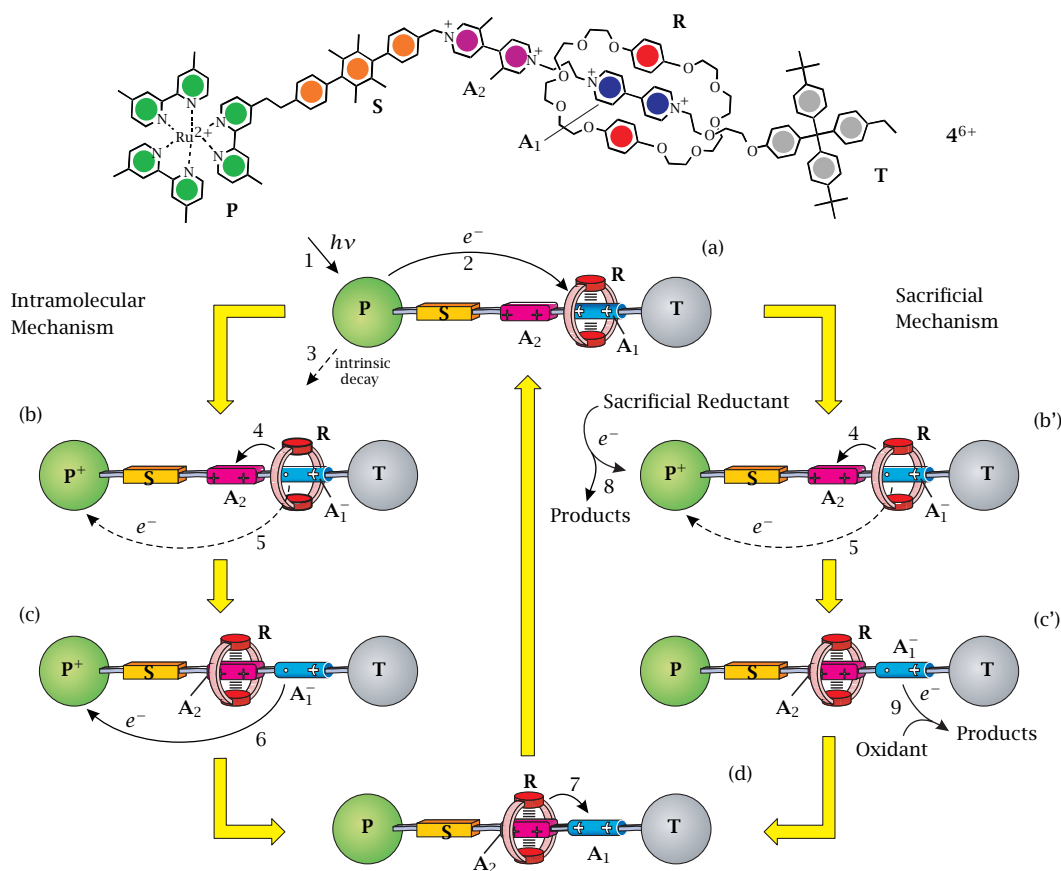(d) *Nuclear reset*, as in the previous mechanism (Step 7).

Figure 10. *Rotaxane 4^{6+} and schematic representation of the intramolecular (left) and sacrificial (right) mechanisms for the photoinduced abacus-like movement of macrocycle R between the two stations A_1 and A_2.*

The results obtained show that such a sacrificial mechanism is fully successful. Of course, this mechanism is less appealing than the intramolecular one because it causes the formation of waste products.

8.2. Rotaxanes as photocarriers.

The photoinduced movement of the ring component along the dumbbell in rotaxanes can be exploited to transport chemical species by light inputs. Such a photocarrier function can be performed by appending to the shuttling macrocycle a guest or host unit capable of recognizing and linking an external species. For example, the shuttling macrocycle can be functionalized with a secondary ammonium function capable of coordinating a crown ether by hydrogen bonding, as schematized in Figure 11(a). Shuttling of the macrocycle is controlled by light inputs as described in the previous section, while loading and unloading of the transported crown ether can be controlled by acid/base inputs.

A number of other functions based on rotaxanes as carriers can be devised, such as, for example, photoinduced stretching of a molecular spring (Figure 11(b)), a movement that could be at the basis of artificial molecular-level muscles [24].

9. $[Ru(bpy)_3]^{2+}$ AS A "LIGHT-FUELED MOTOR" IN CATENANES

In a catenane, structural changes caused by circumrotation of one ring with respect to the other can be evidenced only when one ring contains two non-equivalent units. Examples of catenanes of this type are shown in Figure 12 [25, 26]. In catenane 5^{4+} one ring contains two equivalent electron donors, namely, two dioxybenzene units, while in the other ring two different electron acceptors, namely, a bipypiridinium (A_1) and a *trans*-bis(pyridinium)ethylene (A_2) units, are present. In catenane 6^{4+} the situation is reversed: the electron-acceptor ring contains two equivalent A_1 units, while the electron-donor ring comprises two different units, namely, a tetrathiafulvalene (TTF, D_1) and a 1,5-dioxynaphthalene (D_2) moiety.

In catenane 5^{4+}, the stable translational isomer is that in which the A_1 unit occupies the inside position of the electron-donor ring since A_1 is a better electron acceptor than A_2. In such a structure, indeed, A_1 experiences the effect of both the electron-donor units. Analogous considerations on the donor ability of D_1 and D_2 moieties allow to establish that for catenane 6^{4+}
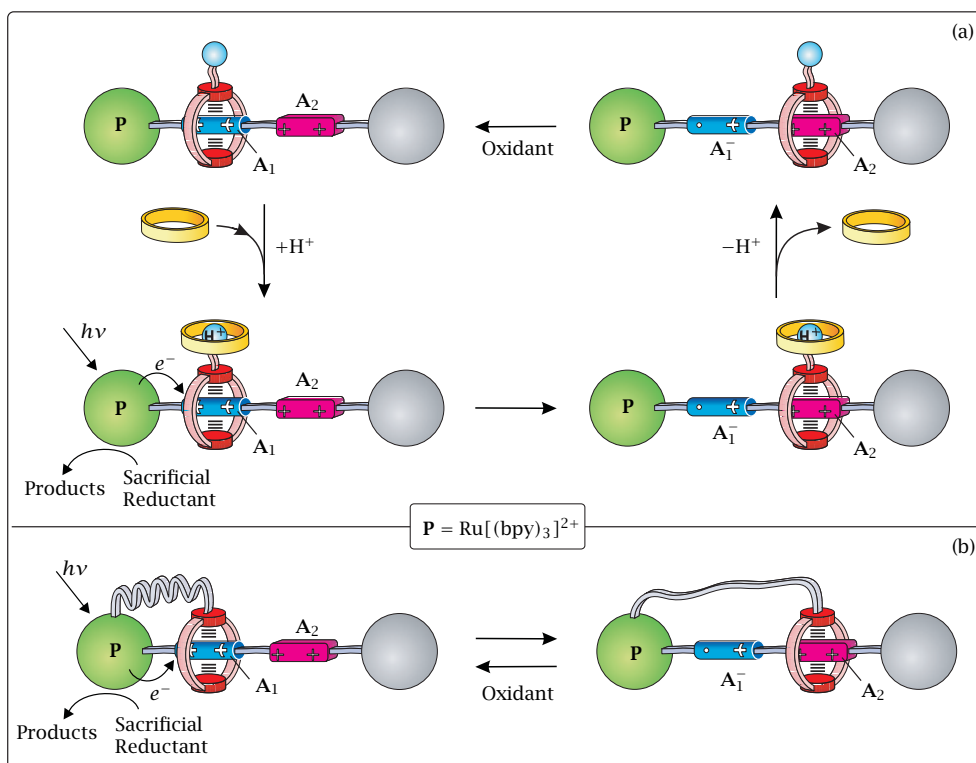
Figure 11. *A rotaxane carrier powered by light inputs designed to perform (a) transport of a crown ether and (b) stretching of a molecular spring.*
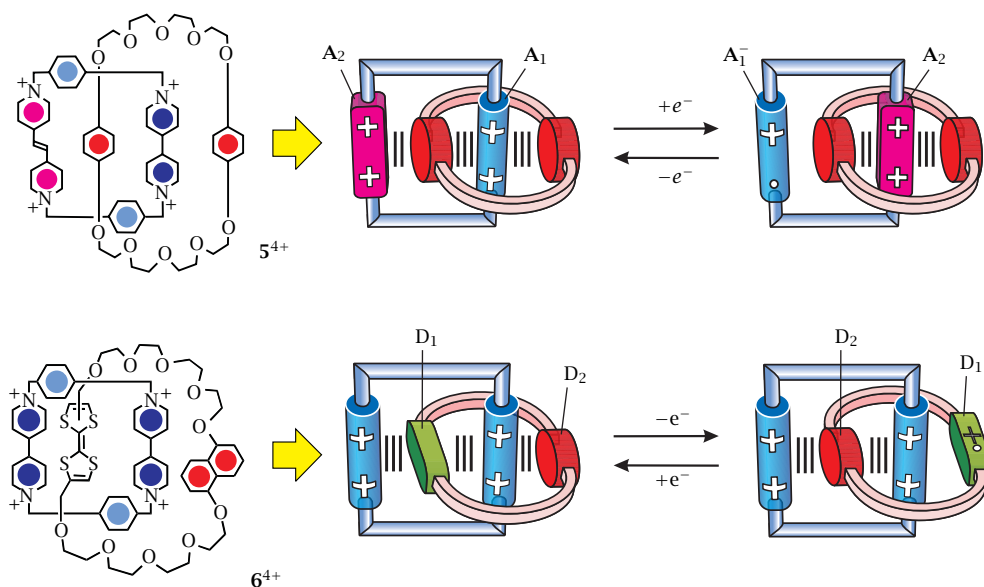

Figure 12. *Examples of catenanes containing a non-symmetric ring and pictorial representation of redox driven ring rotation.*
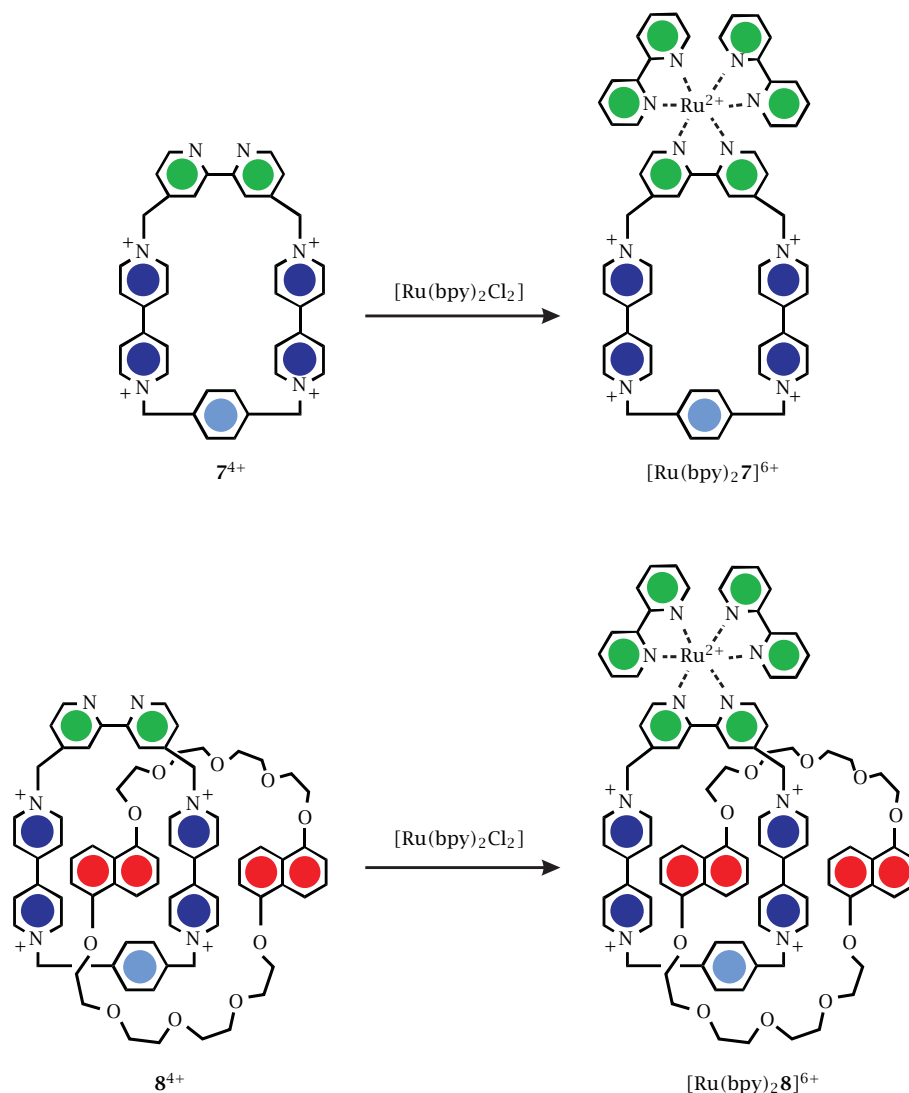
Figure 13. *Cyclophane ligand 7^{4+}, complex* [Ru(bpy)$_2$$7$]$^{6+}$, *catenane ligand 8^{4+} and catenane complex* [Ru(bpy)$_2$$8$]$^{6+}$.

the stable structure is that with TTF inside the electron-acceptor ring.

For catenane 5^{4+} electrochemical reduction of A_1 (easier to reduce than A_2) and for catenane 6^{4+} electrochemical oxidation of D_1 (easier to oxidize than D_2) destroyes the CT interaction that stabilizes the original structure. As a consequence, a circumrotation takes place yielding, for catenane 5^{4+}, the A_2 unit inside the electron-donor ring, and, for catenane 6^{4+}, the D_2 unit inside the electron-acceptor ring. The initial structure of catenanes 5^{4+} and 6^{4+} can be restored by oxidation of A_1^- and reduction of D_1^+, respectively.

Taking into account the redox properties of the excited state of [Ru(bpy)$_3$]$^{2+}$, it should be possible to induce photochemically the reduction of the A_1 unit (oxidative quenching) in catenane 5^{4+}, and the oxidation

of the D_1 moiety (reductive quenching) in catenane 6^{4+}, thereby causing circumrotation. As seen in Section 7, [Ru(bpy)$_3$]$^{2+}$ could be used as an external electron-transfer photosensitizer (intermolecular mechanism) or, more appealing, it can be incorporated in the machine (intramolecular mechanism).

9.1. Incorporation of [Ru(bpy)$_3$]$^{2+}$ *in catenane structures.* Starting from the 7^{4+} cyclophane ligand, used to obtain the previously seen (Section 7, Figure 8(c)) [Ru(bpy)$_2$$7$]$^{6+}$ complex, it was possible to prepare the catenane ligand 8^{4+} and the catenane complex [Ru(bpy)$_2$$8$]$^{6+}$ (Figure 13) [27]. This compound shows an interesting electrochemical behavior (Figure 14), with processes that can be assiged to (i) reduction of the bipyridinium- and bpy-type moieties of the catenane
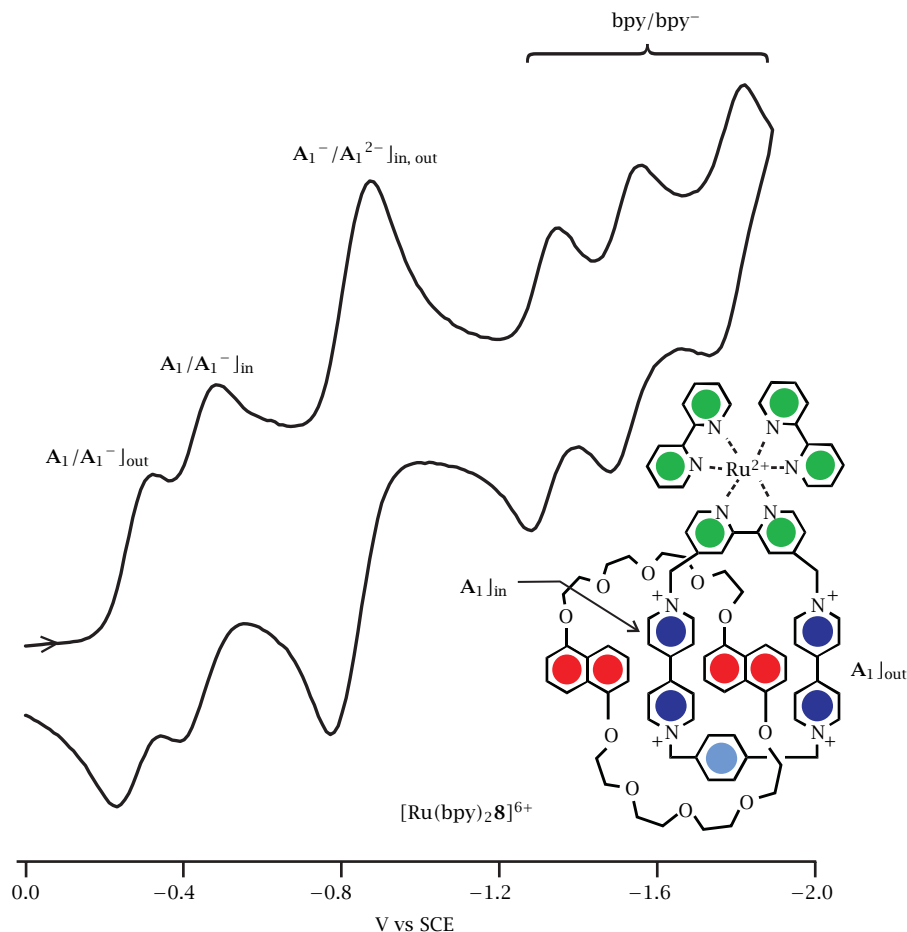
Figure 14. *Electrochemical behavior on reduction of the catenane complex* $[\mathrm{Ru(bpy)_2 8}]^{6+}$ *(*$\mathrm{CH_3 CN}$*, 298 K).*

ligand, (ii) reduction of the bpy ligands, (iii) oxidation of the metal, and (iv) oxidation of the dioxynaphthalene moieties of the crown ether. Catenane $[\mathrm{Ru(bpy)_2 8}]^{6+}$ is "symmetric" and therefore it is not suitable for investigations on ring rotations. For such kind of studies, we propose to incorporate $[\mathrm{Ru(bpy)_3}]^{2+}$ as a "light-fueled motor" in the electron-acceptor rings of catenanes $\mathbf{5}^{4+}$ and $\mathbf{6}^{4+}$, as shown in Figure 15. In such modified systems ring rotation could be photoinduced via intramolecular electron transfer from the excited $[\mathrm{Ru(bpy)_3}]^{2+}$ moiety to the bipyridinium unit in the presence of a reducing sacrificial species (catenane $\mathbf{9}^{6+}$), and from the TTF unit to the excited $[\mathrm{Ru(bpy)_3}]^{2+}$ moiety in the presence of an oxidizing sacrificial species (catenane $\mathbf{10}^{6+}$) [28].

10.   PERSPECTIVES

The results so far achieved with pseudorotaxanes, rotaxanes and catenanes constitute the starting basis for the design of more sophisticated molecular-level machines. An example is described below.

Combination of a catenane and a rotaxane motif in a supramolecular structure, "rotacatenane" [29], can lead to molecular machines capable of coupling distinct mechanical movements. By suitable design it should be possible, for example, to construct a rotacatenane in which a "linear" shuttling motion is coupled with a "rotary" ring motion. In principle, this goal could be reached by the rotacatenane schematized in Figure 16, which is made of (i) a macrocyclic crown ether $\mathbf{C}_1$ containing an electron-donor unit, (ii) a macrocycle $\mathbf{C}_2$ containing a bipyridinium-type electron-acceptor unit, and (iii) a dumbbell-shaped component containing an electron donor, a bulky amine/ammonium function, and a $[\mathrm{Ru(bpy)_3}]^{2+}$ stopper. The working scheme of this machine can be twofold, depending on the relative strength of the hydrogen-bonding and charge-transfer interactions. If the hydrogen-bonding interaction is stronger than the CT one (Figure 16, top), the stable structure is that in which the dumbbell-shaped component occupies macrocycle $\mathbf{C}_1$ with the ammonium function (structure $\mathbf{I}$), while the acceptor unit of macrocycle $\mathbf{C}_2$, because of steric and electrostatic rea-
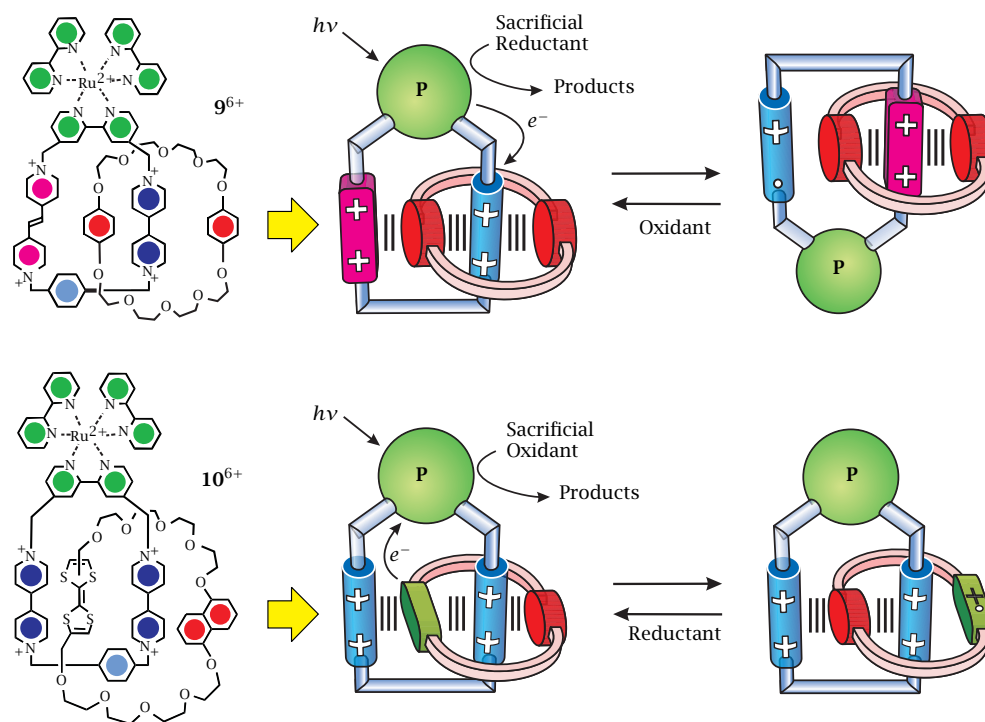
Figure 15. *Suggested systems for obtaining light-driven circumrotation in a catenane.*

sons, cannot be inside the C_1 ring and gives rise to a CT interaction with the donor unit of C_1 from the alongside position. Upon deprotonation, the amine function of the dumbell gets out of macrocycle C_1 and the electron-acceptor moiety of C_2 goes into C_1 together with the electron-donor unit of the dumbell causing coupled "linear" and "rotary" motions which lead to structure **II**, stabilized by a donor-acceptor-donor interaction. Reprotonation of the amine function of the dumbell reverses the movements and leads back to structure **I**. If, however, the CT interaction of the electron-acceptor unit of C_2 with both the donor units of the dumbell component and of C_1 prevails (Figure 16, bottom), the stable structure is **III**. In such a case, reduction of the electron-acceptor unit of C_2 by photoinduced electron transfer from excited $[Ru(bpy)_3]^{2+}$ stopper in the presence of a sacrificial reductant would cause coupled "linear" and "rotary" motions to yield structure **IV**. Addition of a sacrificial oxidant would lead back the system to structure **III**.

Generally speaking, it should be pointed out that the mechanical movements of the above discussed molecular-level machines are associated with a binary logic behavior. This opens the way to the possibility of using these systems as components for the construction of electronic devices [30] and, in the future, of chemical computers [31].

11.   CONCLUSION

$[Ru(bpy)_3]^{2+}$ and related complexes have played a key role in the development of photochemistry, photophysics, photocatalysis, electrochemistry, radiation chemistry, chemi- and electrochemi-luminescence, electron and energy transfer. From the applicative viewpoint, these complexes have been used as photosensitizers in solar energy conversion systems [7], luminescent and electroluminescent sensors [3], non-linear optics devices [32], molecular-level wires [4](b), [33], switches [34], and antennas [5]. Their use as "light-fueled motors" to power mechanical movements in artificial molecular-level machines adds another, future oriented dimension to the chemistry of this peculiar family of compounds. For sure, $[Ru(bpy)_3]^{2+}$ will continue to be one of the most used (and useful) compounds in the coming years.
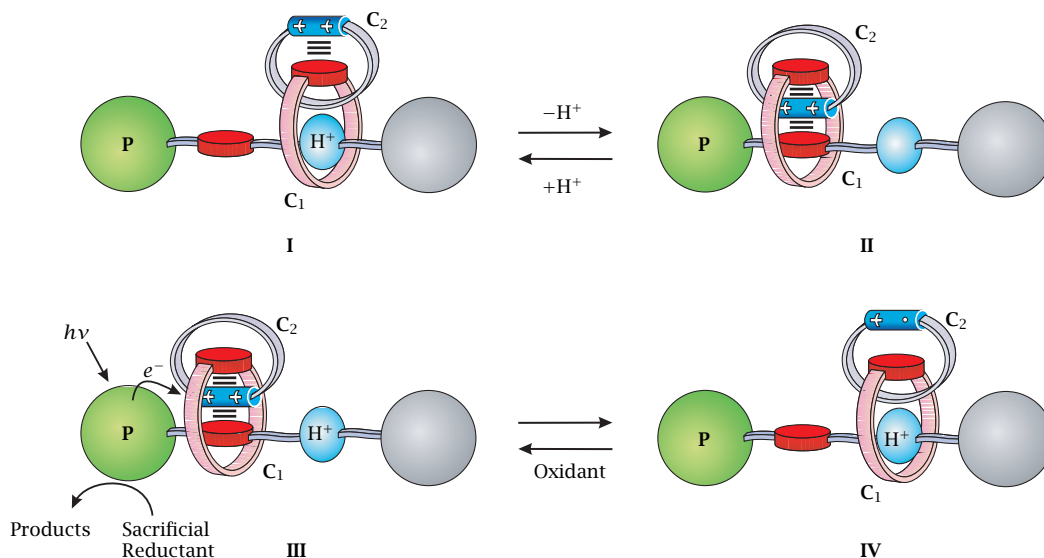
Figure 16. *A rotacatenane designed to couple a linear and a rotary motion upon (top) acid/base stimulation and (bottom) photosensitized electron-transfer reaction assisted by a sacrificial reductant.*

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