

Artificial Molecular Motors Powered by Light

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The bottom-up construction and operation of machines and motors of molecular size is a topic of great interest in nanoscience, and a fascinating challenge of nanotechnology. The problem of the energy supply to make molecular motors work is of the greatest importance. Research in the last ten years has demonstrated that light energy can indeed be used to power artificial nanomotors by exploiting photochemical processes in appropriately designed systems. More recently, it has become clear that under many aspects light is the best choice to power molecular motors; for example, systems that show autonomous operation and do not generate waste products can be obtained. This review is intended to discuss the design principles at the basis of light-driven artificial nanomotors, and provide an up-to-date overview on the prototype systems that have been developed.

Manuscript received: 24 January 2006.

Final version: 22 February 2006.

Introduction

The development of civilization has always been strictly related to the design and construction of devices — from the wheel to the jet engine — capable of facilitating human movement and travel. Nowadays the miniaturization race leads scientists to investigate the possibility of designing and constructing motors and machines at the nanometer scale, that is, at the molecular level. Chemists, by the nature of their discipline, are able to manipulate atoms and molecules and are therefore in the ideal position to develop bottom-up strategies for the construction of nanoscale devices.^[1]

Movement is also a central attribute of life. Nature provides living organisms with complex molecules called motor proteins which work inside a cell like machines.^[2,3] The most important and best known natural molecular motors are adenosine triphosphate (ATP) synthase, myosin, and kinesin. ATP synthase is the ubiquitous enzyme that manufactures ATP and is a rotary motor powered by a proton gradient. The enzymes of the myosin and the kinesin families are linear motors that move along polymer substrates (actin filaments for myosin and microtubules for kinesin), converting the energy of ATP hydrolysis into mechanical work. Motion derives from a mechanochemical cycle, during which the motor protein binds to successive sites along the substrate in

such a way as to move forward on average. Other biological processes are also based on motion, including protein folding and unfolding. Another example is RNA polymerase, which moves along DNA while carrying out transcription. Surely the supramolecular architectures of the biological world are themselves the premier, proven examples of the feasibility and utility of nanotechnology and constitute a sound rationale for attempting the realization of artificial molecular devices.^[4,5]

A molecular motor can be defined as an assembly of a discrete number of molecular components designed to perform mechanical movements under control of appropriate energy inputs. The words *motor* and *machine* are often used interchangeably when referred to molecular systems. It should be recalled, however, that a motor converts energy into mechanical work, while a machine is a device, usually containing a motor component, designed to accomplish a function. Molecular motors and machines operate by means of electronic and/or nuclear rearrangements and make use of thermal fluctuations (Brownian motion).^[6] Like the macroscopic counterparts, they are characterized by the kind of energy input supplied to make them work, the type of motion (such as translation, rotation, or oscillation) performed by their components, the way of monitoring their operation (the



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rearrangements of the component parts should cause readable changes in some chemical or physical property of the system), the possibility to repeat the operation in cycles, and the time scale needed to complete a cycle. According to the view described above, an additional and very important distinctive feature of a molecular machine with respect to a molecular motor is the function performed. As it will be discussed in the next section, the problem of the energy supply to make artificial molecular motors work is of the greatest importance.^[7]

Natural molecular motors are extremely sophisticated systems, and it is clear that the construction of systems of such structural and functional complexity by using the bottom-up molecular approach would be, at present, an impossible task. What can be done in the field of artificial molecular motors and machines is to construct simple prototypes consisting of a few molecular components, capable of moving in a controllable way, and to investigate the challenging problems posed by interfacing such nanodevices with the macroscopic world, particularly as far as energy supply and information exchange are concerned. In recent years synthetic talent — that most distinctive feature of chemists — combined with a device-driven ingenuity evolved from chemists' attention to functions and reactivity have led to outstanding achievements in this field. Among the systems developed are molecular propellers,^[8] rotors,^[9] turnstiles,^[10] gyroscopes,^[11,12] gears,^[13] brakes,^[14] ratchets,^[15] switches,^[16] shuttles,^[17] elevators,^[18] muscles,^[19] valves,^[20] processive artificial enzymes,^[21] walkers,^[22,23] and catalytic self-propelled micro- and nano-rods.^[24] Several excellent reviews^[25–30] and a monograph^[31] are also available.

This short review will focus on the use of light to power artificial molecular motors and machines. Some representative examples taken from recent literature will be described, and the various design strategies and processes that have been employed so far will be discussed.

The Energy Problem

The most obvious way to supply energy to a chemical system is through an exergonic chemical reaction. Not surprisingly, the majority of the molecular motors of the biological world are powered by chemical reactions (e.g. ATP hydrolysis).^[2,3] Richard Feynman, in his famous address^[32] to the American Physical Society in 1959, observed that

... 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 machinery that sustain life.

If an artificial molecular motor 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. Accumulation of waste products, however, will compromise the operation of the device 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 motors based on chemical fuel inputs.

Chemists have since long known that photochemical and electrochemical energy inputs can cause the occurrence of *endergonic* and *reversible* reactions. In the last few years, the outstanding progress made by supramolecular photochemistry^[33] and electrochemistry^[34] has thus led to the design and construction of molecular machines powered by light or electrical energy which work without formation of waste products. Needless to say, the operation of a molecular machine is accompanied by partial conversion of free energy into heat, regardless of the chemical, photochemical, and electrochemical nature of the energy input.

In the context of artificial nanomotors, stimulation by light possesses several advantages compared to stimulation by chemical or electrochemical means. First of all, the amount of energy conferred to a chemical system by using photons can be carefully controlled by the wavelength and intensity of the exciting light, in relation to the absorption spectrum of the targeted species. Such an energy can be transmitted to molecules without physically connecting them to the source (no 'wiring' is necessary), the only requirement being the transparency of the matrix at the excitation wavelength. Other properties of light, such as polarization, can also be used. Lasers provide the opportunity of working in very small spaces and extremely short time domains, and near-field techniques allow excitation with nanometer resolution. On the other hand, the irradiation of large areas and volumes can be conveniently carried out, thereby allowing the parallel (or even synchronous) addressing of a very high number of individual nanodevices.

Photochemical methods are also useful for monitoring the operation of the motor. In general with respect to chemical systems photons can play the dual role of *writing* (causing a change in the system) and *reading* (reporting the state of the system). This is also true in nature, where sunlight's photons are employed both as energy quanta in photosynthetic processes and as information elements in vision and other light-triggered processes (Fig. 1). Specifically, luminescence spectroscopy is a valuable technique, since it is easily accessible and offers good sensitivity and selectivity, along with the possibility of time- and space-resolved studies.

The use of light to power nanoscale devices is relevant for another important reason. If and when nanotechnology-based industries will be developed, its products will have to be powered by renewable energy sources, since it has become clear that the problem of energy supply is a crucial one for human civilization for the years ahead. In this framework, the construction of nanodevices, including natural-artificial hybrids,^[35] that harness solar energy in the form of visible or near-UV light is indeed an important possibility.

Autonomous Operation

An extremely important feature of any molecular motor is its capability to exhibit an autonomous behaviour, namely

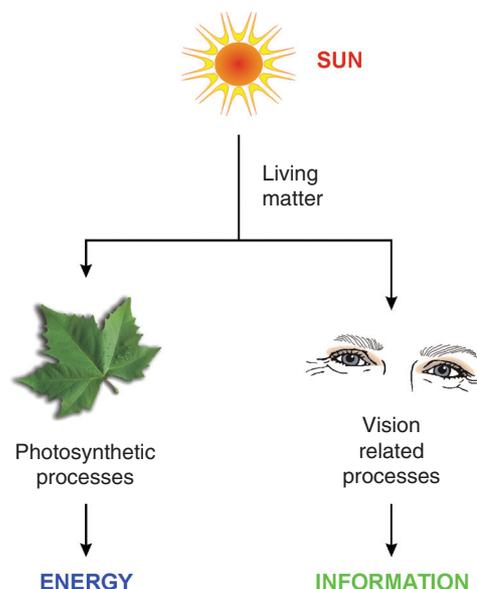


Fig. 1. The dual role of sunlight photons in their interaction with living matter.

able to operate without external intervention (in other words, in a constant environment) as long as the energy source is available. Hence, autonomous molecular motors are free-running devices that do not require controlled and repeated addition of chemicals or other environmental changes. Natural motors are autonomous, in most cases acting as catalysts for the fuelling reaction. Except some recent work on DNA nanomotors,^[36–38] the chemically powered artificial molecular motors reported so far are not autonomous because after the mechanical movement induced by a given input they need another, opposite input to reset. Strictly speaking, such systems should be better referred to as mechanical molecular switches.

The design of autonomous nanomotors can take advantage from reversible photochemical processes. For instance, the operation of the motor could be based on a photoinduced sequence of processes that lead the system through transient electronic and nuclear (mechanical) states; the final deactivation of the system to the ground state provides an automatic reset and closes the cycle of operation. Alternatively, the mechanical motion could be related to the light-triggered switching between two stable states, as it happens in photochromic systems. These approaches will be more conveniently discussed in examples illustrated in the next sections.

Systems Based on Structural Rearrangements in the Excited State

Electronic excited states, by their own nature, possess very different electronic properties compared to the ground state. It is also well known that the electronic excited states of molecules often exhibit a markedly different geometry compared to the ground state. In such cases, light excitation can cause geometric changes of the molecule, which are usually brought about by bond rotation and/or bending. A typical example is represented by compounds exhibiting twisted

intramolecular charge transfer (TICT) excited states.^[39] However, the design of light-powered molecular motors based on structural rearrangements in an excited state is not trivial. The main difficulty arises from the fact that the large-amplitude motions of molecular subunits in multicomponent systems require a period of time (microseconds or longer) somewhat longer than the typical lifetime of most excited states, although long-lived triplet excited states can in principle be exploited.^[40]

The hydrogen bonding ability of a molecule can be greatly enhanced (or depressed) upon light excitation, a property that could be used to cause molecular motions in appropriately designed systems. The complex fluorescence behaviour exhibited by a peptide-based rotaxane bearing an anthracene unit as one of the stoppers was interpreted^[41] in terms of a very fast (subnanosecond) short-amplitude ($\sim 3 \text{ \AA}$) translation of the macrocycle upon light excitation of the anthracene unit. The translation would have originated from the enhancement of the hydrogen bonding between the macrocycle and the anthracene unit in the singlet excited state. However, it seems that alternative explanations, such as the formation of intercomponent exciplexes,^[42,43] cannot be ruled out.

It was also proposed^[44] that unidirectional rotation of a small subunit in an appropriately designed chiral molecule could be driven by linearly polarized picosecond laser pulses. Classical and quantum mechanical calculations showed that the origin of the unidirectional rotation lies in both the asymmetric rotational potential of the chiral molecule and time-correlated forces caused by laser–molecule interactions. However, the experimental demonstration of this concept is expected to be fairly complex and has not been reported yet.

Systems Based on Photoisomerization Processes

Cis–trans photoisomerization reactions involving $-\text{N}=\text{N}-$, $-\text{C}=\text{N}-$, or $-\text{C}=\text{C}-$ bonds are well known processes.^[45] In general, they are extremely clean and reversible reactions, the prototypical case being the *cis–trans* isomerization of azobenzene.^[46] These are ideal processes to obtain light-driven operation of molecular machines because they bring about evident structural changes that can be exploited to cause large amplitude motions in suitably designed molecular and supramolecular systems. It should be noted that photoisomerization processes occur in an electronically excited state and therefore do not differ, from a philosophical point of view, from the processes mentioned in the previous section.

As a matter of fact, molecular tweezers based on the azobenzene unit were perhaps the first examples of light-driven molecular machines reported in the literature.^[47,48] Since then, azobenzene and other photoisomerizable units (e.g. diarylethenes^[49]) have been incorporated in a variety of multicomponent systems,^[50] including macrocyclic receptors,^[51] dendrimers,^[52,53] and polymers.^[54] For instance, compound **1** shown in Fig. 2^[55] mimics the motion exhibited by a pair of scissors but are operated by light. Obviously this species does not carry out a specific function at the present stage; nevertheless it emphasizes that the structural and functional integration of different molecular units

(in this case, a photoelastic handle unit, a ferrocene pivot group, and two phenyl rings as the blade moieties) can lead to the construction of interesting nanodevices. *Cis-trans* photoisomerization reactions have also been investigated on surfaces,^[56] and an optomechanical nanodevice based on atomic force microscopy experiments on single polymer molecules containing azobenzene groups was reported.^[57]

Rotary Motors

Molecular rotary motors are systems capable of undergoing unidirectional and repetitive rotations under the action of external energy inputs. The construction of molecular rotary motors poses several challenges, particularly because it is difficult to satisfy the unidirectional rotation requirement. At present, artificial rotary motors driven by light have only been obtained by exploiting a $\text{C}=\text{C}$ isomerization reaction in carefully designed overcrowded chiral alkenes.

The first motor was based^[58] on a symmetric biphenanthrylidene (**2**, Fig. 3). In such a compound, each one of the two helical subunits linked by a double bond can adopt a right-handed (*P*) or a left-handed (*M*) helicity; as a result, a total of four stereoisomers are possible. The *cis-trans* photoisomerization reactions are reversible and occur upon irradiation at appropriate wavelengths. By contrast, the inversions of helicities, while maintaining a *cis* or a *trans* configuration, are irreversible thermal processes. Upon irradiation (≥ 280 nm, 218 K) of a solution of (*P,P*)-*trans*-**2** (Fig. 3, step a), a mixture of (*P,P*)-*trans*-**2** and (*M,M*)-*cis*-**2** is obtained in a ratio of 5:95. By warming the solution up to 293 K (step b), (*M,M*)-*cis*-**2** is converted irreversibly to (*P,P*)-*cis*-**2**. Subsequent irradiation (≥ 280 nm) of the solution (step c) produces a mixture of (*P,P*)-*cis*-**2** and (*M,M*)-*trans*-**2** in a ratio of 10:90. Upon increasing the temperature further (333 K, step d), (*M,M*)-*trans*-**2** is converted irreversibly to the original isomer (*P,P*)-*trans*-**2**. Thus, a sequence of two energetically uphill light-driven isomerization processes and two energetically downhill thermal helix inversion steps are exploited to move this molecular rotor unidirectionally. The overall process can be followed by monitoring the changes in the circular

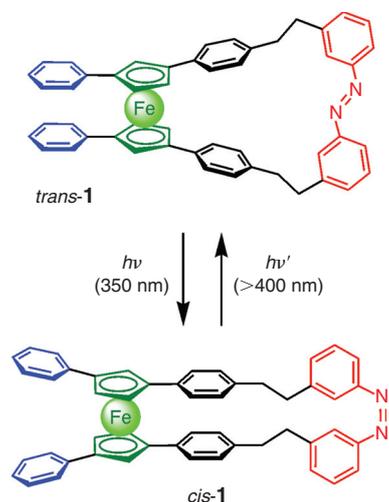


Fig. 2. The light-driven open–close motion of molecular scissors.

dichroism spectra.^[58] Indeed, upon irradiation (≥ 280 nm) of (*P,P*)-*trans*-**2** at a high temperature (293 K) a clockwise 360° rotation occurs and thus the motor exhibits autonomous behaviour. The directionality of rotation is dictated by the energetic preference for the methyl substituents next to the stereogenic centres to adopt an axial orientation, which is less sterically demanding and energetically favourable.

More recently, this molecular motor was redesigned^[59] to improve its performance (Fig. 4); specifically, the major issue is the lowering of the barriers for the rate-determining thermal steps. For the second-generation motors **3** it was established^[60] that unidirectional rotation can be achieved with a single stereogenic centre and that an increase of the size of atoms X and Y increases the steric crowding in the ‘fjord region’, resulting in slower thermal rotation steps. The exchange of a six-membered ring for a five-membered ring in the lower half (from **4** to **5**, Fig. 4) caused^[61] an increase in rotation speed by a factor of 10^8 . The thermal helix inversion step of the ‘fast’ molecular motor **5** exhibited a half-life of 3.17 min at room temperature. The structure was also modified^[62] so that the motor **6** (Fig. 4) could be powered by visible (436 nm) instead of UV light. Light-driven unidirectional rotation of the ‘rotor’ unit when the ‘stator’ of compound **7** is tethered to the surface of gold nanoparticles was recently demonstrated.^[63] Furthermore, the motor was employed as a four-state light-triggered switch to construct a ‘molecular gearbox’ wherein the state of the switch controls the thermal rotation of an appended aromatic moiety.^[64]

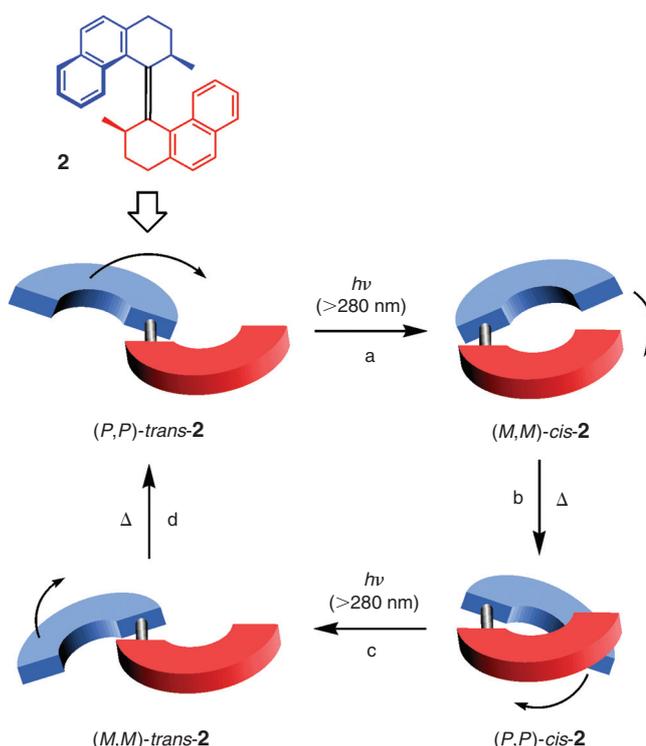


Fig. 3. Mechanism of unidirectional rotation of the two helical subunits of compound **2**. Each light-driven ‘energetically uphill’ process (horizontal) is followed by a thermal ‘energetically downhill’ process (vertical).

Threading–Dethreading Systems

Photoisomerization reactions have been largely used^[50] to gain photocontrol on the self-assembly–disassembly^[65] of host–guest systems. Pseudorotaxanes^[66] are a particular class of supermolecules minimally made of a thread-like guest molecule surrounded by a macrocyclic host, and are interesting in the context of molecular machinery because the assembly–disassembly of the components is reminiscent of the threading–dethreading of a needle.

An example of a pseudorotaxane exhibiting threading–dethreading motions based on a photoisomerization process is shown in Fig. 5.^[67] The thread-like species *trans*-**8**, which contains an electron-rich azobiphenoxy unit, and the

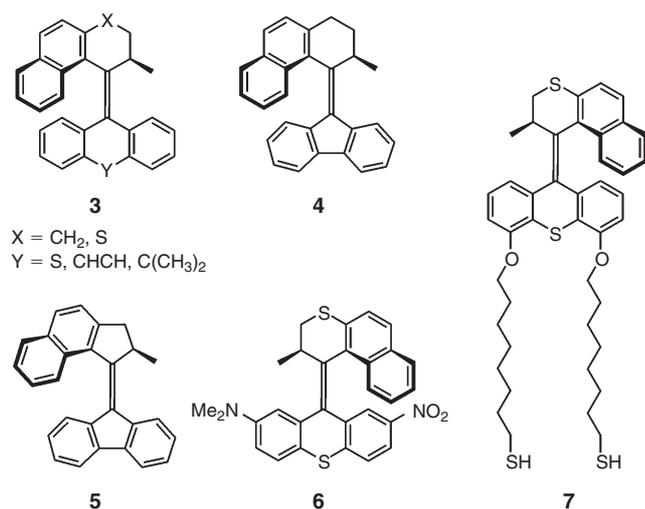


Fig. 4. Molecular formulas of second generation photochemical rotary motors.^[60–63]

electron-acceptor macrocycle **9**⁴⁺ self-assemble very efficiently in acetonitrile solution to give a pseudorotaxane, stabilized by electron donor–acceptor interactions. In the pseudorotaxane structure, the intense fluorescence characteristic of free **9**⁴⁺ ($\lambda_{\max} = 434$ nm) is completely quenched by the donor–acceptor interaction. Irradiation with 365 nm light of a solution containing *trans*-**8** and **9**⁴⁺, in which the majority of the species are assembled to give the pseudorotaxane, causes the *trans* → *cis* photoisomerization of **8**. Since the affinity of the macrocycle for *cis*-**8** is much lower than that for *trans*-**8**, photoexcitation causes a dethreading process (Fig. 5), as indicated by a substantial increase in the fluorescence intensity of free **9**⁴⁺. On irradiation at 436 nm or by warming the solution in the dark *trans*-**8** can be reformed and, as a result, it rethreads inside the macrocycle. Owing to the full reversibility of the photoisomerization process, the light-driven dethreading–rethreading cycle can be repeated at will. A relevant feature of this system is that it exhibits profound changes of a strong fluorescence signal.

Molecular Shuttles

Rotaxanes^[66] are compounds minimally made of an axle-type molecule surrounded by a macrocyclic (ring) component. In contrast to pseudorotaxanes, bulky groups (stoppers) placed at the ends of the axle prevent the disassembly of the components, that are therefore interlocked during the synthesis. Because of their peculiar structure, at least two interesting molecular motions can be envisaged in rotaxanes, namely (a) rotation of the macrocyclic ring around the axle and (b) translation of the ring along the axle (Fig. 6). Hence, rotaxanes are appealing systems for the construction of both rotary and linear molecular motors.

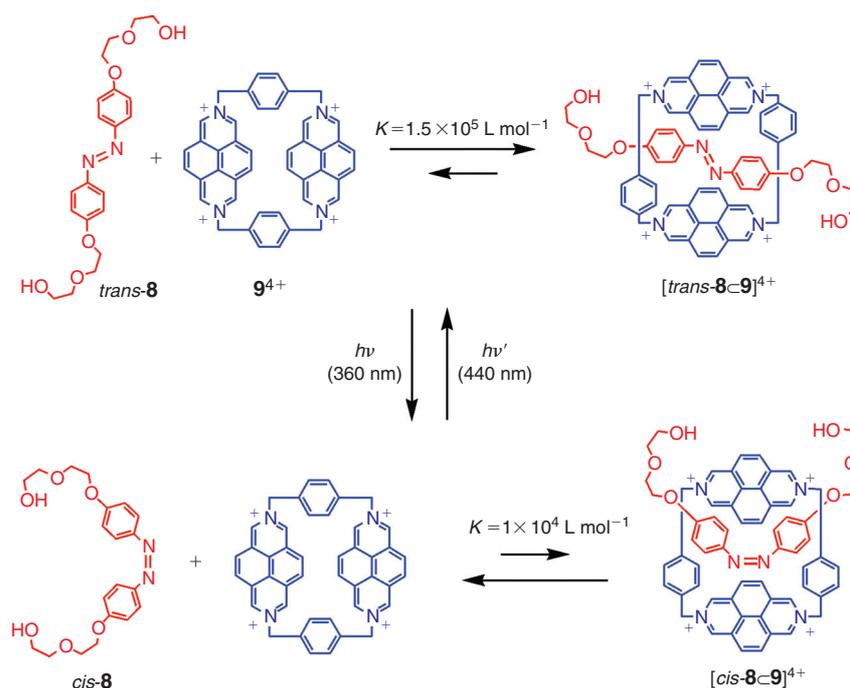


Fig. 5. Dethreading–rethreading of pseudorotaxane $[\mathbf{8}\text{-}\mathbf{9}]^{4+}$ as a consequence of the *cis*–*trans* photoisomerization of the azobenzene-type unit contained in the thread-like component **8**.

The axle and ring components usually exhibit some kind of interaction originating from complementary chemical properties, which is also exploited in the template-directed synthesis of such systems. In rotaxanes containing two different recognition sites in the axle component, it is possible to switch the position of the ring between these two 'stations' by an external stimulus. Systems of this type, termed molecular shuttles,^[68] constitute the most common implementation of the molecular motor concept with rotaxanes.

Examples of molecular shuttles based on photoisomerization reactions have been described in the literature.^[69–71] Recently, peculiar rotaxanes performing as light-driven

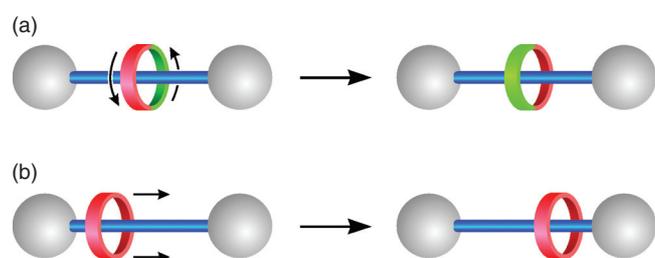


Fig. 6. Schematic representation of long-range (a) rotation and (b) translation (shuttling) motions of the ring component in rotaxanes.

molecular shuttles with a chemical 'lock' and fluorescence output signals were reported.^[72] More complex rotaxanes containing two different photoresponsive stations and one or two macrocyclic rings were found to behave as multistate, multifunctional switches.^[73,74] For instance, rotaxane **10** (Fig. 7)^[74] is a quite interesting species under a photochemical viewpoint because it contains several photoactive units in its axle component. These are an azobenzene and a stilbene groups as the stations, and two slightly different naphthalimide stoppers (A and B) which exhibit strong fluorescence at distinct wavelengths ($\lambda_{\text{max}} = 520$ and 395 nm, respectively). The ring is a α -cyclodextrin (α -CD) macrocycle. The azobenzene and stilbene units can be photoisomerized independently by using light at different wavelengths in the UV-visible region.^[73] At room temperature in dimethylsulfoxide solution, the stable (starting) state is *trans,trans*-**10**, characterized by fast (on the NMR timescale) shuttling of the α -CD ring between the two stations. Irradiation at 380 nm causes the isomerization of the azobenzene unit, leading to the formation of *cis,trans*-**10**, in which the α -CD ring is trapped on the *trans*-stilbene station. Further irradiation at 313 nm causes the isomerization of the stilbene unit, leading to the formation of *cis,cis*-**10**, in which the α -CD ring encircles

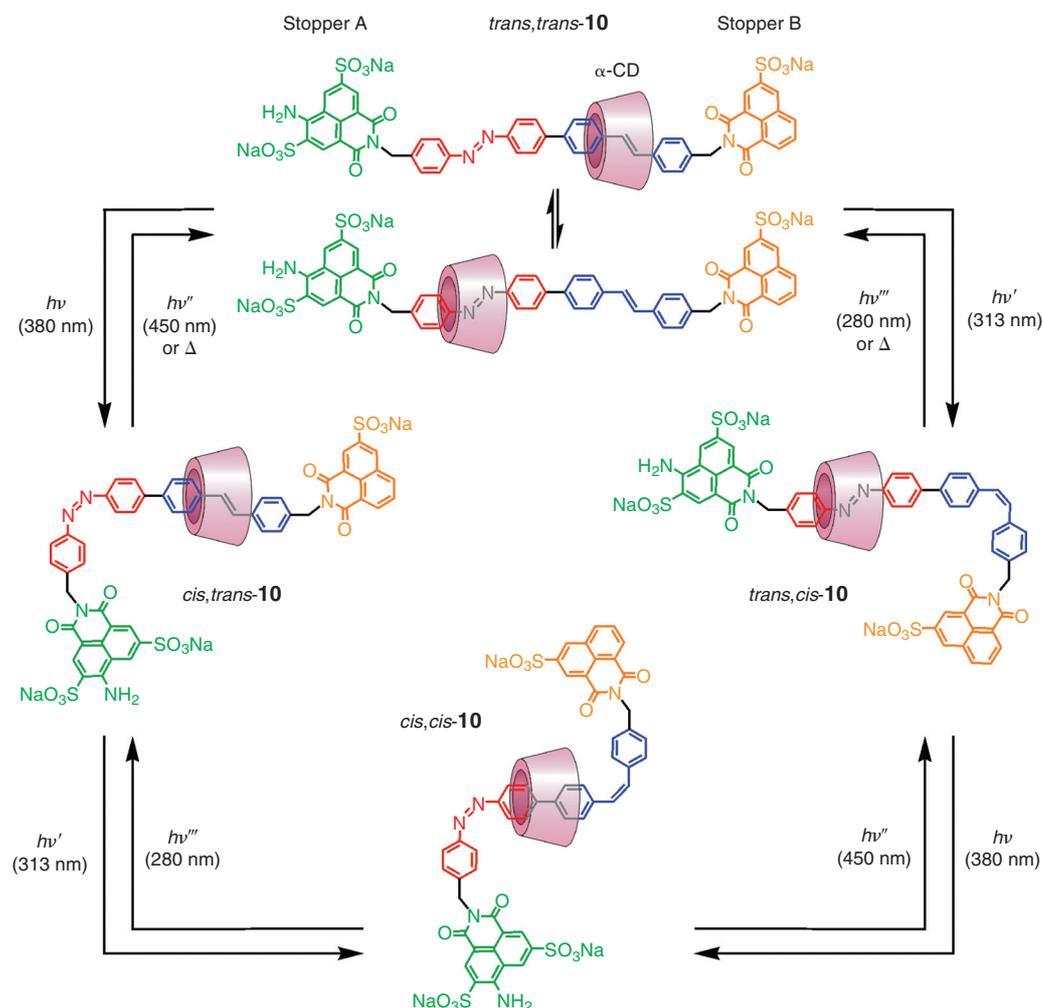


Fig. 7. The four isomeric states of rotaxane **10** and the photoisomerization reactions leading to their interconversion.^[74]

the central biphenyl group. On the other hand, irradiation of *trans,trans*-**10** at 313 nm leads to the formation of the *trans,cis*-**10** isomer, in which the α -CD ring is trapped on the *trans*-azobenzene unit; further irradiation at 380 nm affords *cis,cis*-**10**. As indicated in Fig. 7, the photochemical reactions are fully reversible upon light irradiation or heating. The starting state and the three photostationary states were characterized^[74] by NMR, UV-visible absorption, and luminescence spectroscopies. Interestingly, each state exhibits a different fluorescence spectrum because the emission intensity of a stopper group is enhanced when the α -CD ring is located close to it, owing to the ‘rigidifying’ effect exerted by the macrocycle. Since the absorption and fluorescence spectral changes related to the interconversion between the four states of the system could be interpreted in terms of AND and XOR binary logic functions, rotaxane **10** was shown^[74] to perform as a reversible half-adder device with all-optical input and output signals.

A monolayer of the photoactive rotaxane *trans*-**11** (Fig. 8), which consists of a ferrocene-functionalized β -cyclodextrin (β -CD) macrocycle threaded on a molecule containing a photoisomerizable azobenzene unit and a long alkyl chain, was assembled on a gold electrode.^[75,76] The ring component is prevented from dethreading by a bulky anthracene stopper group. The azobenzene unit in the *trans* configuration is complexed by β -CD; photoisomerization to the *cis* form renders complexation sterically impossible, so that the β -CD ring is displaced to the alkyl component. Back-photoisomerization restores the original *trans* configuration. The position of the β -CD-tethered ferrocene unit was determined by chronoamperometry. A fast current decay ($k = 65 \text{ s}^{-1}$) was observed for the *trans* isomer, implying that the ring component is

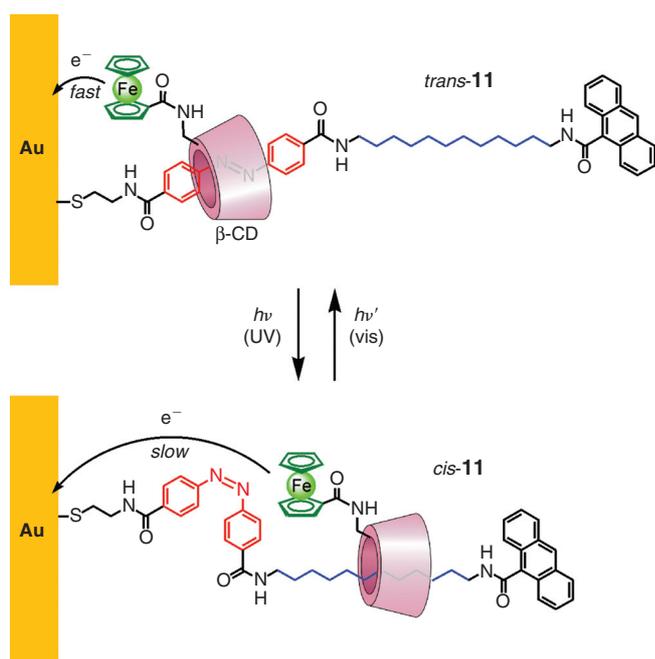


Fig. 8. Schematic representation of the surface-bound photoswitchable rotaxane **11**.^[75,76] Such a device is capable of transducing an optical signal into an electronic signal by means of the photocontrolled ring shuttling in the rotaxane molecules.

close to the electrode surface (Fig. 8). Photoisomerization of the monolayer to the *cis* state resulted in a chronoamperometric transient characterized by a substantially lower electron-transfer rate constant ($k = 15 \text{ s}^{-1}$). This result indicates that in *cis*-**11** the β -CD ring is more distant from the electrode surface. Owing to the reversibility of azobenzene photoisomerization, a cyclic pattern for the rate constant of the heterogeneous electron-transfer process was observed. In this optoelectronic system, optical information is transduced by a mechanical shuttling to an electronic signal.

Peptide-based rotaxanes containing a photoisomerizable fumaramide unit in the axle component were prepared.^[77] In solution, the macrocyclic ring undergoes a large-amplitude thermally driven motion in which it rotates around the axle (Fig. 6a). It was shown^[77] that the rate of rotation can be accelerated by more than six orders of magnitude by isomerizing the fumaramide unit to the maleamide unit by using 254 nm light.

Systems Based on Ligand Photodissociation Reactions

The use of transition metals as templates to construct multi-component chemical systems with interlocked or knotted topologies has been largely exploited.^[66] Some of these species constitute prototypes of nanomachines.^[78] A strategy that takes advantage of the dissociative character of ligand-field excited states in ruthenium diimine complexes to obtain light-driven molecular machines was reported.^[79] In these compounds, one part of the system is set in motion by photochemically expelling a given chelate, the reverse motion being performed by heating the product of the photoreaction so as to regenerate the original state. This idea was implemented to obtain the light-driven rotation of the molecular rings in a catenane.^[80] Visible excitation of the Ru catenane complex **12**²⁺ (Fig. 9) in acetonitrile solution leads to the population of the MLCT (metal-to-ligand charge-transfer) triplet excited state and subsequent formation of the ligand-field state which, in turn, causes the decooordination of the bipyridine ligand. As a result, rotation of the bipyridine-containing ring occurs, and a catenane structure composed of two disconnected rings (e.g. Fig. 9, bottom) is obtained. Simple heating regenerates the starting complex, with both reactions (decoordination–recoordination) being quantitative. The overall process was monitored by NMR and UV-vis spectroscopies. By using the same strategy, light-induced motions on a rotaxane system were also obtained.^[81]

Systems Based on Photoinduced Electron Transfer

Photoinduced electron-transfer (PET) reactions are of primary importance both in natural photosynthetic devices and in artificial systems.^[82] In the present context, it is worth mentioning the conformational changes caused by light excitation in donor–acceptor systems with flexible bridges, which can be viewed as early examples of light-driven molecular motions based on PET.^[83,84] Because the donor and acceptor components are neutral, PET causes the formation of charges of opposite sign at the two ends of the molecule. As a consequence of the resulting electrostatic attraction,

conformational distortion occurs (in competition with charge recombination) and the two ends of the molecule approach each other (harpooning effect). Crucial to the observation of this harpooning motion is that both the ‘stretched’

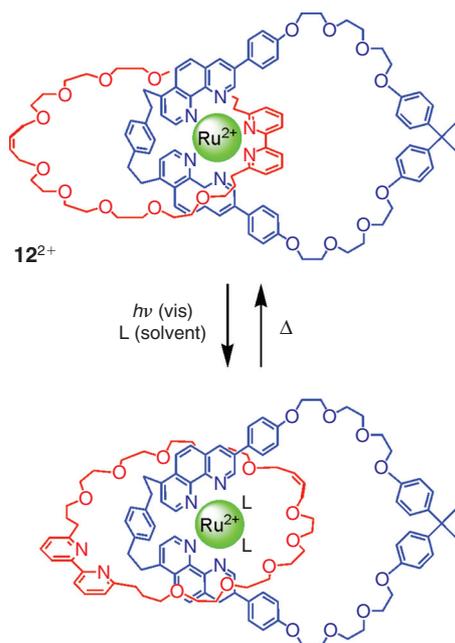


Fig. 9. Photochemically and thermally induced motions taking place in the ruthenium catenane complex 12^{2+} .^[80] The representation of the decoordinated form (bottom) is indicative and does not imply that the actual structure of the photoproduct is that shown.

and ‘folded’ charge-separated states exhibit characteristic luminescence.

Threading–Dethreading Systems

Examples of pseudorotaxanes in which the threading–dethreading of the molecular components is triggered by PET processes are well documented.^[85–89] Recently, a molecular triad for photoinduced charge separation was used^[90,91] as the power supply to drive the dethreading of a pseudorotaxane. A monolayer of the tetrathiafulvalene–porphyrin–fullerene triad **13** (Fig. 10) self-assembled on a gold surface was employed as the working electrode in an electrochemical cell. The solution in contact with the electrodes contained the electron-donor thread **14** and the electron-acceptor macrocycle **15**⁴⁺. Under the conditions employed, such components self-assemble to give the pseudorotaxane $[14\subset 15]^{4+}$, stabilized by electron donor–acceptor interactions. In such a system, excitation of the porphyrin unit at 413 nm (Fig. 10, step a) causes an electron transfer to the fullerene unit (step b), followed by a shift of the positive charge onto the tetrathiafulvalene unit (step c) and subsequent transfer of an electron from the metal surface (step d). The photogenerated fullerene anion can reduce a bipyridinium unit of the **15**⁴⁺ ring (step e) and, as a consequence of the weakening of the donor–acceptor interaction, the pseudorotaxane is disassembled (step f). The dethreading of **14** from **15**³⁺ can be monitored by measuring the increase in the fluorescence intensity of free **14**. After oxidation of the reduced macrocycle **15**³⁺ at the Pt counter-electrode, re-threading of the pseudorotaxane occurs (step g).

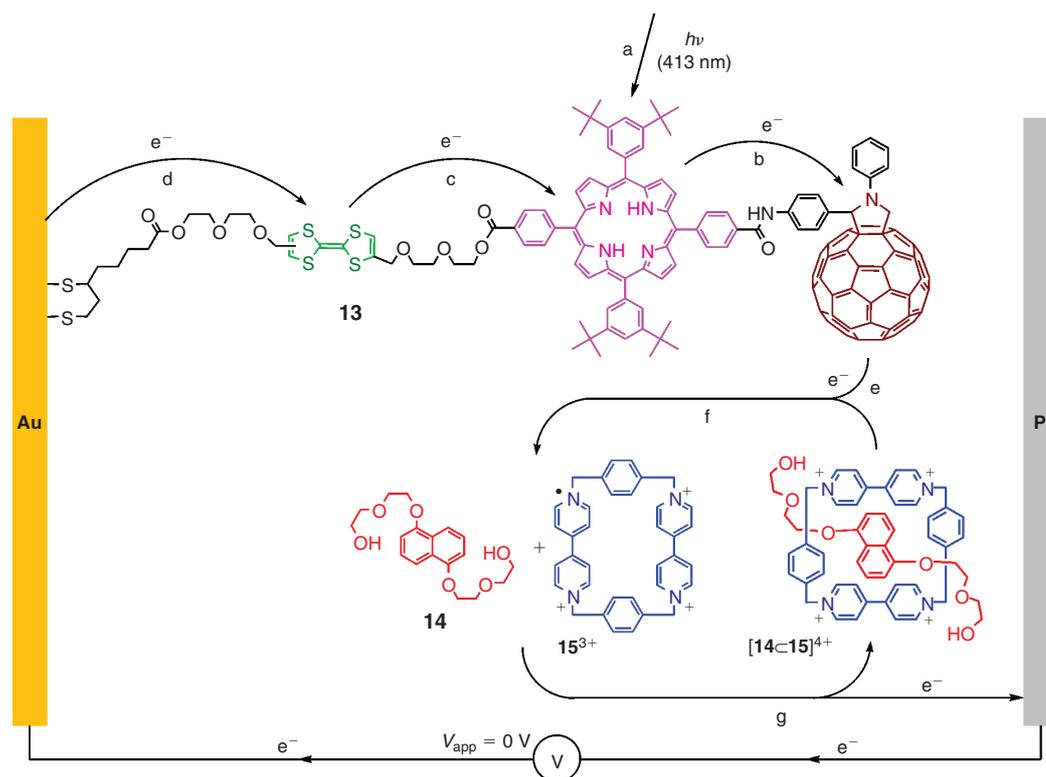


Fig. 10. Schematic representation of the light-driven dethreading–rethreading of pseudorotaxane $[14\subset 15]^{4+}$, powered by a self-assembled monolayer of the molecular triad **13** in a photoelectrochemical cell.^[90,91]

Ring Rotation in Catenanes

PET processes have been engineered within rotaxane- and catenane-type structures with the purpose of obtaining light-driven molecular machines and motors. The copper catenane complex 16^+ (Fig. 11), which incorporates a terpyridine ligand in one of its two macrocyclic components and a phenanthroline ligand in both, constitutes^[92] the first example of a molecular machine based on a catenane. On irradiation of an acetonitrile solution of 16^+ at 464 nm (Fig. 11, step a) the Cu(I)-based chromophoric unit is excited to a metal-to-ligand charge-transfer state. In the presence of the electron acceptor scavenger *p*-nitrobenzylbromide, electron transfer from the photoexcited catenane to *p*-nitrobenzylbromide occurs (step b),^[93] generating a tetracoordinated Cu(II) centre. In response to the preference of the Cu(II) ion for pentacoordinated geometry, the terpyridine-containing macrocycle circumrotates through the cavity of the other (step c) affording a pentacoordinated Cu(II) centre (16^{2+}). On addition of ascorbic acid the pentacoordinated Cu(II) centre is reduced to a pentacoordinated Cu(I) ion (step d). In response to the preference of Cu(I) for a tetracoordinated environment, the terpyridine-containing macrocycle circumrotates again with respect to the other (step e), restoring the original architecture. Therefore, in this system the Cu-based unit plays the role of photosensitizer and *p*-nitrobenzylbromide plays the role of an electron scavenger. The same strategy was used to cause ring shuttling in a related rotaxane.^[94] It should be pointed out that, in addition to light energy, two low-energy fuels (*p*-nitrobenzylbromide and ascorbic acid) are consumed. Moreover, the system does not exhibit autonomous operation, since it requires the alternate addition of the two chemical reactants in order to perform cycles.

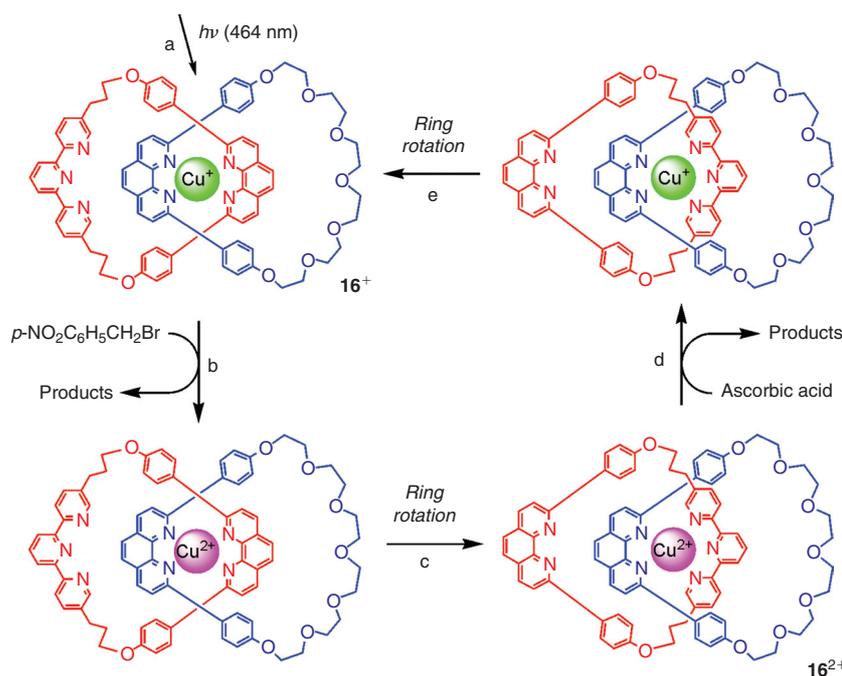


Fig. 11. The photoinduced rotation of the terpyridine-containing macrocyclic ring of the copper catenane complex 16^+ was obtained^[93] by using *p*-nitrobenzylbromide as an electron scavenger and ascorbic acid as a chemical reductant.

It is also worth noting that in the catenane system described above, repeated switching between the two stable states does not necessarily occur through a full rotation. In fact, because of the intrinsic symmetry of the system, the 180° rotations corresponding to both step c and step e can take place clockwise or anticlockwise with equal probability. A full (360°) rotation movement, which is necessary for obtaining a rotary motor, can only occur in ratchet-type systems, namely in the presence of asymmetric elements which can be structural or functional in nature.^[95] This idea was realized^[96] with a carefully designed catenane by relying on a sequence of photochemically, chemically, and thermally activated processes, and the system was characterized using NMR spectroscopy.

Molecular Shuttles

A light-driven molecular shuttle which does not consume chemical fuels and exhibits autonomous operation, based on an external electron donor playing the role of an electron relay, has been described.^[97] Rotaxane **17** (Fig. 12) consists^[98] of a benzylic amide macrocycle that surrounds an axle featuring two hydrogen-bonding stations, namely, a succinamide and a naphthalimide unit, separated by a long alkyl chain. Initially, the macrocycle resides onto the succinamide station because the naphthalimide unit is a much poorer hydrogen-bonding recognition site. Excitation with UV light at 355 nm (Fig. 12, step a) in acetonitrile at room temperature generates the singlet excited state of the naphthalimide unit, which then undergoes high-yield intersystem crossing to the triplet excited state. Such a triplet state can be reduced in bimolecular encounters by an electron donor (1,4-diazabicyclo[2.2.2]octane, DABCO) added to the solution in a sufficiently large amount (step b). Because the back

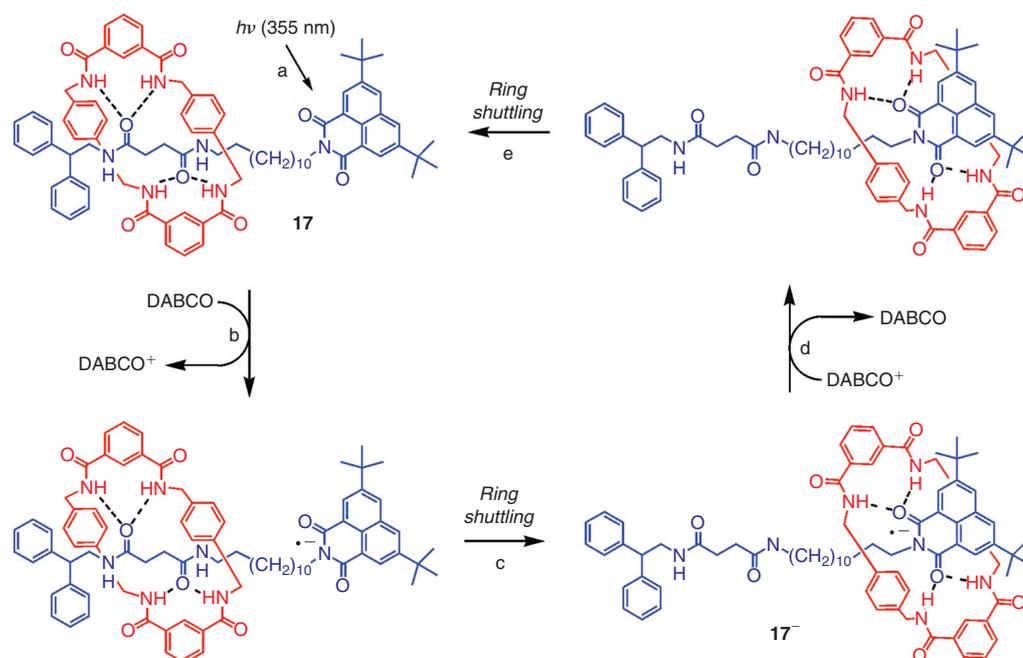


Fig. 12. Mechanism for the autonomous reversible shuttling of the ring component in rotaxane **17**, powered by UV light.^[97] The operation of this system relies on the use of DABCO as an electron relay.

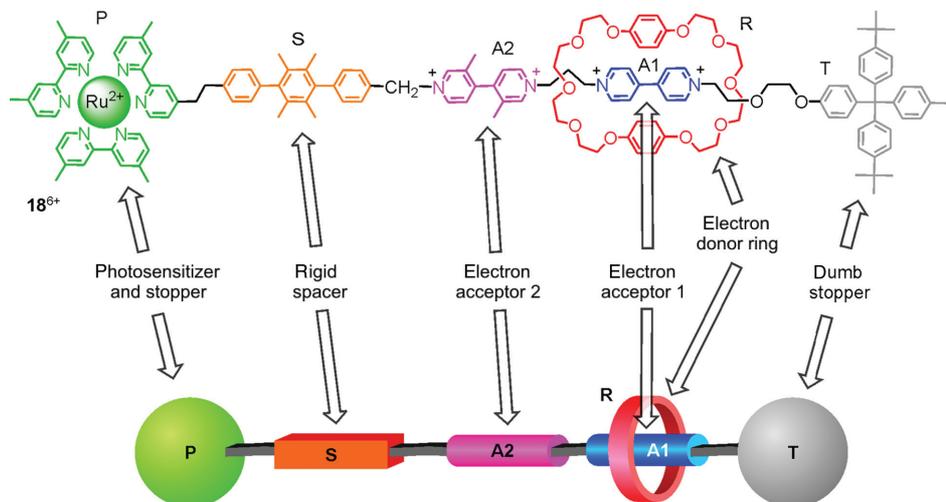


Fig. 13. Chemical formula of the photoactive rotaxane **18**⁶⁺,^[99] showing its modular structure. In solution, this rotaxane behaves^[102] as an autonomous nanomotor powered by sunlight.

electron-transfer process is spin-forbidden and thus slow, the photogenerated ion pair can efficiently dissociate; as a matter of fact, the naphthalimide radical anion survives for hundreds of microseconds before it decays by bimolecular charge recombination with a DABCO radical cation. Since the naphthalimide anion is a much stronger hydrogen-bonding station compared to the succinamide, upon reduction of the naphthalimide unit the macrocycle is expected to shuttle from the latter to the former station (step c); this has been demonstrated by cyclic voltammetric experiments and confirmed by laser flash photolysis. The time required for ring shuttling ($\sim 1 \mu\text{s}$) is much shorter than the lifetime of the naphthalimide radical anion ($\sim 100 \mu\text{s}$). After bimolecular charge recombination (step d), the macrocycle moves back to its original position (step e). This rotaxane constitutes a remarkable example of

a linear molecular motor driven exclusively by light (UV), although its operation still relies on the presence of an external reactant which, however, is not consumed. The motor can be cycled at a frequency depending on the charge recombination rate of the rotaxane radical anion. It can be estimated that if the shuttle is pumped by a laser at the frequency of its ‘recovery stroke’ (step d), 10^4 s^{-1} , this molecular-level machine generates about 10^{-15} W of mechanical power per molecule.^[97]

On the basis of the experience gained with previous studies on pseudorotaxane model systems,^[85,86,88,89] the rotaxane **18**⁶⁺ (Fig. 13) was specifically designed^[99] to achieve photoinduced ring shuttling in solution. This compound has a modular structure; its ring component R is an electron donor bis-*p*-phenylene[34]crown-10, whereas its axle component

is made of a Ru(II) polypyridine complex (P) covalently linked to a 4,4'-bipyridinium (A1) and a 3,3'-dimethyl-4,4'-bipyridinium (A2) electron-accepting stations by means of a *p*-terphenyl-type rigid spacer (S); the axle component is finally stoppered by a tetraarylmethane group (T). The ruthenium-based unit plays the dual role of a light-fuelled power station^[100] and a stopper, whereas the mechanical switch consists of the two electron-accepting stations and the electron donor macrocycle. The strategy devised in order to obtain the photoinduced shuttling movement of the macrocycle between the two stations A1 and A2 is based on a 'four stroke' synchronized sequence of electronic and nuclear processes. A more detailed description of the system can be found in the paper by Balzani et al.^[101] in this issue. Steady-state and time-resolved spectroscopic experiments together with electrochemical measurements in acetonitrile solution showed^[102] that the absorption of a visible photon by **18**⁶⁺ can cause the occurrence of a forward and backward ring movement, that is, a full mechanical cycle. It was estimated that the fraction of the excited state energy used for the motion of the ring amounts to about 10%, and the motor can generate a mechanical power of approximately 3×10^{-17} W per molecule. The somewhat disappointing quantum efficiency for ring shuttling (2% at 30°C) is compensated by the fact the investigated system is a unique example of an artificial linear nanomotor because it gathers together the following features:

- it is powered by visible light (in other words, sunlight).
- it exhibits autonomous behaviour, like motor proteins.
- it does not generate waste products.
- its operation can rely only on intramolecular processes, allowing in principle operation at the single-molecule level.
- it can be driven at a frequency of ~ 1 kHz.
- it works in mild environmental conditions (i.e. fluid solution at ambient temperature).
- it is stable for at least 10^3 cycles.

Owing to its modular design, the rotaxane **18**⁶⁺ is amenable to be structurally modified in the attempt of improving its performance as a light-driven nanomotor. For instance, the effects of the exchange of the position of the two electron accepting stations along the axle are discussed by Balzani et al.^[101,102]

Summary and Outlook

The results described here show that compounds capable of performing large amplitude, non-trivial, and controlled mechanical movements upon light stimulation can be obtained by using careful incremental design strategies, the tools of modern synthetic chemistry, and the paradigms of supramolecular chemistry, together with some inspiration from natural systems.

Such achievements enable to devise future developments which are under investigation in our and other laboratories, namely:

- the design and construction of more sophisticated artificial molecular motors and machines, showing complex

motions and better performances in terms of stability, speed, switching, among others.

- the use of such systems to do tasks such as molecular-level transportation, catalysis, and mechanical gating of molecular channels.
- the possibility of exploiting their logic behaviour for information processing at the molecular level and, in the long run, for the construction of chemical computers.

The majority of the artificial molecular motors developed so far operate in solution, that is, in an incoherent fashion and without control of spatial positioning. The studies in solution of complicated chemical systems such as molecular motors and machines are indeed of fundamental importance to understand their operation mechanisms; moreover, for some uses (e.g. drug delivery) molecular machines will have to work in liquid solution. In this regard, it should be recalled that motor proteins operate in — or at least in contact with — an aqueous solution. However, it seems reasonable that, before artificial molecular motors and machines can find applications in many fields of technology, they have to be interfaced with the macroscopic world by ordering them in some way so that they can behave coherently and can be addressed in space. New generations of molecular machines and motors organized at interfaces,^[103] deposited on surfaces,^[63,104,105] or immobilized into membranes^[106] or porous materials,^[20,107] have started to appear. On the basis of recent experiments^[108,109] showing that the collective operation of artificial nanomotors in carefully engineered surface-deposited monolayers can indeed develop mechanical work at a larger scale, one can optimistically hope that useful devices based on artificial nanomachines will see the light in a not-too-distant future. Apart from more or less futuristic applications, the study of motion at the molecular level and the extension of the concept of motor and machine to the nanoscale are fascinating topics for basic research. Looking at molecular and supramolecular species from the viewpoint of functions with references to devices of the macroscopic world is indeed a very interesting exercise which introduces novel concepts into chemistry as a scientific discipline.

Acknowledgments

I thank Vincenzo Balzani and Margherita Venturi for stimulating discussions, and J. Fraser Stoddart and his group for a long lasting and fruitful collaboration. Financial support from European Union (STREP 'Biomach' NMP2-CT-2003-505487) and the University of Bologna is gratefully acknowledged.

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