Using light to induce energy and electron transfer or molecular motions in multicomponent systems†‡

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Light-induced processes are at the basis of fundamental natural phenomena as well as of a variety of applications. Since the functions that can arise from the interaction between light and matter depend on the degree of complexity and organization of the receiving 'matter', the research on these processes has progressively moved from molecular to supramolecular (multicomponent) systems, thereby originating the field of supramolecular photochemistry. In this context, examples of photochemical molecular devices and machines—that is, multicomponent chemical systems capable to perform specific functions under light stimulation—have been developed. Here we report examples of molecular devices in solution, where light is employed (i) to create and transport electronic energy, (ii) to displace electrons, and (iii) to set molecular components in motion, mimicking the operation of mechanical machines and motors. These studies are of interest not only for increasing the basic understanding and testing of current theoretical treatments of photoinduced processes but also eventually for the growth of nanoscience.

Introduction

The interaction between light and matter lies at the heart of the most important processes of life.[1] Photons are exploited by natural systems as both quanta of energy and elements of information. In fact, light constitutes an energy source and is consumed (or, more precisely, converted) in large amount in photosynthesis, while it functions as a signal in vision-related processes, the energy used to run the operation being biological in nature. There is a variety of functions that can be obtained from the interaction between light and matter in natural as well as in artificial systems.[2] The type and utility of such functions depend on the degree of complexity and organization of the chemical systems that receive and process the photons.

About three decades ago a new branch of chemistry called supramolecular chemistry[3–5] emerged and developed very rapidly, and its importance was established by the assignment of the 1987 Nobel prize in chemistry.[6–8] Supramolecular chemistry deals with the "*organised entities of higher complexity that result from the association of two or more chemical species held together by intermolecular forces*",[4,6] and is strongly related to the systems and processes of the biological world. Owing to the progress of synthetic chemistry, it has become possible to design and synthesize supramolecular systems composed of a remarkable number of molecular components capable of self-assembling under appropriate experimental conditions. Chemical systems can also be constructed where distinct molecular components are held together by coordination and covalent bonds (as in grids, racks, arrays or dendrimers)[3–5,9] or even mechanically linked to each other (as in catenanes and rotaxanes).[10] According to the above definition, such systems would not belong to the supramolecular realm; however, some authors pointed out[11,12] that species that are not strictly supramolecular under the 'bonding' point of view can exhibit in fact a supramolecular behaviour as far as the physico-chemical properties (and the related emerging functions) are concerned. All these species have in common their multicomponent nature, *i.e.*, the fact that they are made by a discrete number of molecular units linked together by a variety of forces—from weak electrostatic interactions to covalent bonds. Broadly speaking, one can say that with supramolecular chemistry there has been a change in focus from molecules to molecular assemblies or multicomponent systems. The study of the interaction between supramolecular species and light is the realm of the fast-growing field of supramolecular photochemistry.[13,14]

In the frame of research on supramolecular chemistry, the idea began to arise[6,15,16] that the concept of macroscopic device and machine can be transferred to the molecular level. In short, a molecular device can be defined[17] as an assembly of a discrete number of molecular components designed to perform a function under appropriate external stimulation. A molecular machine[17,18] is a particular type of device where the function is achieved through the mechanical movements of its molecular components. In analogy to their macroscopic counterparts, molecular devices and machines need energy to operate and signals to communicate with the operator. As discussed above, light provides an answer to this dual requirement, and possesses several advantages compared to other forms of stimulation (*e.g.*, chemical or electrochemical).[19]

By using photons, the amount of energy conferred to a chemical system can be carefully controlled by the wavelength and intensity

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of the exciting light, depending on the absorption spectrum of the targeted species. Such an energy can be transmitted to molecules without physically connecting them to the source (no 'wiring'), the only requirement being the transparency of the matrix at the excitation wavelength. Laser sources provide the opportunity of working in very small spaces and extremely short time domains, and near-field techniques enable excitation and probing with nanometre 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 molecular devices. Last but not least, spectroscopic methods (*e.g.*, luminescence spectroscopy) are a powerful tool to read the state of a chemical system.

It should be pointed out that mechanical molecular devices cannot be considered merely as 'shrunk' versions of macroscopic counterparts, because the operational mechanisms of motion at the molecular level have to deal with phenomena different from those that govern the macroscopic world.[20,21] Gravity and inertia motions we are familiar with in our everyday experience are fully negligible at the molecular scale, where the viscous forces resulting from intermolecular interactions (including those with solvent molecules) largely prevail. This means that while we can describe the bottom-up construction of a nanoscale device as an assembly of suitable (molecular) components by analogy with what happens in the macroscopic world, we should not forget that the design principles and the operating mechanisms at the molecular level are different.

Here we describe some examples of multicomponent molecular systems, taken from our own work, where light is employed (i) to create and transport electronic energy, (ii) to displace electrons from one molecular component to another, and (iii) to cause the motion of some molecular parts with respect to the rest of the structure. Systems of type (i) and (ii) are interesting for the development of antennas for light harvesting, molecular wires, switches, and logic gates, whereas systems of type (iii) can be viewed as simple prototypes of mechanical machines and motors.

Photoinduced energy- and electron-transfer processes

A dinuclear Ru[II]–Os[II] polypyridine complex containing a shape-persistent macrocyclic bridging ligand

Ru[II] and Os[II] polypyridine-type complexes have long been known[22] to exhibit favourable excited-state and redox properties to play the role of building blocks for the construction of photoactive multicomponent systems. An interesting class of such systems are polynuclear complexes, where the metal-based units are linked together by bridging ligands.[23] The choice of suitable bridging ligands is crucial to obtain polynuclear complexes capable of showing desired spectroscopic and electrochemical properties, and of giving rise to photoinduced energy- and electron-transfer processes. In the past 15 years, several polynuclear complexes based on Ru[II] and Os[II] ions have been synthesized and studied.[23,24]

The heterodinuclear complex 1^{4+} (Fig. 1)—having a shape-persistent phenylacetylene macrocycle incorporating 2,2′-bipyridine (bpy) units as the bridging ligand[25]—has been recently prepared, and its photophysical properties have been
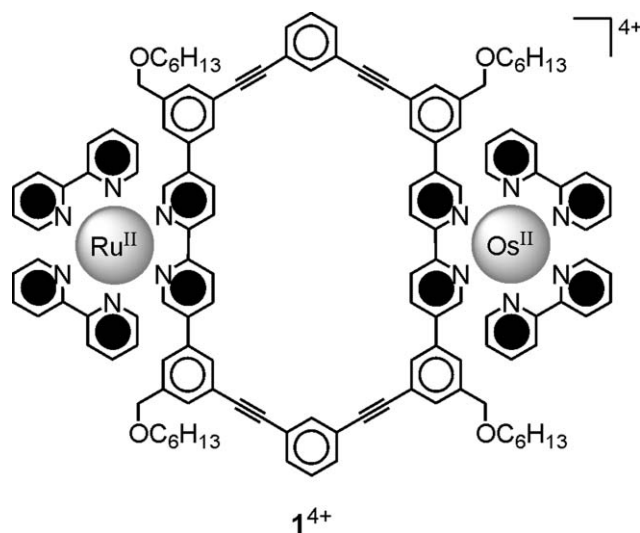

Fig. 1 Structural formula of the Ru[II]–Os[II] heterodinuclear complex 1^{4+}.

investigated.[26] The absorption spectrum of 1^{4+} in acetonitrile solution coincides with the average of the spectra of the parent Ru[II]–Ru[II] and Os[II]–Os[II] homodinuclear complexes. However, the emission spectra (Fig. 2) show that 97% of the MLCT (metal-to-ligand charge-transfer) luminescence intensity of the Ru-based unit ($\lambda_{max} = 645$ nm) is quenched, with respect to the Ru homodinuclear model compound, by the presence of the Os-based component. A comparison with the Os homodinuclear complex indicates that a concomitant sensitisation of the Os-based MLCT luminescence ($\lambda_{max} = 780$ nm) occurs. This result shows that, under the experimental conditions employed, the quenching of the Ru-based luminescence takes place by intramolecular energy transfer to the Os-based unit.[26]
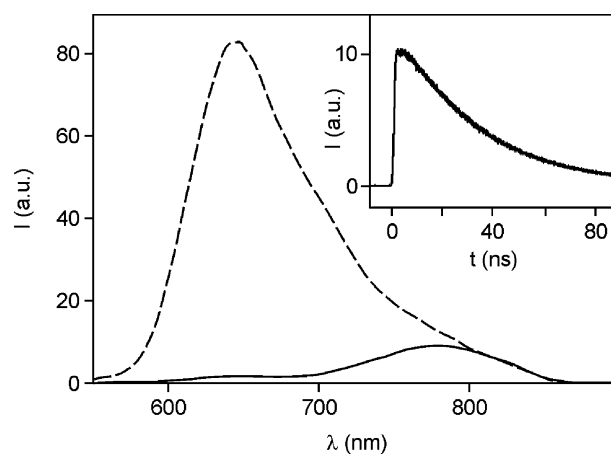

Fig. 2 Comparison of the luminescence spectra (air-equilibrated acetonitrile solution, room temperature, 5.0×10^{-5} mol L^{-1}, $\lambda_{exc} = 475$ nm; uncorrected for the spectral response of the detector) of 1^{4+} (full line) and of a 1 : 1 mixture of the corresponding homodinuclear Ru[II]–Ru[II] and Os[II]–Os[II] compounds (dashed line). The inset shows the rise and the decay of the Os-based excited state ($\lambda_{exc} = 406$ nm, $\lambda_{em} = 780$ nm).

As expected for an energy-transfer process, the quenching of the luminescence intensity of the Ru-based unit is accompanied by the quenching of its excited-state lifetime. Moreover, the decay of

the Ru-based excited state is accompanied by the rise of the Os-based excited state (Fig. 2, inset). Interestingly, the decay of the Ru-based luminescence in 1^{4+} follows a double exponential kinetic law with rate constants of 2.0×10^8 and $2.2 \times 10^7 \, \text{s}^{-1}$, respectively, as determined from luminescence lifetime measurements. This result indicates that each dinuclear complex exists as a mixture of two different conformers whose interconversion is slow compared to the excited-state decay. Different conformers can indeed be expected because steric hindrance between hydrogen atoms of pyridine and phenyl rings in the bis-chelating macrocyclic ligand forces the dinuclear complexes to assume a 'cis' or 'trans' structure. In the 'cis' structure the two metal ions lie on the same side of the plane defined by the shape-persistent macrocycle and the metal–metal distance is estimated to be 1.5 nm from a space filling model, whereas for the 'trans' conformer the two metal ions lie on opposite sides of the plane and their distance is about 1.7 nm. The through-bond distance, of course, is the same (ca. 2.7 nm) for both structures, but this does not mean that the through bond electronic coupling has to be the same in the two conformers. Calculations indicate that the most plausible mechanism for the energy-transfer process is the Förster (Coulombic) one.[26] However, it cannot be excluded that a Dexter (exchange) mechanism is also involved, because the experimental values of the energy-transfer rate constants can be accounted for by small (<1 cm^{-1}) electronic interactions.

Complex 1^{4+} (Fig. 1) is also interesting because its Os^{II}-based unit can be quantitatively oxidised to obtain the Ru^{II}–Os^{III} complex 1^{5+}.[26] Titration of 1^{4+} with the oxidant ammonium Ce^{IV} nitrate in acetonitrile is accompanied by profound changes in the absorption spectrum, namely (i) the decrease of the MLCT absorption bands of the Os^{II} moiety between 400 and 700 nm, and (ii) the appearance of a broad and weak band with maximum at 720 nm that is assigned to a ligand-to-metal charge-transfer (LMCT) transition of the Os^{III} moiety.

Oxidation of 1^{4+} to 1^{5+} causes changes also in the emission spectrum (Fig. 3). As discussed above, in 1^{4+} the Ru^{II}-based emission is strongly, but not completely quenched by energy transfer to the Os^{II}-based one (Fig. 2). After addition of one equivalent of oxidant, the Os^{II}-based emission band ($\lambda_{max} = 780$ nm) can no longer be observed, showing that the Os^{II} unit has

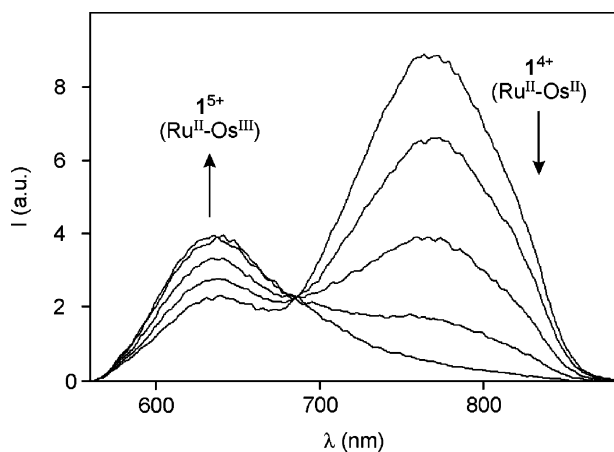**Fig. 3** Changes in the luminescence spectrum observed during the titration of 1^{4+} with Ce^{IV} in acetonitrile (2.0×10^{-5} mol L^{-1}, $\lambda_{exc} = 400$ nm). The curves are not corrected for the spectral response of the detector.

been quantitatively oxidised. The disappearance of the Os^{II} unit, however, causes only a small recovery (7%) of the Ru^{II}-based band ($\lambda_{max} = 645$ nm, Fig. 3). In other words, the Ru^{II}-based emission in 1^{5+} is still strongly quenched by the Os^{III}-based unit, although slightly less quenched than it is in 1^{4+}. Transient absorption experiments indicate that the emission quenching takes place by intercomponent electron transfer via direct formation of the Ru^{III}–Os^{II} species, which is formed within the laser pulse (ca. 10 ns) and subsequently relaxes to the Ru^{II}–Os^{III} ground species by back electron transfer.[26]

The presence of a double exponential decay for the Ru^{II}-based luminescence supports the hypothesis of the two conformers discussed above for 1^{4+}. The rate constants for the forward electron-transfer process (Ru^{II}–Os^{III} → Ru^{III}–Os^{II}) in the two conformers are estimated to be respectively 1.6×10^8 and $2.7 \times 10^7 \, \text{s}^{-1}$ by luminescence lifetime measurements, whereas the rates of the back electron-transfer process (Ru^{III}–Os^{II} → Ru^{II}–Os^{III}), measured by laser flash photolysis, are respectively 9.1×10^7 and $1.2 \times 10^7 \, \text{s}^{-1}$.

It can be noticed that the rate for the forward electron-transfer process in 1^{5+} is relatively slow compared with those reported for other dinuclear Ru^{II}–Os^{III} complexes.[24] This result can be accounted for by considering that the presence of *meta*-disubstituted phenyl rings as the connectors between the polypyridine ligand and alkyne spacers causes a dramatic reduction in the extent of electron delocalization.

A plug–socket device based on a pseudorotaxane

Supramolecular species whose components are connected by means of non-covalent forces can be disassembled and re-assembled[27] by modulating the interactions that keep the components together, with the consequent possibility of switching energy-transfer processes. Two-component systems of this type are reminiscent of plug–socket electrical devices because, like their macroscopic counterparts, are characterised by (i) the possibility of connecting–disconnecting the two components in a reversible way, and (ii) the occurrence of an electronic energy flow from the socket to the plug when the two components are connected (Fig. 4a). Hydrogen-bonding interactions between ammonium ions and crown ethers are particularly suitable for constructing molecular-level plug–socket devices, since they can be switched on and off quickly and reversibly by means of acid–base inputs.

A plug–socket system which deals with the transfer of electronic energy is illustrated in Fig. 4b.[28] The absorption and fluorescence spectra of a CH$_2$Cl$_2$ solution containing equal amounts of ($\pm$)-binaphthocrown ether **2** and amine **3** indicate the absence of any interaction between the two compounds. Addition of a stoichiometric amount of acid, capable of protonating compound **3**, causes profound changes in the fluorescence behaviour of the solution, namely (i) the fluorescence of **2** is completely quenched, and (ii) the fluorescence of **3**-H$^+$ is sensitised upon excitation with light absorbed exclusively by the crown ether. These observations are consistent with the formation of an adduct between **2** and **3**-H$^+$, wherein very efficient electronic energy transfer takes place from the photoexcited binaphthyl unit of the crown ether to the anthracenyl group incorporated within the **3**-H$^+$ component. Such an adduct belongs to the class of pseudorotaxanes,[10] i.e. supermolecules made (at minimum) of a

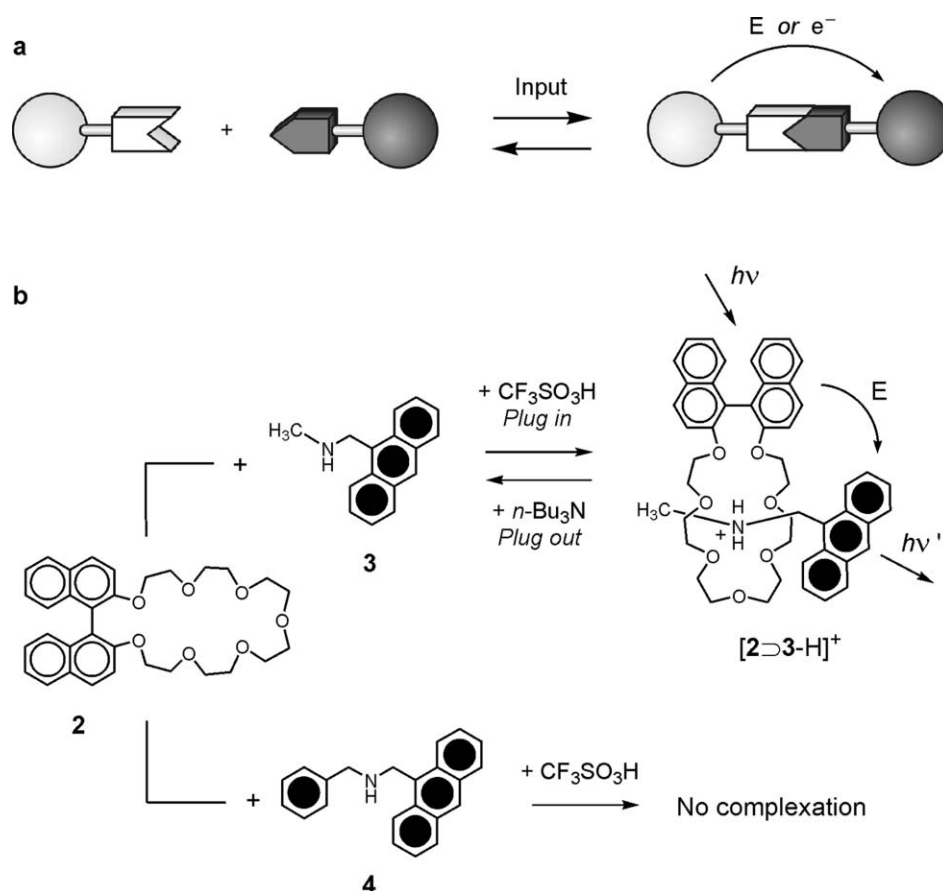This journal is © The Royal Society of Chemistry and Owner Societies 2007

Fig. 4 (a) Schematic representation of the working mechanism of a plug–socket system. (b) Switching of photoinduced energy transfer by the acid–based controlled plug in–plug out of binaphthocrown ether **2** and anthracenylammonium ion **3**-H^{+}.

thread-like guest molecule surrounded by a macrocyclic host, because dialkylammonium ions are known[29] to penetrate the cavity of crown ethers like **2**. The very fast ($k > 4 \times 10^9$ s^{-1}) rate constant for the energy-transfer process[28] can be accounted for by a Coulombic mechanism, as molecular models show that the maximum distance between binaphthyl and anthracene units in the **2**⊃**3**-H^{+} complex (≈15 Å) is much shorter than their Förster radius (26 Å).

The pseudorotaxane **2**⊃**3**-H^{+} can be disassembled by the subsequent addition of a stoichiometric amount of base, capable of deprotonating **3**-H^{+}, thereby interrupting the photoinduced energy flow, as indicated by the restoring of the initial absorption and fluorescence spectra. Moreover, the stability of this pseudorotaxane can be influenced by changing the nature of the counteranion of **3**-H^{+}.[30] Interestingly, the plug-in process does not take place when a plug component incompatible with the size of the socket, such as the benzyl-substituted amine **4**, is employed (Fig. 4b).

Mimicking electrical extension cables at the molecular level

The plug–socket concept described above can be used to design molecular systems which mimic the function played by a macroscopic electrical extension cable. The operation of an extension cable is more complex than that of a plug–socket system, since it involves *three* components that must be hold together

by *two* connections that have to be controllable *reversibly* and *independently*; in the fully connected system, an electron or energy flow must take place between the remote donor and acceptor units (Fig. 5).

In the attempt of constructing a molecular-level extension cable for electron transfer, the pseudorotaxane shown in Fig. 6a, made of the three components **5**[2+], **6**-H^{3+}, and **7**, has been obtained and studied.[31] Component **5**[2+] consists of two moieties: a [Ru(bpy)$_3$]$^{2+}$ unit, which behaves as an electron donor under light excitation,[22] and a dibenzo[24]crown-8 macrocycle, capable of playing the role of a hydrogen-bonding first socket.[29] The dialkylammonium-based moiety of **6**-H^{3+}, driven by hydrogen-bonding interactions, threads as a plug into the first socket, whereas the π-electron accepting 4,4′-bipyridinium unit threads as a plug into the third component, the π-electron rich 1,5-dinaphtho[38]crown-10 macrocycle (**7**), which plays the role of a second socket. In CH$_2$Cl$_2$–CH$_3$CN (98 : 2 v/v) solution, reversible connection–disconnection of the two plug–socket junctions can be controlled independently by acid–base and red–ox stimulation, respectively, and monitored by changes in the absorption and emission spectra, owing to the different nature of the interactions (hydrogen-bonding and π-electron donor–acceptor) that connect the components. In the fully assembled triad, **5**[2+]⊃**6**-H^{3+}⊂**7**, light excitation of the [Ru(bpy)$_3$]$^{2+}$ unit of the component **5**[2+] is followed by electron transfer to the bipyridinium unit of the component **6**-H^{3+}, which is plugged into component **7**.
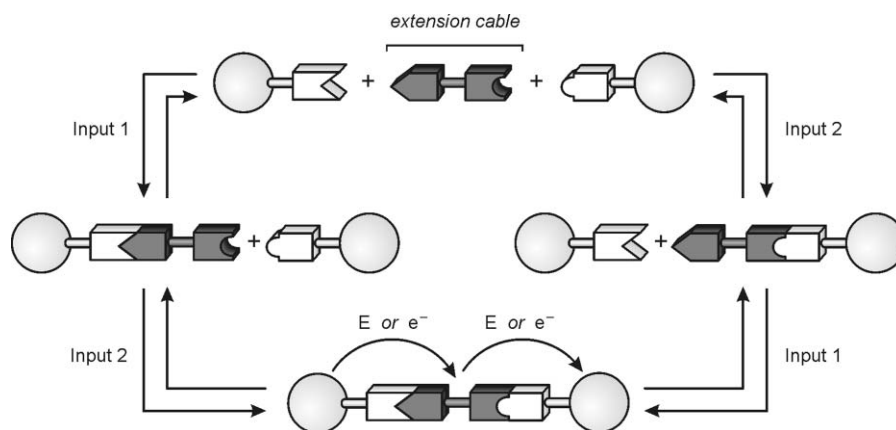
extension cable

Fig. 5 Schematic representation of the working mechanism of an electrical extension cable.

It should be noted that in the system described above the transferred electron does not reach the final component of the assembly. Moreover, a true extension cable should contain a plug and a socket at the two ends, instead of two plugs as component **6-H**$^{3+}$. An improved system of that type has been recently investigated (Fig. 6b).[32] The electron-source component is again **5**$^{2+}$, whereas the new extension cable **8-H**$^+$ is made up[33] of a dialkylammonium ion, that can insert itself as a plug into a dibenzo[24]crown-8 socket, a biphenyl spacer, and a benzonaphtho[36]crown-10 unit, which fulfills the role of a π-electron rich socket. Finally, the 1,1′-dioctyl-4,4′-bipyridinium dication **9**$^{2+}$ can play the role of an electron drain plug. As for the previously studied system, the two plug–socket connections **5**$^{2+}$⊃**8-H**$^+$ and **8-H**$^+$⊃**9**$^{2+}$ can be controlled by acid–base and red–ox stimuli, respectively. In the complete ensemble, **5**$^{2+}$⊃**8-H**$^+$⊃**9**$^{2+}$, light excitation of the Ru-based unit of **5**$^{2+}$ is followed by electron transfer to **9**$^{2+}$, with **8-H**$^+$ playing the role of an extension cable (Fig. 6b). The occurrence of this process is confirmed by nanosecond laser flash photolysis experiments, showing a transient absorption signal assigned to the 4,4′-bipyridinium radical cation formed by photoinduced electron transfer within the self-assembled triad. Such a second-generation system exhibits two conceptual and quite significant advancements: (i) **8-H**$^+$ consists of a plug and a socket components, and thus it really mimics an extension cable; (ii) the photoinduced electron transfer does take place from the first component—the Ru-based unit of **5**$^{2+}$—to the remote **9**$^{2+}$ unit, whereas in the previous system the electron receiving bipyridinium unit was a component of the cable.

Ru^{II} bis(terpyridine) complexes containing rotaxanes as ligands

Rotaxanes[10] are compounds made, at minimum, of a dumbbell-shaped molecule surrounded by a macrocyclic (ring) component. Because of the bulky groups (stoppers) placed at the ends of the thread-like portion of the dumbbell, the components cannot disassemble and are therefore interlocked during the synthesis.

As discussed above, it is well known that the cavity of crown ethers like [24]crown-8 can host thread-like dialkylammonium ions.[29] In more recent times, it was shown that such macrocycles can form hydrogen-bonded pseudorotaxane-type adducts also with 1,2-bis(pyridinium)ethane derivatives.[34] Taking advantage of such an observation, rotaxanes based on the 1,2-bis(pyridinium)ethane⊂24-crown-8 ether motif have been prepared, which contain a terminal terpyridine (tpy) group for coordination to a transition metal ion on one side of their dumbbell-shaped component, and an electron accepting 4,4′-bipyridinium unit on the other side. These rotaxane ligands have been utilised in the preparation of a series of heteroleptic [(tpy)Ru(tpy-rotaxane)]$^{2+}$ complexes.[35] The investigated model compound for the Ru-based unit, **10**$^{3+}$, dumbbell-shaped species **11**$^{5+}$ and rotaxanes **12**$^{5+}$–**14**$^{5+}$ are shown in Fig. 7. It should be noted that these compounds are in fact complicated multichromophoric systems, that contain several different units capable of interacting one another, and provide an interesting combination of structural features and photophysical properties.

At room temperature in acetonitrile, compound **10**$^{3+}$ exhibits a luminescence band in the near infrared (Fig. 8) and a relatively long-lived (τ = 125 ns) triplet MLCT excited state, whereas parent [Ru(tpy)$_2$]$^{2+}$ do not show an appreciable luminescence under the same conditions. This difference is due to the presence of a strong electron withdrawing pyridinium substituent on one of the two tpy ligands. Visible light excitation of the Ru-based chromophore in complexes **11**$^{3+}$–**14**$^{5+}$ causes a partial quenching of the MLCT luminescence (Fig. 8) because of an electron transfer to the covalently linked 4,4′-bipyridinium unit (*e.g.*, $k = 1.0 \times 10^8$ s^{-1} for **11**$^{5+}$). The rotaxane structure affects the absorption and luminescence properties of the complexes. In particular, for compounds **13**$^{5+}$ and **14**$^{5+}$ a weak absorption tail that reaches down to 600 nm ($\varepsilon \approx$ 500 L mol^{-1} cm^{-1} at 450 nm) is observed. Such a band is assigned to π-donor–acceptor interactions between the electron rich dioxyaromatic units of the macrocycles and the electron poor pyridinium and 4,4′-bipyridinium units of the cationic thread.[36] Interestingly, when a crown ether surrounds the cationic thread the luminescence quenching process is slowed down by a factor from 2 to 3, an effect attributed to the presence of the macrocycle in the rotaxane complexes which prevents the formation of folded conformations. The excited state obtained upon photoinduced electron transfer can relax to the ground state by a back electron-transfer process or, in the case of **13**$^{5+}$ and **14**$^{5+}$, by intramolecular energy transfer to the level originating from π-donor–acceptor interactions between the bipyridinium unit and the aromatic moieties of the crown ether rings (see above). The fact that the electron-transfer state cannot be detected by transient absorption experiments suggests that the decay of such a state is
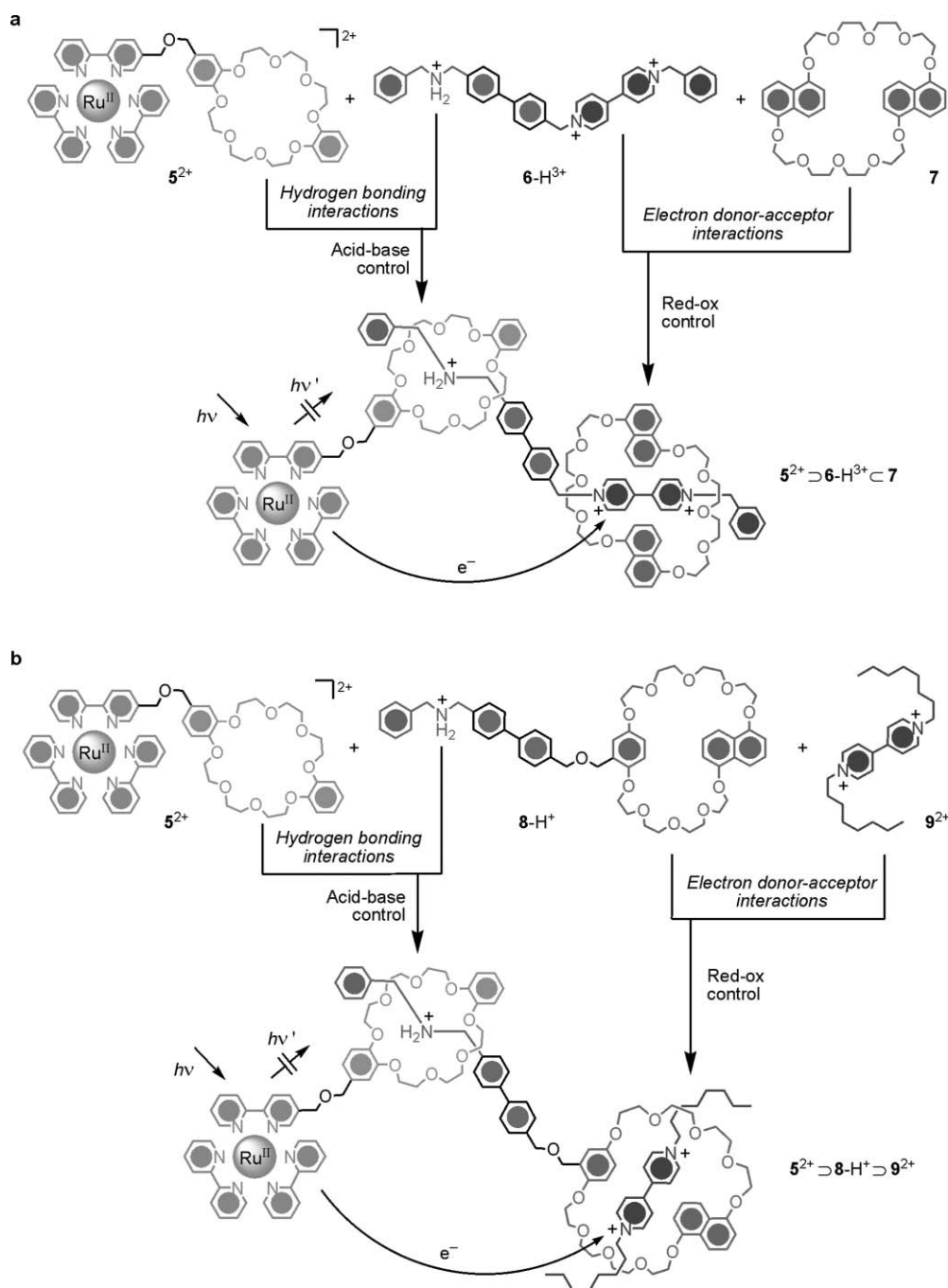
Fig. 6 First- and second-generation systems for mimicking an electrical extension cable. (a) Structural formulas of the three molecular components 5^{2+}, 6-H^+ and 7, which self-assemble in solution to give the $5^{2+} \supset 6$-$H^{3+} \subset 7$ triad. The photoinduced electron-transfer process from the Ru-based unit of 5^{2+} to the bipyridinium unit of 6-H^{3+} taking place in the fully connected system is also represented. (b) Structural formulas of the three molecular components 5^{2+}, 8-H^+ and 9^{2+} which self-assemble in solution to give the $5^{2+} \supset 8$-$H^+ \supset 9^{2+}$ triad. In the fully connected system, excitation with visible light of the Ru-based unit of 5^{2+} is followed by electron transfer to 9^{2+}, with 8-H^+ playing the role of an extension cable.

faster than its formation, thereby preventing its accumulation after light excitation.

The favourable luminescence properties, together with the synthetic and structural advantages offered by $[Ru(tpy)_2]^{2+}$-type complexes compared to, *e.g.*, $[Ru(bpy)_3]^{2+}$-type compounds, render these rotaxane metal complexes promising candidates for the construction of photochemical molecular devices having a wire-type structure.

Light-triggered molecular motions

In green plants the energy needed to sustain the machinery of life[37] is provided by sunlight. In general, light energy is not used as such to produce mechanical movements, but it is used to produce a chemical fuel, namely ATP, suitable for feeding natural molecular machines.[1] Light energy, however, can directly cause photochemical reactions involving large nuclear movements.[13] A simple
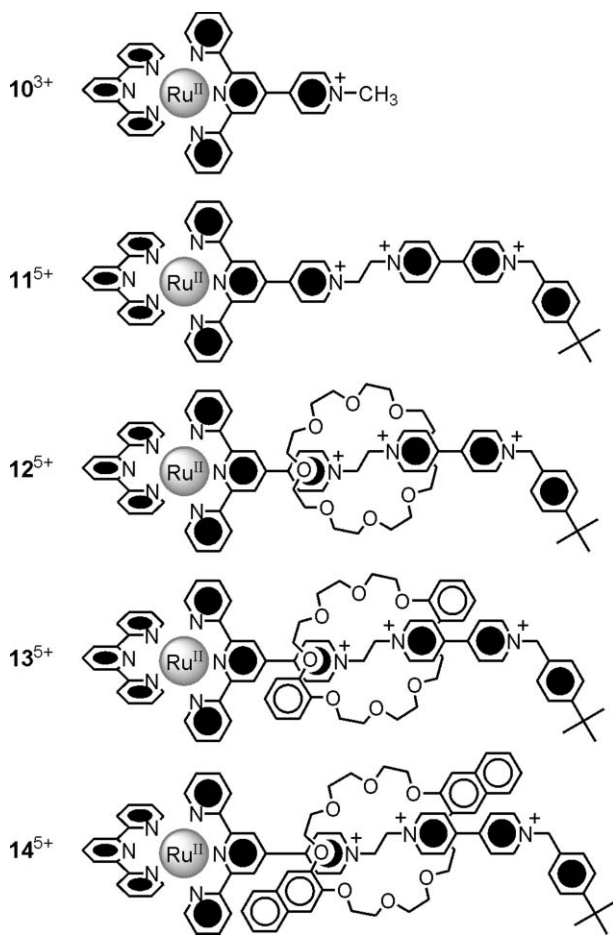
Fig. 7 Structural formulas of the model compound 10^{3+}, dumbbell-shaped species 11^{5+} and rotaxanes 12^{5+}–14^{5+}.
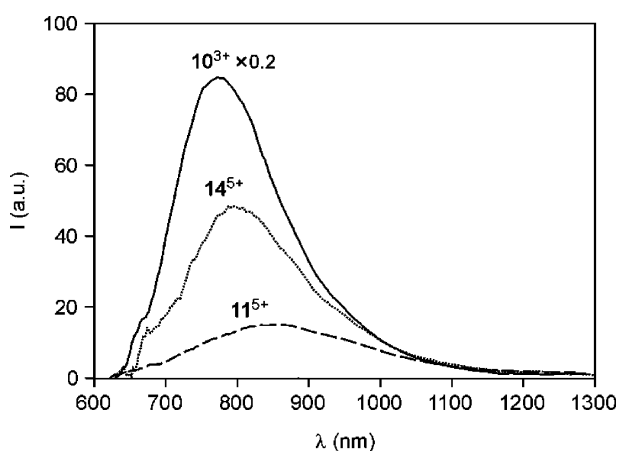

Fig. 8 Luminescence spectra of the Ru[II]-complex 10^{3+} (full line), dumbbell-shaped compound 11^{5+} (dashed line) and rotaxane 14^{5+} (dotted line) in acetonitrile at room temperature. Excitation is performed in the maximum of the MLCT absorption band. The curves are corrected for the spectral response of the detector.

example is a photoinduced isomerization from the lower energy *trans* to the higher energy *cis* form of a molecule containing –C=C– or –N=N– double bonds, which is followed by a spontaneous or

light-induced back reaction. Such photoisomerization reactions have indeed been used to design early prototypes of molecular machines driven by light energy inputs.[38,39] In supramolecular species photoinduced electron-transfer reactions can often cause large displacement of molecular components.[13,17–19] In principle, working with suitable systems, an endless sequence of cyclic molecular-level movements can be performed making use of light-energy inputs without generating waste products.[19,40] In the last few years, a great number of light-driven molecular machines have been developed and the field has been extensively reviewed.[17–19,41,42] Here we will briefly describe two examples: the first one is based on a photoisomerisation reaction, while the second one relies on photoinduced electron-transfer processes.

Threading-dethreading of an azobenzene-based pseudorotaxane

Pseudorotaxanes are interesting in the context of molecular machinery, because the assembly-disassembly of the thread-like and macrocyclic components reminds the threading-dethreading of a needle. They can hardly be used to make unimolecular machines because of the chemical equilibrium between the components, but they represent good models for the development of rotaxane- and catenane-based systems (*vide infra*).

An example of a pseudorotaxane exhibiting threading-dethreading motions based on a photoisomerization process is shown in Fig. 9.[43] The thread-like species *trans*-**15**, which contains a π-electron rich azobiphenoxy unit, and the π-electron deficient macrocycle 16^{4+} self-assemble very efficiently to give a pseudorotaxane, stabilised by electron donor–acceptor interactions.[36] The association constant, obtained by fluorescence titration in acetonitrile solution at room temperature, is $K_a = (1.5 \pm 0.2) \times 10^5$ L mol^{-1}. In the pseudorotaxane structure, the intense fluorescence characteristic of free 16^{4+} ($\lambda_{max} = 434$ nm, Fig. 10) is completely quenched by the donor–acceptor interaction.

Irradiation of an acetonitrile solution containing 1.0×10^{-4} mol L^{-1} *trans*-**15** and 16^{4+} (*ca.* 80% complexed species) with 365-nm light—almost exclusively absorbed by the *trans*-azobiphenoxy unit—causes strong absorption spectral changes, as expected for the well known *trans* $\rightarrow$ *cis* photoisomerisation of the azobenzene-type moiety. Such spectral changes are accompanied by a parallel increase in the intensity of the fluorescence band with $\lambda_{max} = 434$ nm (Fig. 10), characteristic of free 16^{4+} (see above). This behaviour shows that photoisomerisation is accompanied by dethreading (Fig. 9), a result which is confirmed by the finding that the association constant of 16^{4+} with *cis*-**15** is much smaller [$K_a = (1.0 \pm 0.1) \times 10^4$ L mol^{-1}] than that with *trans*-**15**. On irradiation at 436 nm or by warming the solution in the dark the *trans* isomer of **15** can be reformed. This process is accompanied by a parallel decrease in the fluorescence intensity at $\lambda_{max} = 434$ nm, indicating that the *trans*-**15** species rethreads through the cyclophane 16^{4+}.

Although this systems is a rudimental attempt towards the making of light-driven molecular machines, it should be noted that it exhibits a number of valuable features. Firstly, threading-dethreading is controlled exclusively by light energy, without generation of waste products. Furthermore, owing to the reversibility of the photoisomerization process, the light-driven dethreading-rethreading cycle can be repeated at will (Fig. 10, inset). Another relevant feature of this system is that it exhibits profound changes of a strong fluorescence signal.
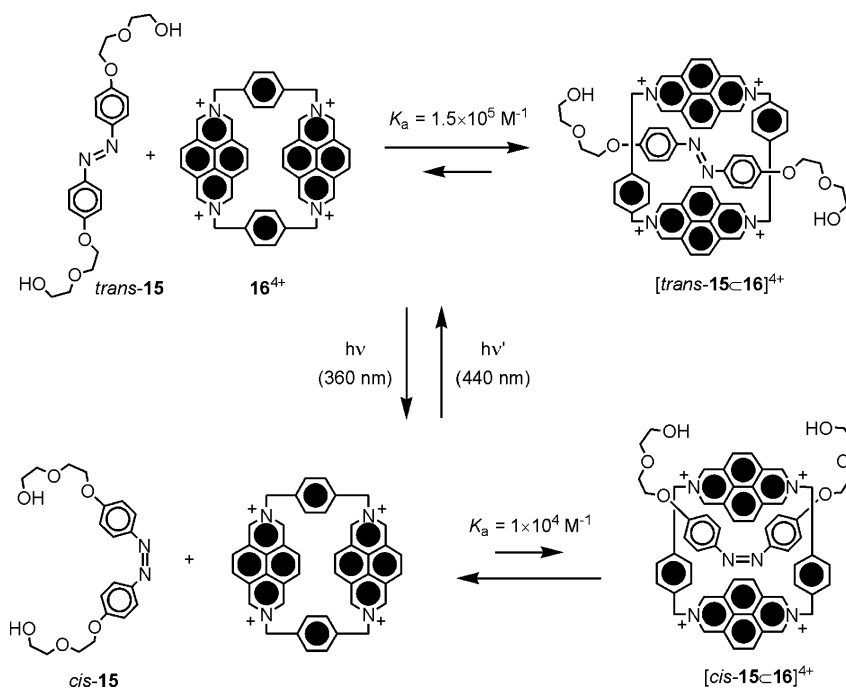
Fig. 9 Threading-dethreading of **15** and **16**[4+] as a consequence of the *cis-trans* photoisomerization of the azobenzene-type unit contained in the thread-like component **15**.
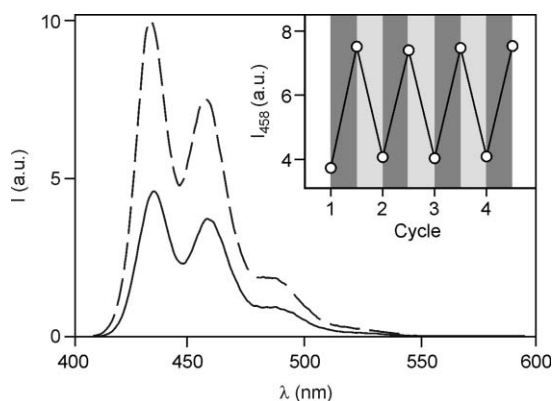

Fig. 10 Fluorescence spectrum of an equimolar mixture (1.0 × 10⁻⁴ mol L⁻¹) of *trans*-**15** and **16**[4+] in acetonitrile at room temperature (full line), and fluorescence spectrum of the same mixture after irradiation at 365 nm until a photostationary state is reached (dashed line). The inset shows the changes in intensity of the fluorescence associated with the free macrocyclic ring **16**[4+] upon consecutive *trans* → *cis* (irradiation at 365 nm, dark areas) and *cis* → *trans* (irradiation at 436 nm, light areas) photoisomerisation cycles. Excitation is performed in an isosbestic point at 411 nm.

Photoinduced shuttling in multicomponent rotaxanes

Rotaxanes are appealing systems for the construction of molecular machines because the mechanical binding of the macrocyclic host with its dumbbell-shaped substrate leaves the former free to displace itself along and/or around the latter without losing the system's integrity. Two interesting molecular motions can be envisaged in rotaxanes, namely (i) rotation of the macrocyclic ring around the thread-like portion of the dumbbell-shaped component, and (ii) translation of the ring along the same portion. The molecular components of a rotaxane usually exhibit some kind of interaction originating from complementary chemical properties, which is also exploited in the template-directed synthesis of such systems.[10] In rotaxanes containing two different recognition sites in their thread-like portion, 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,[44] constitute probably the most common examples of artificial molecular machines. Interestingly, the dumbbell component of a molecular shuttle exerts a restriction on the ring motion in the three dimensions of space, similar to that imposed by the protein track for linear biomolecular motors kinesin and dynein.[37]

On the basis of the experience gained with pseudorotaxane model systems,[45] the rotaxane **17**[6+] (Fig. 11) was specifically designed[46] to achieve photoinduced ring shuttling in solution. This compound has a modular structure; its ring component R is a π-electron donating bis-*p*-phenylene[34]crown-10, whereas its dumbbell component is made of several covalently linked units. They are a Ru[II] polypyridine complex (P[2+]), a *p*-terphenyl-type rigid spacer (S), a 4,4′-bipyridinium (A₁[2+]) and a 3,3′-dimethyl-4,4′-bipyridinium (A₂[2+]) π-electron accepting stations, and a tetraarylmethane group as the terminal stopper (T). The Ru-based unit plays the dual role of a light-fueled power station and a stopper, whereas the mechanical switch consists of the two electron accepting stations and the electron donating macrocycle. The stable translational isomer of rotaxane **17**[6+] is the one in which the R component encircles the A₁[2+] unit, in keeping with the fact that this station is a better electron acceptor than the other one. The strategy devised in order to obtain the photoinduced shuttling movement of the macrocycle between the two stations A₁[2+] and
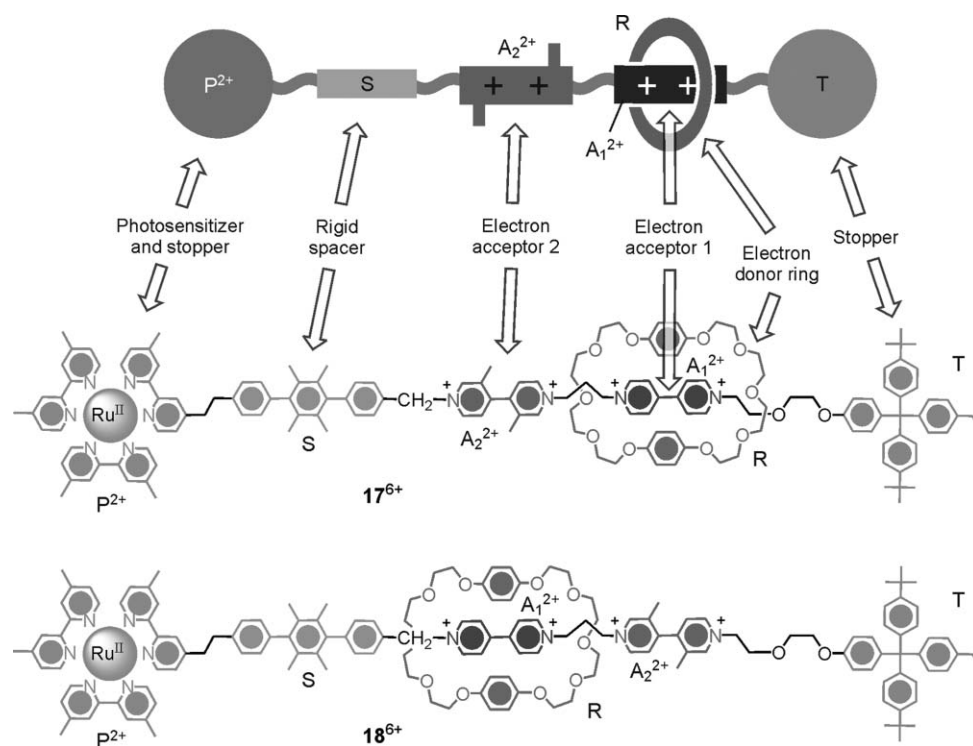
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Fig. 11 Structural formulas of multicomponent rotaxanes 17^{6+} and 18^{6+}, designed to work as photochemically driven molecular shuttles. A cartoon representation of 17^{6+} is also shown.

A_2^{2+} is based on the following 'four stroke' synchronised sequence of electronic and nuclear processes (Fig. 12):

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

(b) *Ring displacement*: the ring moves (process 4) for 1.3 nm from the reduced station A_1^+ to A_2^{2+}, a step that is in competition with the back electron-transfer process from A_1^+ (still encircled by R) to the oxidised unit P^{3+} (process 5).

(c) *Electronic reset*: a back electron-transfer process from the 'free' reduced station A_1^+ to the oxidised unit P^{3+} (process 6) restores the electron acceptor power to such a station. At this point the machine is reset, and the ring has been 'pumped' into an energetically higher state.

(d) *Nuclear reset*: as a consequence of the electronic reset, thermally activated back movement of the ring from A_2^{2+} to A_1^{2+} takes place (process 7).

Steady-state and time-resolved spectroscopic experiments together with electrochemical measurements in acetonitrile solution showed[47] that the absorption of a visible photon by 17^{6+} can cause the occurrence of a forward and back ring movement, that is, a full mechanical cycle according to the mechanism illustrated in Fig. 12.[48] It was estimated that the fraction of the excited state energy used for the motion of the ring amounts to ∼10%, and the system can generate a mechanical power of about 3×10^{-17} W per molecule. The somewhat disappointing quantum efficiency for ring shuttling (2% at 30 °C) is compensated by the fact that

the investigated system gathers together the following features: (i) it is powered by visible light (in other words, sunlight); (ii) it exhibits autonomous behaviour, like motor proteins; (iii) it does not generate waste products; (iv) its operation can rely only on intramolecular processes, allowing in principle operation at the single-molecule level; (v) it can be driven at a frequency of about 1 kHz; (vi) it works in mild environmental conditions (*i.e.*, fluid solution at ambient temperature); and (vii) it is stable for at least 10^3 cycles.

The molecular shuttle 17^{6+} can also be operated, with a higher quantum yield, by a sacrificial mechanism[46] based on the participation of external reducing (triethanolamine) and oxidizing (dioxygen) species, and by an intermolecular mechanism[47] involving the kinetic assistance of an external electron relay (phenothiazine), which is not consumed. However, operation by the sacrificial mechanism does not afford an autonomous behaviour and leads to consumption of chemical fuels and formation of waste products. On the other hand, the assistance by an electron relay affords autonomous operation in which only photons are consumed, but the mechanism is no longer based solely on intra-rotaxane processes.

Owing to its modular design, the rotaxane 17^{6+} is amenable to be structurally modified in the attempt of improving its performance as a light-driven molecular shuttle. For instance, a rotaxane 18^{6+} (Fig. 11), that differs from 17^{6+} only for the exchange in the position of the two electron accepting stations along the dumbbell-shaped component, has been recently synthesized and its photochemical properties investigated.[49] It has been found that the shorter distance of the electron-transfer photosensitiser P^{2+} to the better (A_1^{2+}) of the two electron acceptors in 18^{6+} results in an increase in the rate—and hence the efficiency—of the photoinduced
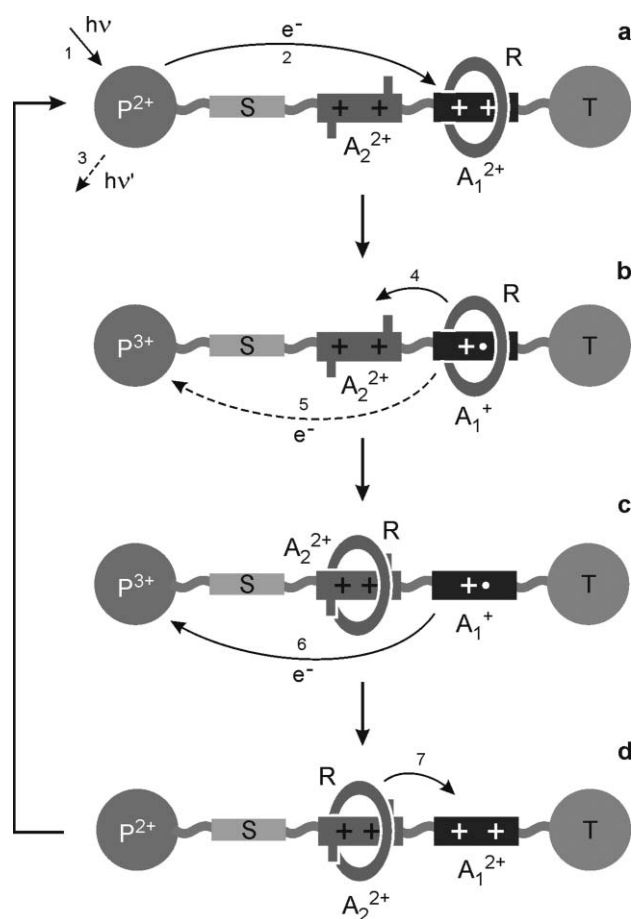
Fig. 12 Schematic representation of the working mechanism of rotaxane **17**[6+] as an autonomous 'four stroke' molecular shuttle powered by visible light. See Fig. 11 for a legend of the cartoons.

electron-transfer step compared to **17**[6+]. The rate of the back electron transfer, however, also increases. As a consequence, such a second-generation molecular shuttle performs better than **17**[6+] in a sacrificial mechanism, but much worse when it is powered by visible light (*e.g.*, sunlight) alone. Another interesting difference between these two parent rotaxanes lies in the fact that the macrocyclic ring R, which initially surrounds the A_1^{2+} station, moves in opposite directions upon light excitation, *i.e.*, towards the photosensitiser P^{2+} in **17**[6+] and towards the stopper T in **18**[6+].

This study shows that the structural and functional integration of different molecular subunits in a multicomponent structure is a powerful strategy for constructing nanoscale machines.[50] Nevertheless, the molecular shuttle **17**[6+] in its present form could not perform a net mechanical work in a full cycle of operation[51] (as for any reversible molecular shuttle, the work done in the 'forward' stroke would be cancelled by the 'backward' stroke).[52] To reach this goal, a more advanced design of the molecular machine and/or a better engineering of its operating environment (*e.g.*, a surface or a membrane) is indeed required.[17]

Conclusion

One of the most interesting aspects of supramolecular (multi-component) systems is their interaction with light. The systems described in this paper show that, in the frame of research on supramolecular photochemistry, the design and construction of nanoscale devices capable of performing useful light-induced functions can indeed be attempted.

The potential applications of photochemical molecular devices are various—from energy conversion to sensing and catalysis—and, to a large extent, still unpredictable. As research in the area is progressing, two interesting kinds of non-conventional applications of these systems begin to emerge: (i) their behaviour can be exploited for processing information at the molecular level[53] and, in the long run, for the construction of chemical computers;[54] (ii) their mechanical features can be utilised for transportation of nanoobjects, mechanical gating of molecular-level channels, and nanorobotics.[55]

However, it should be noted that the species described here, as most multicomponent systems developed so far, operate in solution, that is, in an incoherent fashion and without control of spatial positioning. Although the solution studies are of fundamental importance to understand their operation mechanisms and for some use (*e.g.*, drug delivery), it seems reasonable that before such systems can find applications in many fields of technology, they have to be interfaced with the macroscopic world by ordering them in some way. The next generation of multicomponent molecular species will need to be organised so that they can behave coherently and can be addressed in space. Viable possibilities include deposition on surfaces, incorporation into polymers, organisation at interfaces, or immobilisation into membranes or porous materials. Recent achievements in this direction[56–59] let one optimistically hope that useful devices based on functional (supra)molecular systems could be obtained in a not too distant future.

Apart from foreseeable applications related to the development of nanotechnology, investigations on photochemical molecular devices are important to increase the basic understanding of photoinduced reactions and other important processes such as self-assembly, as well as to develop reliable theoretical models. This research has also the important merit of stimulating the ingenuity of chemists, thereby instilling new life into chemistry as a scientific discipline.

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