Artificial nanomachines based on interlocked molecular species: recent advances

Vincenzo Balzani, Alberto Credi,* Serena Silvi and Margherita Venturi

Received 14th June 2006
First published as an Advance Article on the web 6th September 2006
DOI: 10.1039/b517102b

The bottom-up construction and operation of nanoscale machines and motors, that is, supramolecular systems wherein the molecular components can be set in motion in a controlled manner for ultimately accomplishing a function, is a topic of great interest in nanoscience and a fascinating challenge of nanotechnology. The field of artificial molecular machines and motors is growing at an astonishing rate and is attracting a great deal of interest. Research in the last decade has shown that species made of interlocked molecular components like rotaxanes, catenanes and related systems are most attractive candidates. In recent times, the evolution of the structural and functional design of such systems has led to the construction and operation of complex molecular machines that, in some cases, are able to do specific tasks.

This *tutorial review* is intended to discuss the design principles for nanomachines based on interlocked molecules, and to provide a timely overview on representative prototype systems.

1. Introduction

The construction of useful devices is the essence of technology, and has always been a key issue for human development. In general, a device is an assembly of components designed to achieve a specific function, resulting from the cooperation of the acts performed by each component. Another distinctive feature of a device is indeed its size. Many fields of technology, in particular information processing, have benefited from progressive miniaturisation of the components of devices in the last fifty years. A common prediction is that further progress in miniaturisation will not only decrease the size and increase the power of computers, but could also open the way to new technologies in the fields of medicine, environment, energy and materials.

The top-down approach used so far for the construction of miniaturised devices is reaching fundamental and practical limits, which include severe cost limitations, for sizes below 50 nanometres.[1] Miniaturisation, however, can be pushed further on since 'there is plenty of room at the bottom', as Richard Feynman stated in his famous talk in 1959.[2] Research on supramolecular chemistry has shown that molecules are convenient nanometre-scale building blocks that can be used, in a bottom-up approach, to construct ultraminiaturised devices and machines. Chemists are in an ideal position to develop such a molecular approach to functional

Dipartimento di Chimica "G. Ciamician", Università di Bologna, via Selmi 2, 40126 Bologna, Italy. E-mail: alberto.credi@unibo.it; Fax: (+39)-051-2099456

Vincenzo Balzani

Vincenzo Balzani is professor of Chemistry at the University of Bologna, Italy. He has obtained several awards, including the Italgas European Prize for Research and Innovation and the Porter Medal on Photochemistry. He is a fellow of the American Association for the Advancement of Science (USA) and the Accademia Nazionale dei Lincei, and a member of the Editorial Boards of several international journals. His scientific activity is documented by three monographs and about 500 papers in the fields of photochemistry, supramolecular chemistry, molecular-level devices and machines, and solar energy conversion. He is one of the 50 most cited scientists in the field of Chemistry according to the ISI classification.

Alberto Credi

Alberto Credi was born in 1970. He received his "Laurea" (1994) from the University of Bologna where, after a research period in the United States, he also earned his PhD (1999). He is currently associate professor of chemistry at his Alma Mater. He has received several scientific awards, including the IUPAC Prize for young chemists, and co-authored about 120 scientific papers in the fields of molecular and supramolecular photochemistry and electrochemistry. He is also the co-author (together with V. Balzani and M. Venturi) of a monograph entitled "Molecular Devices and Machines", and of a handbook of photochemistry.

nanostructures because they are able to design, synthesise, investigate and operate with molecules—for instance, make them react or get them together into larger assemblies.

Much of the inspiration to construct molecular devices and machines comes from the outstanding progress of molecular biology that has begun to reveal the secrets of the natural nanodevices which constitute the material base of life.[3] 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 realisation of artificial molecular devices.[4,5] The bottom-up construction of devices as complex as those present in Nature is, of course, a prohibitive task. Therefore chemists have tried to construct much simpler systems, without mimicking the complexity of the biological structures, and to investigate the challenging problems posed by interfacing artificial molecular devices with the macroscopic world, particularly as far as energy supply and information exchange are concerned. In the last few years the development of powerful synthetic methodologies, combined with a device-driven ingenuity evolved from the attention to functions and reactivity, have led to remarkable achievements in this field.[6–12]

In the first part of this tutorial review we will briefly discuss the design principles for molecular machines, and illustrate the potential of rotaxanes, catenanes, and related species as nanomechanical devices. We will then describe recent prominent work in the field, and discuss potential applications, limitations and future directions.

2. Basic features and "scaling rules" for molecular machines

A molecular machine can be defined as a particular type of molecular device designed to perform mechanical movements under control of appropriate energy inputs. As for any device, a molecular machine is supposed to carry out a function, and should contain a motor, namely a component (or an assembly of components) capable of using a form of energy to bring about controllable molecular displacements. It should be noted that the dynamic behaviour is a distinctive feature of molecules, even in the solid state; however, the term molecular machine is reserved to systems performing reactions that can cause large amplitude, non-trivial motions leading to real translocation of some component parts of the system itself.

Like the macroscopic counterparts, molecular machines are characterised by (i) the kind of energy input supplied to make them work, (ii) the type of motion (such as translation, rotation, or oscillation) performed by their components, (iii) the way of monitoring their operation (the motion of the component parts should cause readable changes in some chemical or physical properties of the system), (iv) the possibility to repeat the operation in cycles, and (v) the time scale needed to complete a cycle. An additional and very important distinctive feature of a molecular machine with respect to a molecular motor is (vi) the function performed. Under these aspects, molecular machines are indeed the result of the extension of the concept of macroscopic machine to the molecular world.

However, nanoscale machines and motors cannot be considered merely as 'shrunk' versions of the corresponding macroscopic counterparts. In fact, the operation mechanisms of molecular machines cannot be devised on the basis of scaling rules, because they have to deal with phenomena different from those that govern the macroscopic world.[5,13] For example, inertia-dominated motion we are familiar with in our everyday experience is fully negligible at the molecular scale, where viscous forces resulting from intermolecular interactions (including those with solvent molecules) largely prevail. Another fundamental difference between the macroscopic and the nanoscale realms is represented by the importance of thermal fluctuations (Brownian motion).[5,13,14] This random motion can be neglected for "big" objects, but dominates the mechanical behaviour of small (sub-micrometre) particles. Nanometre-scale systems are thus inherently subjected to Brownian motion, and it was estimated[13] that a typical biomolecular motor is subjected to a thermal noise power that is several orders of magnitude greater than the power originating from an exoergonic chemical reaction (ATP hydrolysis) to drive directed movement. Chemists have known for a long time that molecules utilise thermal fluctuations to react, since the vast majority of chemical processes include

Serena Silvi

Serena Silvi was born in 1978. She received her "Laurea" in Chemistry in 2002 from the University of Bologna, where she also earned her PhD in 2006 under the supervision of professor Alberto Credi. In 2005 she spent a research period in the laboratory of professor Angel E. Kaifer at the University of Miami, working on cucurbituril-based supramolecular species. Her research focuses on the design of artificial molecular machines and the investigation of their photochemical, photophysical and electrochemical behaviour in solution.

Margherita Venturi

Margherita Venturi is professor of Chemistry at the University of Bologna, Italy. From 1972 to 1991 she worked at the National Research Council of Bologna where she mainly studied, by means of pulsed and continuous radiolytic techniques, the electron-transfer processes involved in model systems for the conversion of solar energy. In 1992 she moved to the group of Prof. Balzani, where she is still now. Her present research interests are in the field of supramolecular photochemistry and electrochemistry. She is co-author of about 150 publications in international journals, including several reviews and a monograph entitled "Molecular Devices and Machines".

thermally activated steps. Molecular machines are no exception: thermal fluctuations allow the energy barriers associated with the transition between the different mechanical states of the system to be overcome.[14]

Because of the second law of thermodynamics, molecular machines cannot simply be driven by thermal energy at a constant temperature: in analogy with macroscopic machines, they need to be fuelled by an energy source in order to carry out a task. Thus, the problem of the energy supply to make artificial molecular machines work [point (i)] is of the greatest importance. The most obvious way to supply energy to a chemical system is through an exergonic chemical reaction. Richard Feynman observed:[2] *''An internal combustion engine of molecular size is impossible. Other chemical reactions, liberating energy when cold, can be used instead.''* This is exactly what happens in our body, where the chemical energy supplied by food is used in long series of slightly exergonic reactions to power the biological machines that sustain life. If an artificial molecular machine has to work by inputs of chemical energy, it will need addition of fresh reactants ('fuel') at any step of its working cycle, with the concomitant formation of waste products. Accumulation of waste products, however, will compromise the operation of the device unless they are removed from the system, as 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 machines based on chemical fuel inputs.

Photochemical and electrochemical energy inputs can indeed cause the occurrence of *endergonic* and *reversible* reactions. In recent years, the progresses made by supramolecular photochemistry and electrochemistry has thus led to the design and construction of molecular machines powered by light or electrical energy, which work without formation of waste products. In the case of photoexcitation, the commonly used endergonic and reversible reactions are isomerisation and electron-transfer processes.[15] In the case of electrochemical energy inputs, the induced endergonic and reversible reactions are, of course, heterogeneous electron transfer processes. Photochemical and electrochemical techniques offer further advantages, since lasers provide the opportunity of working in very small space and very short time domains, and electrodes represent one of the best way to interface molecular-level systems with the macroscopic world.

A very important feature of molecular machines, related to energy supply [point (i)] and cyclic operation [point (iv)], is their capability to exhibit an *autonomous* behaviour; that is, to keep operating, in a constant environment, as long as the energy source is available. Natural motors are autonomous, but most of the artificial systems reported so far are *not autonomous* since, after the mechanical movement induced by a given input, they need another, opposite input to reset. Obviously, the operation of a molecular machine is accompanied by partial degradation of free energy into heat, regardless of the chemical, photochemical, and electrochemical nature of the energy input.

Finally, as far as point (vi) is concerned, the functions that can be performed by exploiting the movements of the component parts in molecular motors and machines are various and, to a large extent, still unpredictable. In natural systems the molecular motions are always aimed at obtaining specific functions, *e.g.*, catalysis, transport, gating. It is worth noting that the changes in the physicochemical properties related to the mechanical movements in molecular machines usually obey binary logic, and can thus be taken as a basis for information processing at the molecular level.

The majority of the artificial molecular machines investigated so far operates in solution, *i.e.*, without control of spatial positioning and in an incoherent fashion. It is likely that immobilisation of nanomachines[16] on surfaces, interfaces, membranes or porous materials will be mandatory for application in many fields of technology, where spatial control and/or coherent operation of the individual nanomechanical devices is required to accomplish the desired function. Nevertheless, the solution studies remain of fundamental importance both to gain understanding on the operation mechanisms of such machines for development of prototypes of increasing complexity, and to investigate applications (*e.g.*, drug delivery) for which operation in liquid solution is required.

3. Interlocked molecular species as nanoscale machines

In principle, molecular motors and machines can be designed starting from several kinds of molecular and supramolecular systems,[6–12] including DNA.[17] However, for the reasons mentioned below, most of the systems constructed so far are based on interlocked molecular species such as rotaxanes, catenanes, and related species. The names of these compounds derive from the Latin words *rota* and *axis* for wheel and axle, and *catena* for chain. Rotaxanes[18] are minimally composed (Fig. 1a,b) of a dumbbell-shaped molecule surrounded by a macrocyclic compound (the 'ring') and terminated by bulky groups ('stoppers') that prevent disassembly. Catenanes[18] are made of (at least) two interlocked macrocycles (Fig. 1c). Important features of these systems derive from noncovalent interactions between components that contain complementary recognition sites. Such interactions, that are also responsible for the efficient template-directed syntheses[19] of rotaxanes and catenanes, include electron donor–acceptor ability, hydrogen bonding, hydrophobic–hydrophylic character, π–π stacking, electrostatic forces and, on the side of the strong interaction limit, metal–ligand bonding.

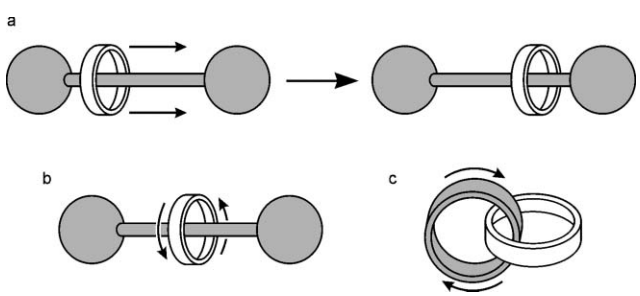

Fig. 1 Schematic representation of the intercomponent motions that can be obtained with simple interlocked molecular architectures: ring shuttling in rotaxanes (a), and ring rotation in rotaxanes (b) and catenanes (c).

Rotaxanes and catenanes are appealing systems for the construction of molecular machines because (i) the mechanical bond allows a large variety of mutual arrangements of the molecular components, while conferring stability to the system, (ii) the interlocked architecture limits the amplitude of the intercomponent motion in the three directions, (iii) the stability of a specific arrangement (co-conformation) is determined by the strength of the intercomponent interactions, and (iv) such interactions can be modulated by external stimulation. The large-amplitude motions that can be achieved with rotaxanes and catenanes are represented schematically in Fig. 1. Particularly, two interesting molecular motions can be envisaged in rotaxanes, namely (i) translation, *i.e.*, shuttling, of the ring along the axle, and (ii) rotation of the ring around the axle. Hence, rotaxanes are good prototypes for the construction of both linear and rotary molecular motors. Systems of type (i), termed molecular shuttles (Fig. 1a), constitute indeed the most common implementation of the molecular machine concept with rotaxanes.

The cartoons shown in Fig. 1, while providing a simple structural and topological representation, are somewhat misleading because they give the impression that rotaxanes and catenanes are made of rigid molecular components, which is not the case for the vast majority of the systems reported so far. However, in order to obtain clear-cut mechanical movements the molecular components should exhibit at least some stiffness. As will be evidenced by the examples in the following sections, this feature for molecular machines is most commonly fulfilled by utilising molecular components that possess rigid subunits in their structures.

Interestingly, the dumbbell component of a molecular shuttle exerts on the ring motion the same type of directional restriction imposed by the protein track for linear biomolecular motors (an actin filament for myosin and a microtubule for kinesin and dynein).[3] It should also be noted that interlocked molecular architectures are largely present in natural systems—for instance, DNA catenanes and rotaxanes are known.[18] Many processive enzymes, *i.e.*, enzymes that remain attached to their biopolymer substrates (DNA, RNA or proteins) and perform multiple rounds of catalysis before dissociating, are thought to exhibit a rotaxane structure, as confirmed for example by the observation of the crystal structure of DNA λ-exonuclease.[20] Clearly, the unique aspect of the rotaxane architecture, that is, the mechanical binding of the catalyst with the substrate which leaves the former free to displace itself along the latter without losing the system's integrity, is utilised by Nature to enhance the activity of processive enzymes.

4. Linear motions

4.1 Photochemically driven molecular shuttles with luminescence readout

Several examples of rotaxanes that behave as light-driven molecular shuttles based on photoisomerisation reactions are known.[6,7] Rotaxanes containing two different photoresponsive 'stations' (*i.e.*, recognition sites for the ring) on the axle and one or two macrocyclic rings, and exhibiting fluorescence output signals, were described recently.[21,22] For instance, rotaxane **1** (Fig. 2)[22] contains in its dumbbell component an azobenzene and a stilbene stations, and two slightly different naphthalimide stoppers (A and B) which exhibit strong fluorescence at distinct wavelengths (λ_{max} = 520 and 395 nm, respectively). The ring is a α-cyclodextrin (α-CD) macrocycle. The azobenzene and stilbene units can be photoisomerised independently by using light at different wavelengths in the UV–visible region. At room temperature in dimethyl sulfoxide solution, the stable (starting) state is *E,E*-**1**, characterised by fast (on the NMR timescale) shuttling of the α-CD ring between the two stations. Irradiation at 380 nm causes the isomerisation of the azobenzene unit, leading to the formation of *Z,E*-**1**, in which the α-CD ring is trapped on the *E*-stilbene station. Further irradiation at 313 nm causes the isomerisation of the stilbene unit, leading to the formation of *Z,Z*-**1**, in which the α-CD ring encircles the central biphenyl group. On the other hand, irradiation of *E,E*-**1** at 313 nm leads to the formation of the *E,Z*-**1** isomer, in which the α-CD ring is trapped on the *E*-azobenzene unit; further irradiation at 380 nm affords *Z,Z*-**1**. The photochemical reactions are fully reversible upon light irradiation or heating. The starting state and the three photostationary states were characterised by NMR and UV-visible absorption and luminescence spectroscopy. 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 steric and electronic effects 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 **1** was shown[22] to perform as a reversible half-adder device with all-optical input and output signals.

4.2 Autonomous shuttling in a rotaxane powered by visible light

On the basis of the experience gained with pseudorotaxane model systems,[6,7] the rotaxane $\mathbf{2}^{6+}$ (Fig. 3) was specifically designed[23] 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 (A_1^{2+}) and a 3,3′-dimethyl-4,4′-bipyridinium (A_2^{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-fuelled power station and a stopper, whereas the mechanical switch consists of the two electron accepting stations and the electron donor macrocycle. The stable translational isomer of rotaxane $\mathbf{2}^{6+}$ is the one in which the R component encircles the A_1^{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 A_1^{2+} and A_2^{2+} is based on the following 'four stroke' synchronised sequence of electronic and nuclear processes (Fig. 3):

a) *Destabilisation of the stable translational isomer*: light excitation of the photoactive unit P^{2+} (process 1) is followed by

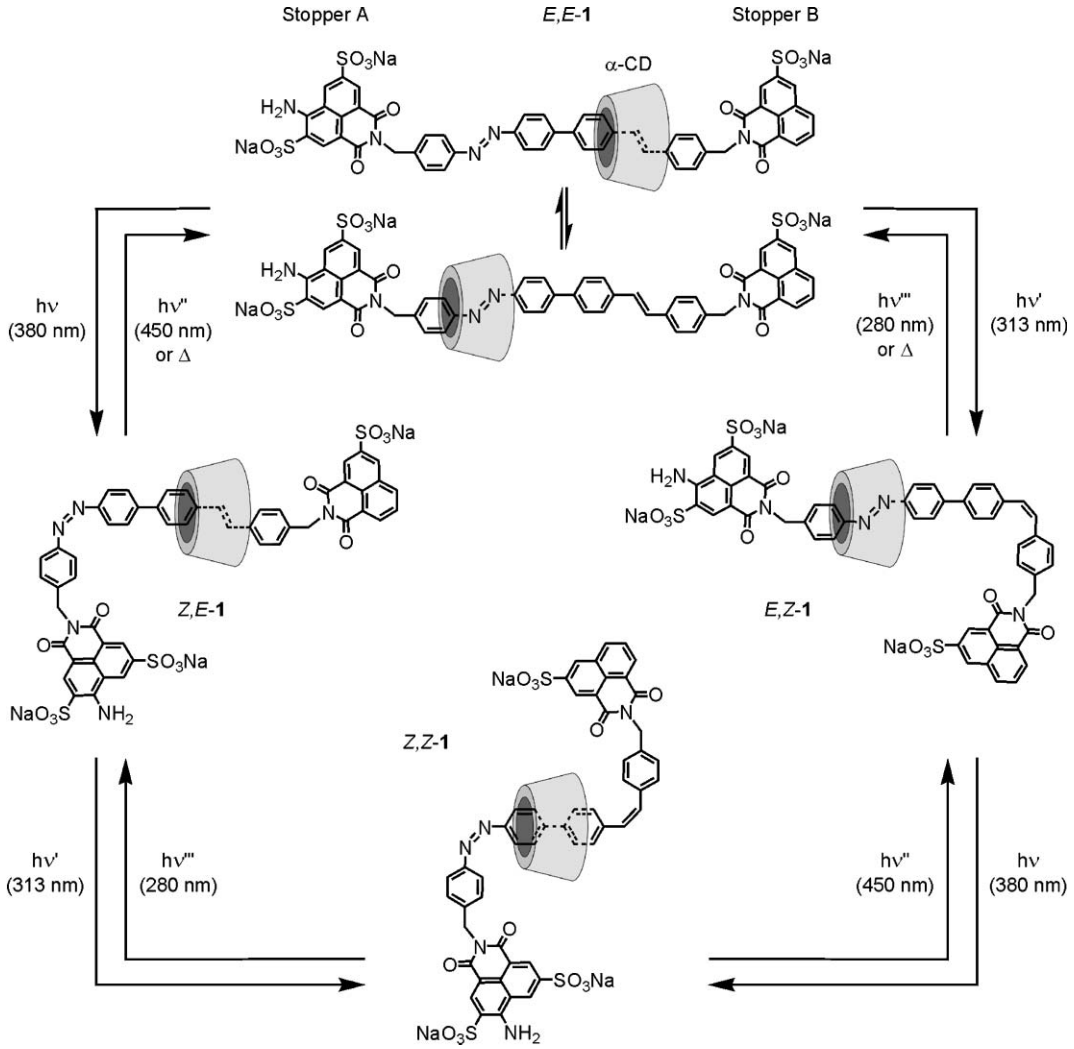

Fig. 2 The four isomeric states of rotaxane **1** and the photoisomerisation reactions leading to their interconversion.

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 the A_1^{2+} 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[24] that the absorption of a visible photon by $\mathbf{2}^{6+}$ can cause the occurrence of a forward and back ring movement, that is, a full mechanical cycle according to the mechanism illustrated in Fig. 3. It was estimated that the fraction of the excited state energy used for the motion of the ring amounts to $\sim$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. Although the system in its present form could not develop a net mechanical work in a full cycle of operation[25] (as for any reversible molecular shuttle, the work done in the 'forward' stroke would be cancelled by that performed in the 'backward' stroke),[26] it shows that the structural and

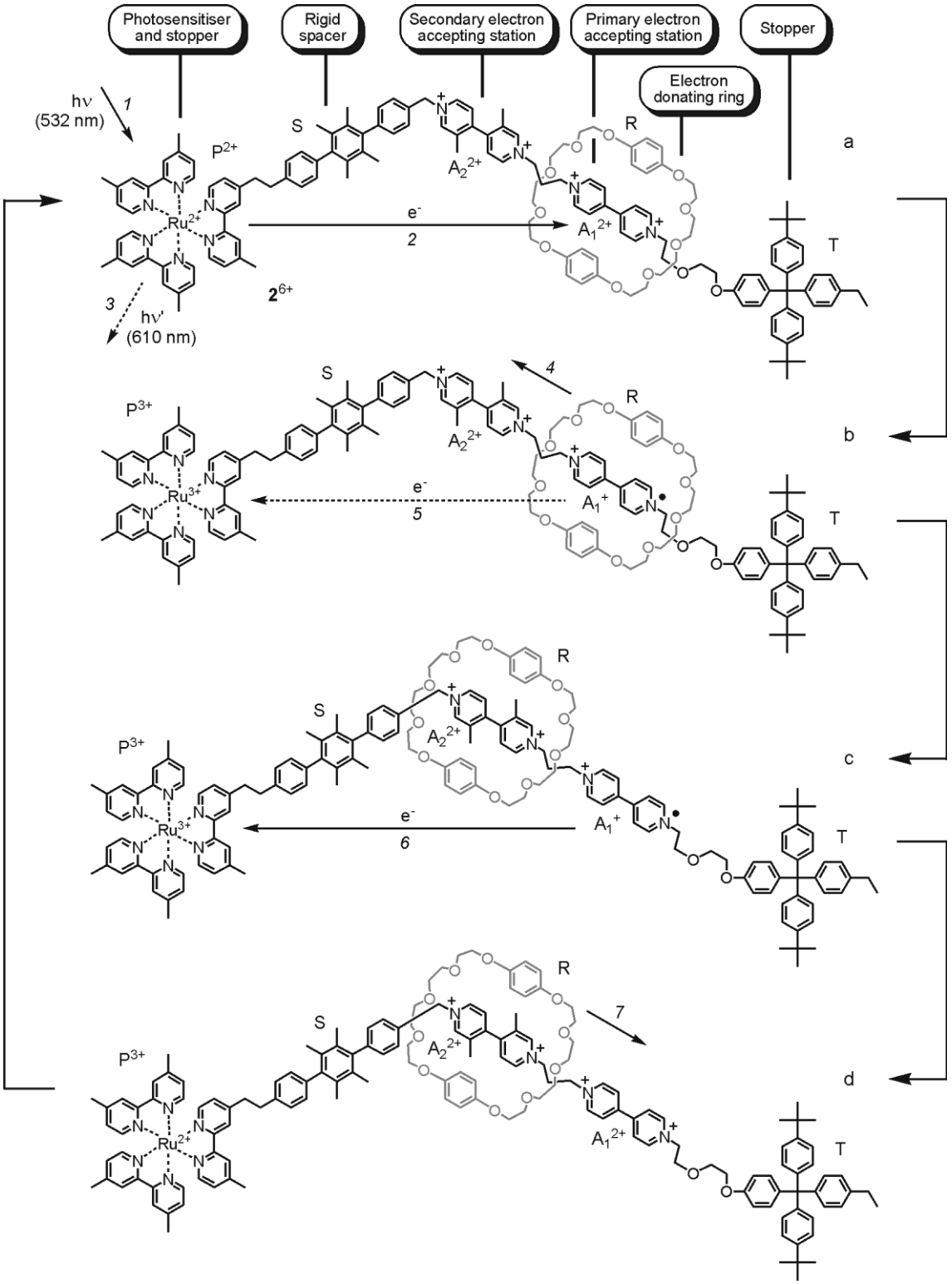

Fig. 3 Chemical formula and working mechanism of rotaxane $\mathbf{2}^{6+}$ as an autonomous 'four stroke' molecular shuttle powered by visible light.

functional integration of different molecular subunits in a multicomponent structure is a powerful strategy to construct nanoscale machines. Owing to its modular design, the rotaxane $\mathbf{2}^{6+}$ is amenable to be structurally modified in the attempt of improving its performance as a light-driven molecular shuttle.[27]

4.3 A rotaxane-terminated surface with switchable wettability properties

Rotaxane **3** (Fig. 4a)[28] contains two different stations on its axle, namely a fumaramide (FUM) and a tetrafluorosuccinamide (TFS) units. The former station has a high binding

affinity for the ring, that can be switched off by photoisomerisation to the maleamide (MAL) isomeric form. As a result, the ring is expected to move onto the tetrafluorosuccinamide station. Therefore, the light-controlled shuttling of the ring in **3** can be used to expose or conceal the fluorinated portion of the axle, and it was envisaged that such a process could be exploited to produce a rotaxane-covered surface whose hydrophobic/hydrophilic character can be modulated. In fact, it is known that the contact angles of both polar and apolar liquids are highly sensitive to small variations in the concentration of fluoroalkane groups.

The rotaxane **3** was anchored to a monolayer of 11-mercaptoundecanoic acid self-assembled on a Au(111) surface deposited on glass or mica (Fig. 4b).[28] Such a modified surface was found to exhibit photoswitchable wettability characteristics because the contact angle of small droplets of various types of liquids changed upon UV irradiation of the surface. Specifically, the hydrophilicity of surface was found to increase upon irradiation. By performing spatially-controlled irradiation experiments, a microlitre droplet of diiodomethane could be displaced on the surface, and even transported up to a 12° incline. These results were interpreted in terms of the light-induced shuttling in some of the surface-deposited rotaxanes which causes a decrease in the number of exposed fluoroalkane residues, thereby reducing the hydrophobicity of the surface (Fig. 4b). This sound interpretation is in agreement with the results of control experiments. However, because of the strategy employed for chemical modification of the surface, the definitive control system (namely, a surface covered with the photoactive dumbbell component of **3**) could not be prepared.

4.4 A surface-bound electrochemically driven molecular shuttle

A monolayer of the rotaxane $\mathbf{4}^{4+}$ (Fig. 5), which consists of an electron accepting cyclophane threaded on a molecular axle which includes an electron donating diiminobenzene unit and is stoppered by an adamantane moiety, was assembled on a gold electrode.[29] The cyclophane ring, which is originally located on the diiminobenzene unit (Fig. 5a) by virtue of electron donor–acceptor interactions, is displaced towards the electrode upon one-electron reduction of its two bipyridinium units at −0.53 V *vs* SCE (Fig. 5b), owing to disruption of the donor–acceptor interactions and electrostatic attraction to the electrode. Oxidation of the reduced cyclophane at −0.33 V *vs* SCE causes ring shuttling to the original diiminobenzene site.

The position of the oxidised and reduced cyclophane rings and the shuttling rate constants (320 s^{-1} and 80 s^{-1} at 298 K for reduction- and oxidation-induced processes, respectively) were determined by chronoamperometry and impedance measurements. Investigation of the temperature dependence of the shuttling rates showed[30] that the reduction-induced shuttling is an energetically downhill process with no measurable activation barrier, whereas oxidation-induced shuttling requires thermal activation. The lack of an energy barrier in the former case is in agreement with the fact that the shuttling is mainly driven by coulomb attraction of the positively

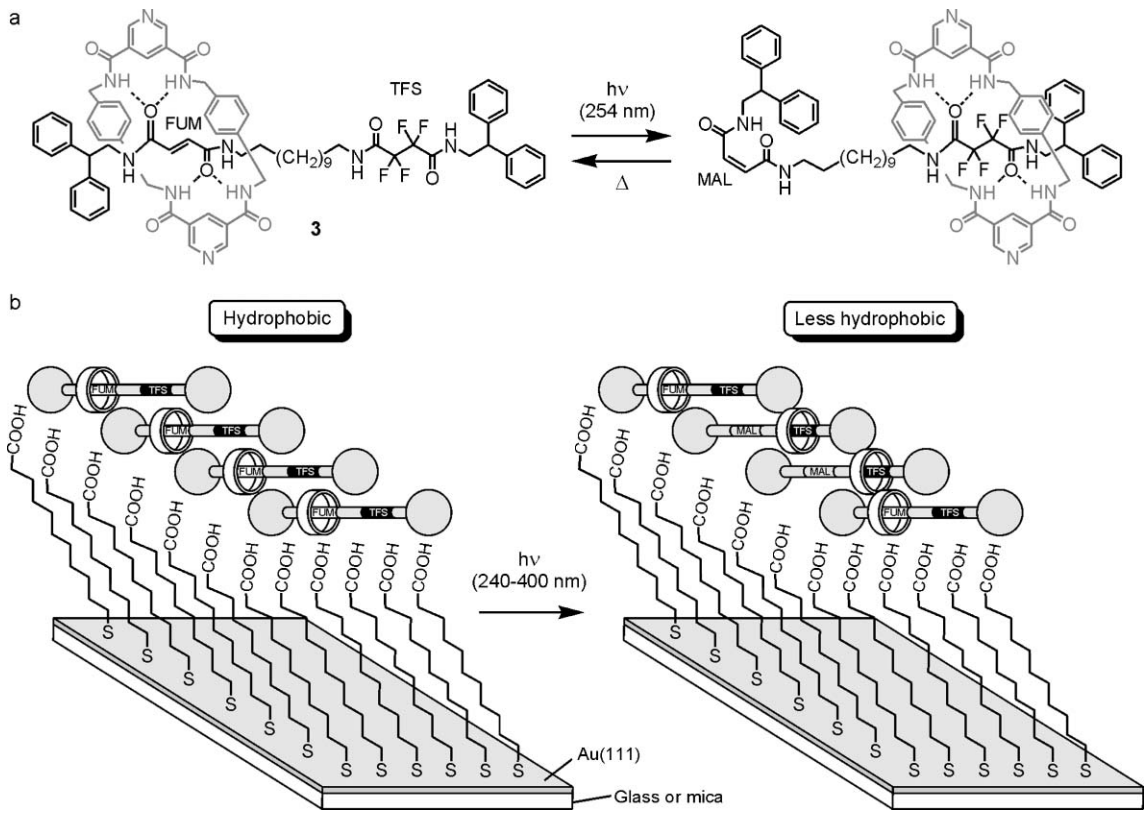

Fig. 4 (a) Chemical formula of rotaxane **3** and its operation as a light-controlled molecular shuttle. (b) Schematic representation of the photoinduced change of the hydrophobic/hydrophilic character of a gold surface covered with a self-assembled monolayer of rotaxane **3**/11-mercaptoundecanoic acid.

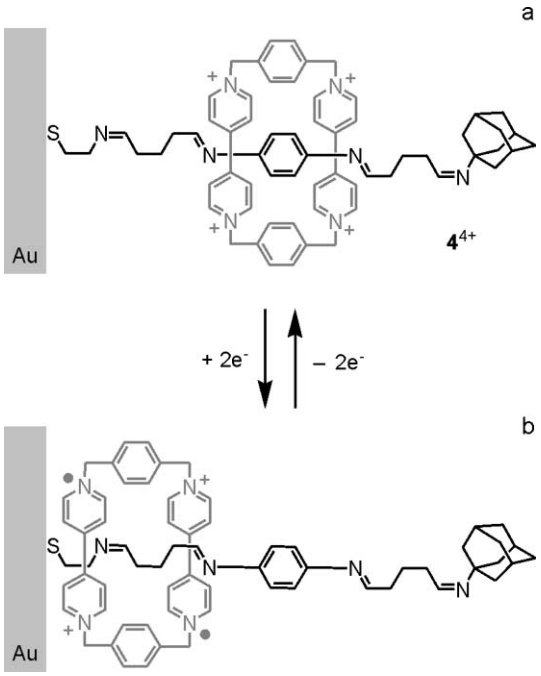

Fig. 5 The electrochemically driven ring shuttling in the surface-bound rotaxane $\mathbf{4}^{4+}$.

charged cyclophane towards the negatively polarised electrode. Therefore, ring shuttling does not need assistance by thermal noise, in contrast with the typical operation of biomolecular motors. Also, *in situ* electrochemical/contact angle measurements revealed that the electrochemically driven translocation of the cyclophane along the axle in $\mathbf{4}^{4+}$ provides a means to control reversibly the wetting properties of the surface, and was used to displace a water droplet.[29]

4.5 A molecular lift

By using an incrementally staged strategy, the architectural features of the acid-controllable molecular shuttle $\mathbf{5}H^{3+}$ (Fig. 6a) were integrated with those of the supramolecular bundle obtained by self-assembly of the trifurcated compound $\mathbf{6}H_3^{3+}$ and the tris-crown ether **7** (Fig. 6b) to design and construct the two-component molecular device $\mathbf{8}H_3^{9+}$ (Fig. 7a) that behaves as a nanoscale lift.[31] This interlocked compound, which is *ca*. 2.5 nm in height and has a diameter of *ca*. 3.5 nm, consists of a tripod component containing two different notches—one ammonium centre and one 4,4′-bipyridinium unit—at different levels in each of their three legs. The latter are interlocked by a tritopic host, which plays the role of a platform that can be made to stop at the two different levels. The three legs of the tripod carry bulky feet that prevent the loss of the platform. Initially, the platform resides exclusively on the 'upper' level, *i.e.*, with the three rings surrounding the ammonium centres (Fig. 7b). This preference results from strong N^+–H···O hydrogen bonding and weak stabilizing π–π stacking forces between the aromatic cores of the platform and tripod components. Upon addition of a strong, non-nucleophilic phosphazene base to an acetonitrile solution of $\mathbf{8}H_3^{9+}$, deprotonation of the ammonium centre occurs and, as a result, the platform moves to the 'lower' level, that is, with the three macrocyclic rings surrounding the bipyridinium units (Fig. 7c). This co-conformation is stabilised mainly by electron donor–acceptor interactions between the electron rich aromatic units of the platform and the electron deficient bipyridinium units of the tripod component. Subsequent addition of acid to $\mathbf{8}^{6+}$ restores the ammonium centres, and the platform moves back to the upper level. The 'up and down' lift-like motion, which corresponds to a quantitative switching and can be repeated many times, can be monitored by NMR spectroscopy,

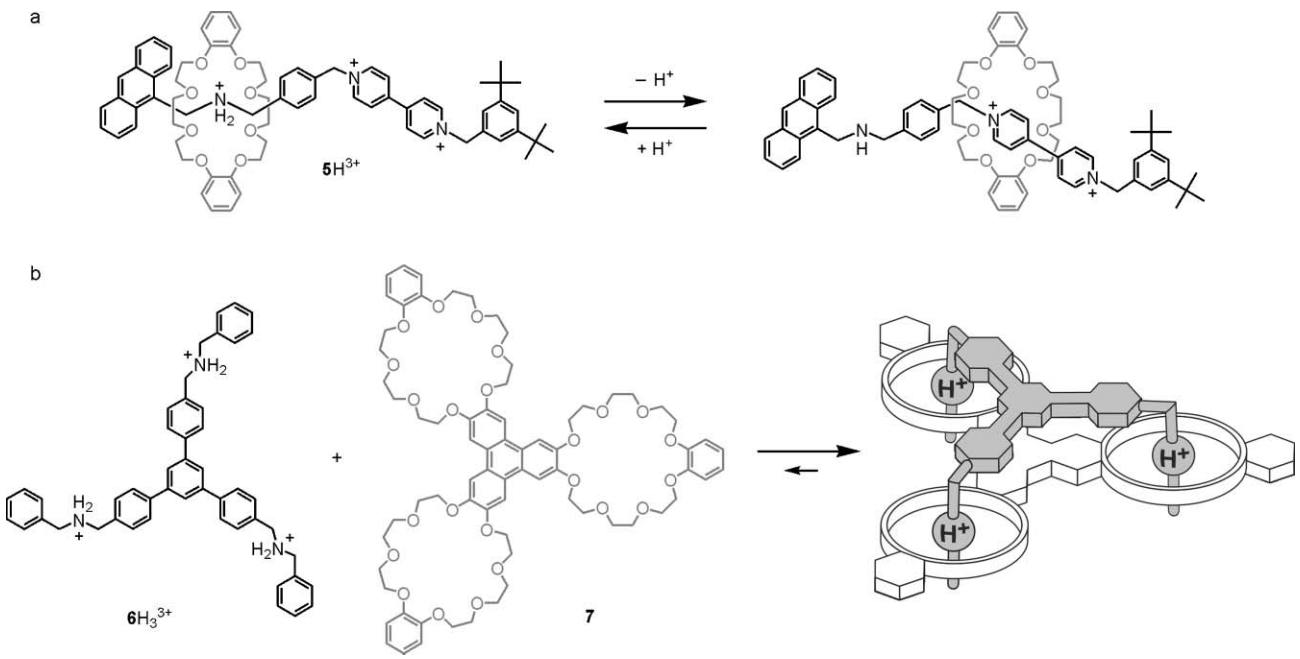

Fig. 6 (a) Chemical formula and working scheme of the acid–base switchable rotaxane $\mathbf{5}H^{3+}$. (b) The equilibrium between the tris-ammonium ion $\mathbf{6}H_3^{3+}$ and the tris-crown ether **7** which lies to the right in favor of the supramolecular bundle in solution.

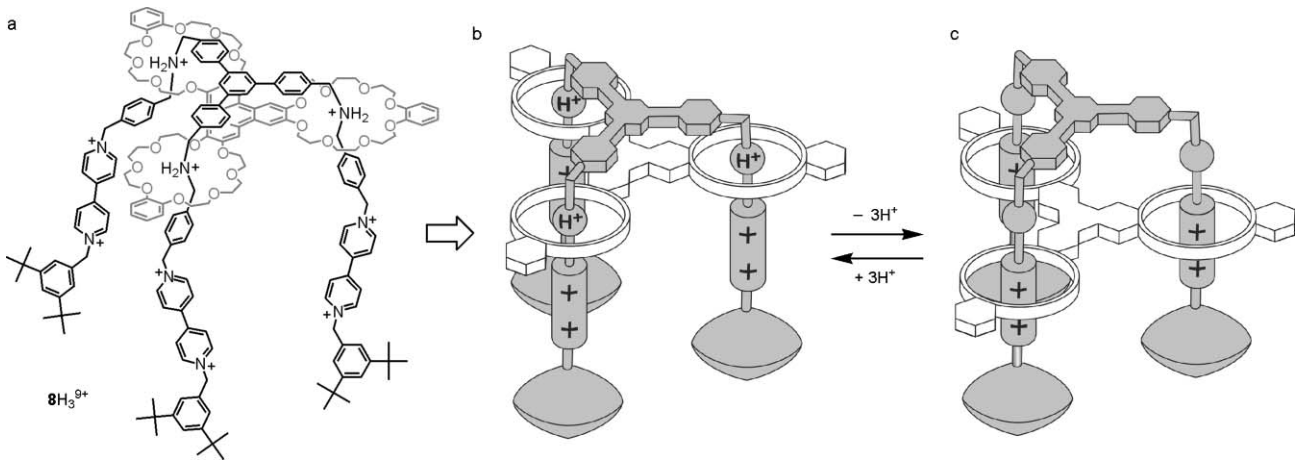

Fig. 7 Chemical formula (a) and operation scheme in solution (b, c) of the molecular lift $\mathbf{8}H_3^{9+}$.

electrochemistry, and absorption and fluorescence spectroscopy.[32] Interestingly, the experimental results show also that the platform operates by taking three distinct steps associated with each of the three deprotonation/reprotonation processes. Hence, this molecular machine is more reminiscent of a legged animal than it is of a lift. It can also be noted that the acid–base controlled mechanical motion in $\mathbf{8}H_3^{9+}$ is associated with remarkable structural modifications, such as the opening and closing of a large cavity and the control of the positions and properties of the bipyridinium legs. This behaviour can in principle be used to control the uptake and release of a guest molecule, a function of interest for the development of drug delivery systems.

4.6 Artificial molecular muscles

The construction of molecular machines that exhibit controlled extension–contraction motions, reminiscent of the operation of sarcomere units in skeletal muscles (Fig. 8a), is a topic of great interest. The molecular muscle concept was first implemented with artificial molecules by designing a doubly threaded rotaxane dimer.[9] Recently, mechanical actuation in a submillimetre-scale device was observed[33] by means of a self-assembled monolayer of cleverly designed rotaxane molecules exhibiting redox-switchable muscle-like motions. The motor molecule is the palindromic three-component rotaxane $\mathbf{9}^{8+}$ (Fig. 8b), consisting of two mechanically mobile rings encircling the same dumbbell. The two electron deficient rings are initially located on the electron rich tetrathiafulvalene (TTF) stations, and the inter-ring distance is approximately 4.2 nm. Chemical or electrochemical oxidation of the TTF units leads to the displacement of the two rings onto the naphthalene (NP) stations, and to an inter-ring distance of 1.4 nm. Reduction of the TTF cationic units restores the original mechanical state (Fig. 8b). Owing to the disulfide tether covalently linked to each ring, a monolayer of $\mathbf{9}^{8+}$ could be assembled onto a gold surface. An array of flexible silicon microcantilever beams (500 × 100 × 1 μm), coated on one side with a monolayer of rotaxane molecules (Fig. 9a), was shown to undergo controllable and reversible bending up and down when exposed to the successive addition of an aqueous chemical oxidant ($Fe(ClO_4)_3$) and reductant (ascorbic acid) in a transparent fluid cell. The position of each cantilever beam was monitored by an optical lever. Since a monolayer of the dumbbell component alone does not bend the cantilevers under the same conditions, the beam bending can be correlated with flexing of the surface bound molecular muscles (Fig. 9b). Hence, the rotaxane molecules employ the free energy of a chemical reaction to do mechanical work against the spring force of the cantilever. It is worth noting that no alignment of the rotaxane molecules with respect to the cantilevers is required to observe a bending effect because only the component of the contraction that is parallel to the long axis of the cantilever contributes effectively to the bending.

These experiments demonstrate[33] that the collective effect of billions of molecular machines in carefully engineered systems can be harnessed to do mechanical work on a larger scale; in fact, the contraction and extension of the molecular muscles lead to the bending of a beam that is five orders of magnitude larger in size. It is worth noticing that individual molecular muscles, when making cycles of operation, cannot develop net mechanical work at the nanometre scale (*vide infra*); however, their collective action does generate work at the macroscopic level (bending up and down) that can be used to operate mechanical devices.

4.7 Catalytically active rotaxanes as processive enzyme mimics

As discussed in the Introduction, the rotaxane geometry is adopted by many enzymes that operate on nucleic acids and proteins. In the case of processive enzymes, the catalytic reaction drives the sequential motion of the enzyme on its polymeric substrate. Therefore, these enzymes can be viewed as molecular motors powered by chemical reactions and moving one-dimensionally on a track, in which fuel is provided by the track itself. An initial attempt to carry out processive catalysis with a synthetic rotaxane has been described.[34]

The catalyst $\mathbf{10}^{+}$ is a macrocycle consisting of a substrate binding cavity that incorporates a Mn(III) porphyrin complex (Fig. 10) able to oxidise alkenes to the corresponding epoxides. It was shown that oxidation occurs within the cavity, provided that a ligand (such as **11** in Fig. 10) is complexed by the outer face of the porphyrin for both activating the catalytic complex and prevent the oxidation reaction from taking place outside

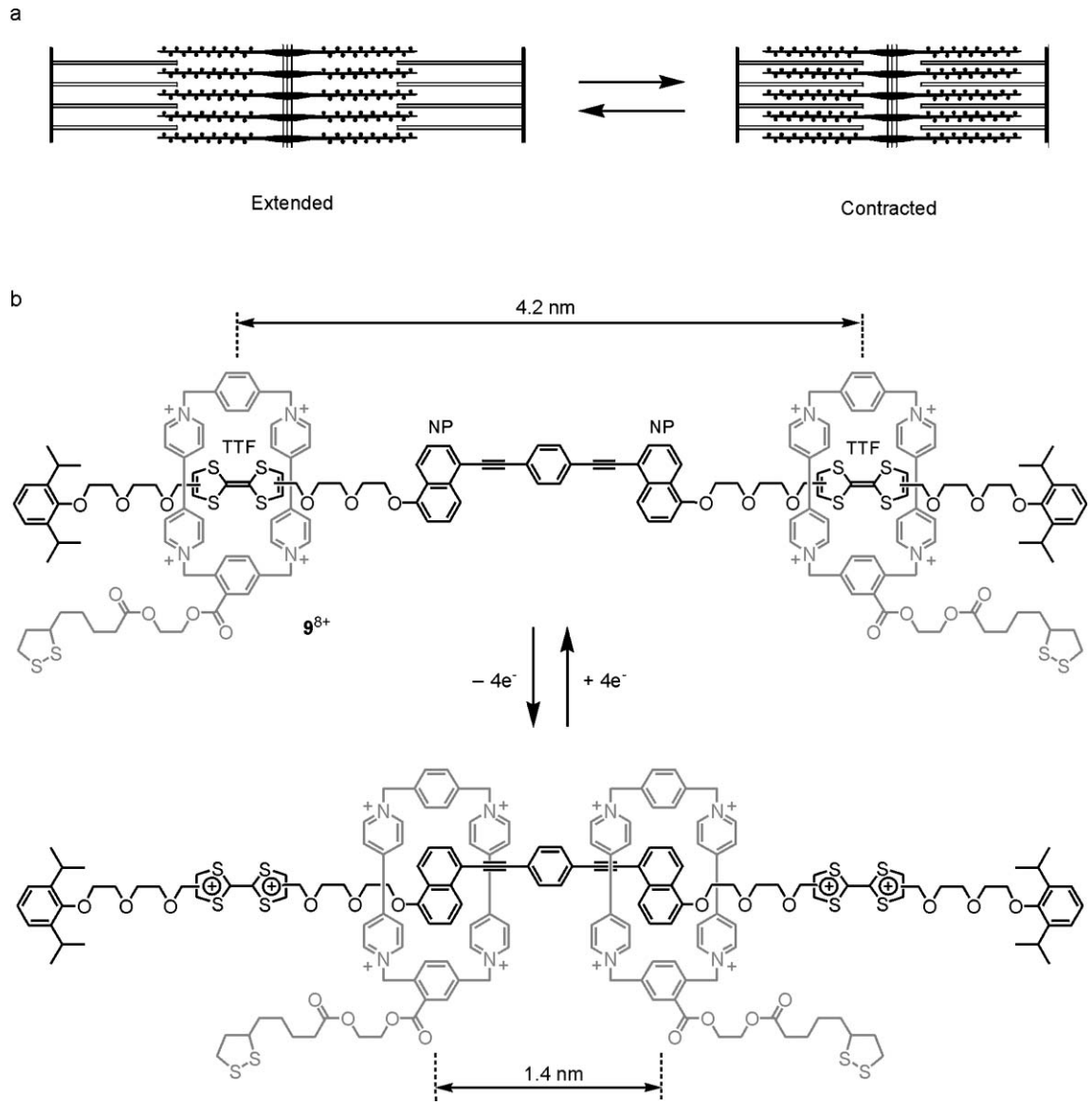

Fig. 8 (a) Schematic representation of the extension–contraction of a sarcomere unit of skeletal muscles. (b) Chemical formula of the palindromic rotaxane $\mathbf{9}^{8+}$ and the redox-controlled switching between its contracted and extended forms.

the cavity. In the presence of an oxygen donor (for example, PhIO) and the activating axial ligand, a Mn(V)=O species is formed, which transfers its oxygen atom to the alkene substrate. Macrocycle $\mathbf{10}^{+}$ was employed as the ring to make the three-component rotaxane $\mathbf{12}^{6+}$ (Fig. 10), in which two $\mathbf{10}^{+}$ rings surround an axle containing a polybutadiene chain. It was shown[34] that the macrocyclic components of $\mathbf{12}^{6+}$ are able to catalyze the conversion of the polybutadiene chain incorporated in the axle into the corresponding polyepoxide. This result indicates that the macrocyclic catalysts can surround each diene unit of the polybutadiene chain by moving along the axle.

The rotaxane $\mathbf{12}^{6+}$ can indeed be described as a simple mimic of topologically linked enzymes. A feature that is not mimicked is the sequential nature of the reaction, which gives rise to processive behaviour. It is not straightforward to determine whether the macrocyclic units of $\mathbf{12}^{6+}$ convert each butadiene unit into the corresponding epoxide function in a sequential manner or randomly hop along the chain. However, calculations on the basis of the catalytic rate suggested[34] that the rate of displacement of the macrocycle by the effect of the reaction would be much slower than the thermal shuttling rate, pointing to a random hopping mechanism. To make the system sequentially processive, one has to precisely balance the speed of the movement of the catalyst and the rate of the catalytic reaction. In such a case the unidirectional linear motion of the macrocycle along the axle would be powered by the exoergonic chemical reaction between the 'fuels' PhIO and the diene units.

5. Oscillatory and rotary motions

5.1 Electrochemically driven swinging of a molecular ring in a rotaxane

The use of transition metal ions as templates to construct multicomponent chemical systems with interlocked or knotted

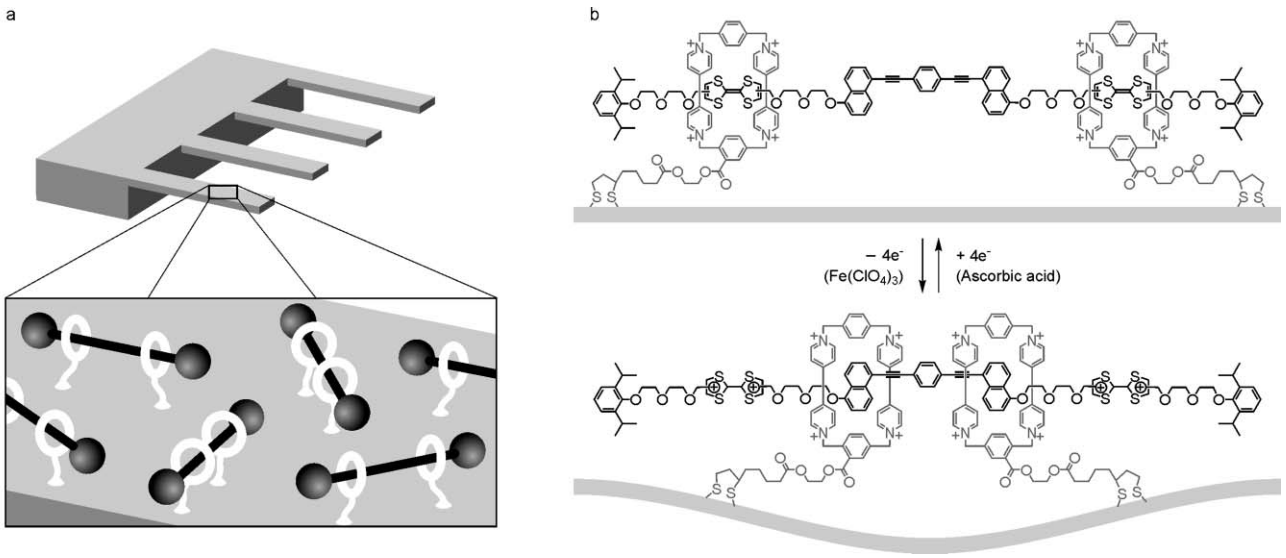

Fig. 9 Schematic illustration of (a) flexible microcantilever beams coated on one side with a monolayer of $\mathbf{9}^{8+}$ rotaxane molecules, and (b) the proposed mechanism for the bending of the cantilevers by the chemically driven operation of $\mathbf{9}^{8+}$. Note that the various parts of the diagrams are not to scale, and that the rotaxane molecules are randomly oriented on the surface.

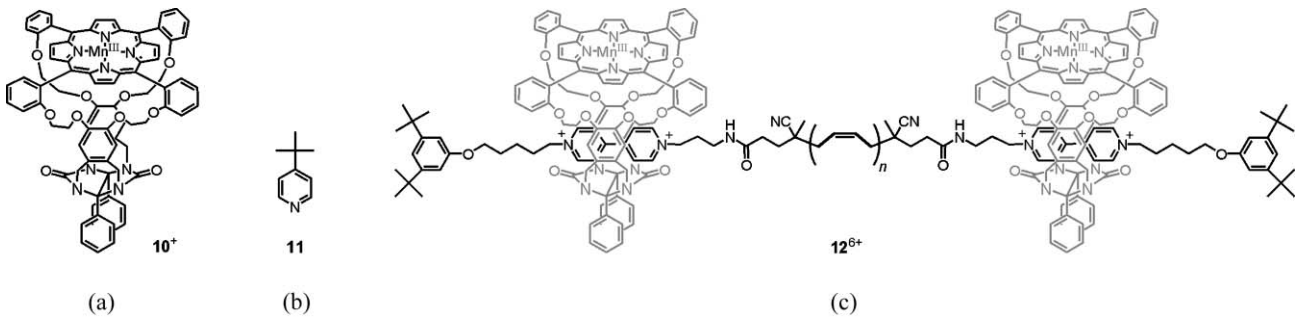

Fig. 10 Chemical formulae of the macrocyclic catalyst $\mathbf{10}^{+}$, ligand **11** and three-component rotaxane $\mathbf{12}^{6+}$ which mimics the operation of topologically linked enzymes.

topologies has been largely exploited.[18] Some of these species constitute nice prototypes of nanomachines that can be operated chemically, electrochemically and photochemically.[9] In suitably designed rotaxanes the swinging movement of the ring around the axle can be electrochemically driven.

Compound $\mathbf{13}^{+}$ (Fig. 11a) represents the last generation of this class of rotaxanes,[35] and contains a Cu(I) ion coordinated tetrahedrically by the 2,2′-bipyridine and 1,10-phenanthroline ligands present in the dumbbell and ring components, respectively. Electrochemical oxidation of the Cu(I) centre in acetonitrile leads to a transient tetracoordinated Cu(II) species. In response to the preference of Cu(II) for a pentacoordination geometry and by exploiting the presence in the ring component of a second coordination site—namely, the terdentate terpyridine ligand—the transient species rearranges through the swinging of the ring around the axle. This rearrangement leads to a co-conformation in which the Cu(II) centre reaches its most stable environment, being pentacoordinated by the phenanthroline of the axle and the terpyridine of the ring (Fig. 11b). Upon electrochemical reduction of Cu(II) a transient pentacoordinated Cu(I) species is obtained, which relaxes by another swinging motion to the most stable co-conformation with Cu(I) tetrahedrically coordinated (Fig. 11a).

The rate constants for each of the rearrangement steps in these compounds can be determined using voltammetric techniques, and it was evidenced that the swinging rate depends greatly on the copper oxidation state (the rearrangement of the Cu(I) complex is much faster than that of the Cu(II) one).[9] In the first examples of such Cu-based rotaxanes, the swinging motion took minutes or even hours to occur after the electrochemical stimulus had been applied. Rotaxane $\mathbf{13}^{+}$ features a swinging motion in the Cu(II) state with a half-life of 60 ms in acetonitrile at −40 °C, and the rearrangement in the Cu(I) state is likely to occur 2–3 orders of magnitude faster.[35] Such an improvement in the swinging rate has been accomplished by a careful molecular design. The rearrangement processes involve several coordination–decoordination steps, an important factor being the accessibility of the copper centre and its ability to undergo fast ligand exchange. To this aim, the 1,10-phenanthroline ligand present on the axle of the previously studied systems has been replaced in $\mathbf{13}^{+}$ by a less hindering 2,2′-bipyridine, and the bulky stoppers have been located far away from the central complex.

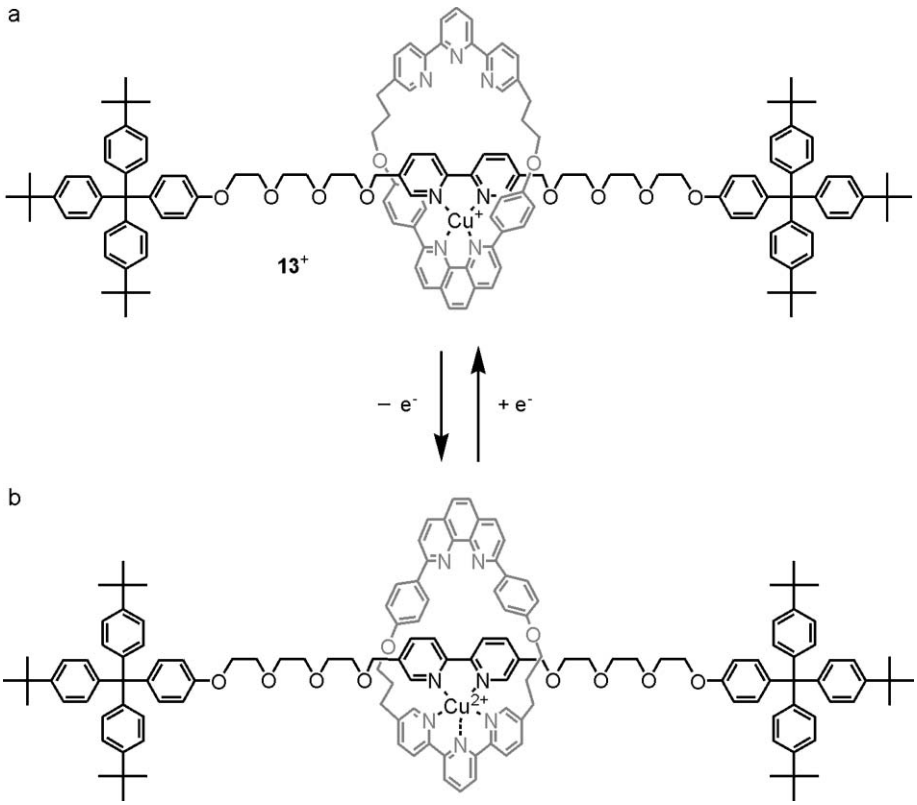

Fig. 11 Structural formula of rotaxane $\mathbf{13}^{+}$, and schematic representation of the electrochemically driven swinging motion of the ring around the axle.

5.2 Photochemically driven swinging of a molecular ring in a catenane

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.[36] 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.[37] Visible excitation of the Ru catenane complex $\mathbf{14}^{2+}$ (Fig. 12a) 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 decoordination 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. 12b) 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 spectroscopy. By using the same strategy, light-induced motions on a rotaxane system were also obtained.[38]

5.3 Controlled unidirectional ring rotation in a catenane

It should be pointed out that repeated switching between the two states of bistable swinging systems such as those described in Sections 5.1 and 5.2 does not need to occur through a full rotation. In fact, because of the intrinsic symmetry of the system, both the half-turns of the 'moving' ring can take place,

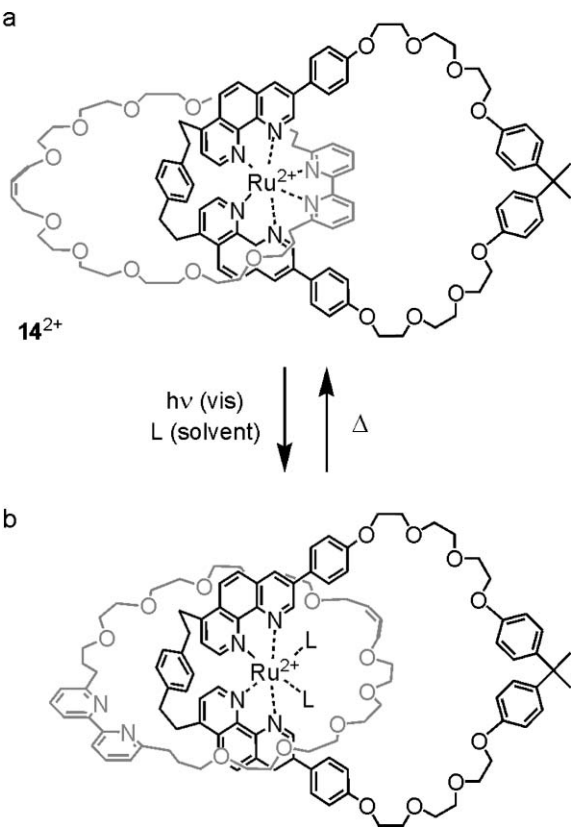

Fig. 12 Photochemically and thermally induced motions taking place in the Ru catenane complex $\mathbf{14}^{2+}$. The representation of the decoordinated form (b) is indicative and does not imply that the actual structure of the photoproduct is that shown.

with equal probabilities, along a clockwise or anticlockwise direction. A full (360°) rotation movement, which would be much more interesting from a mechanical viewpoint because it is a requirement for the construction of a rotary motor,[12] can only occur in ratchet-type systems, *i.e.*, in the presence of dissymmetry elements which can be structural or functional in nature. Of course, according to the second law of thermodynamics, a fundamental requirement for unidirectional motion even in such desymmetrised systems is the coupling with an exoergonic reaction that ultimately provides the free energy for the directed movement.

A bistable catenane can be a starting point to make a rotary motor, but an additional control element has to be added. Unidirectional rotation could be achieved with a catenane according to the design illustrated in Fig. 13.[7] Its 'track' ring contains two different recognition sites, A and B, a hindering group K and a blocking group X. In the starting co-conformation I, the 'moving' ring surrounds the most efficient site (A) on the track ring. Upon application of the stimulus 1, site A is switched off (A′) and must leave from the cavity of the ring. The system has to reach the new stable co-conformation II wherein the moving ring surrounds site B. The presence of a blocking group X makes clockwise rotation faster compared to anticlockwise rotation. At this stage, application of stimulus 2 causes the cleavage of the blocking group, and a reset stimulus −1 restores the recognition ability to site A. The system has now to reach the starting co-conformation wherein the moving ring surrounds site A. The presence of the hindering group K again makes clockwise rotation faster compared to anticlockwise rotation. The original catenane structure is then obtained with a reset stimulus −2 by which the blocking group X is put back in place. Unidirectional rotation in such a catenane occurs by a 'flashing ratchet' mechanism,[13,14] which is based on a periodic change of the potential energy surface viewed by the moving part (Fig. 13) by orthogonal (*i.e.*, independent) reactions. It is worth noting that the direction of rotation can be inverted by reversing the order of the two input stimuli.

This concept was cleverly realised[39] with the catenane **15** shown in Fig. 14. Its larger ring contains two recognition sites

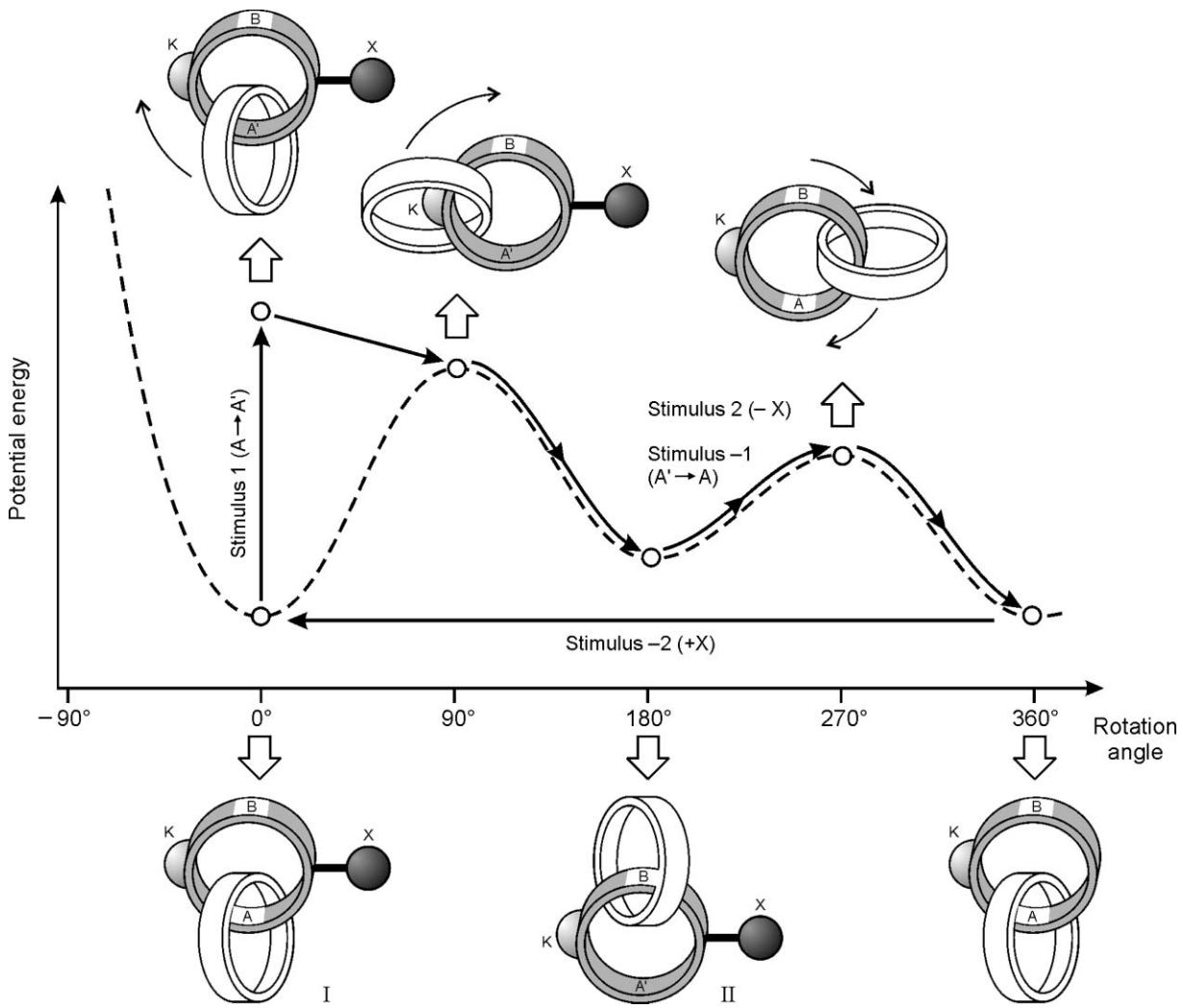

Fig. 13 The design of a bistable catenane that performs as a molecular rotary motor controlled by two independent stimuli. The working scheme is based on the potential energy changes expected for the chemical reactions and co-conformational rearrangements brought about by stimulation with the orthogonal inputs 1 and 2. For more details, see the text.

for the smaller ring—namely, a succinamide (SUC) and a photoisomerisable fumaramide (FUM) unit—and two bulky substituents that can be selectively detached–reattached—namely, a triphenylmethyl (TRI) and a silyl (SIL) group. In the starting isomer (Fig. 14a) the smaller ring surrounds the fumaramide site. Upon photoisomerisation of such a unit to the maleamide (MAL) isomeric form with 254 nm light (Fig. 14b) and subsequent desilylation–resilylation, the smaller ring moves in the clockwise direction to surround the succinamide site (Fig. 14c). Piperidine-assisted back-isomerisation of the maleamide unit to the fumaramide one (Fig. 14d), followed by detritylation–retritylation, causes another half-turn of the smaller ring in the clockwise direction to surround the fumaramide unit, thereby regenerating the starting isomer (Fig. 14a). The overall result is a net clockwise rotation of the smaller ring about the larger one. The structures of the compounds obtained after each of the above reaction steps, and particularly the position of the smaller ring, were determined by ^{1}H NMR spectroscopy.[39]

This system is more complex than that described in Fig. 13 because it contains two independently addressable blocking groups. Hence, unidirectional rotation is achieved with three different stimuli (one for driving the co-conformational rearrangement, and two for the ratcheting of the energy barriers). The time scales and number of reactions involved for unidirectional ring rotation in **15** make its operation as a rotary motor somewhat impractical. Nevertheless, the analysis of the thermodynamic and kinetic aspects of the operation mechanism of catenane **15** provides a fundamental insight on how energy inputs can be used to harness thermal fluctuations and drive unidirectional motion.

6. Conclusions

Interlocked molecular species like suitably designed rotaxanes and catenanes are ideal structures to obtain artificial nanomachines. Depending on the nature of the molecular components, mechanical motions in these systems can be promoted by chemical, electrochemical and photochemical energy inputs. In the last few years remarkable progress has been made in this field. Linear motion in rotaxanes has been exploited to construct artificial molecular muscles, enzymes,

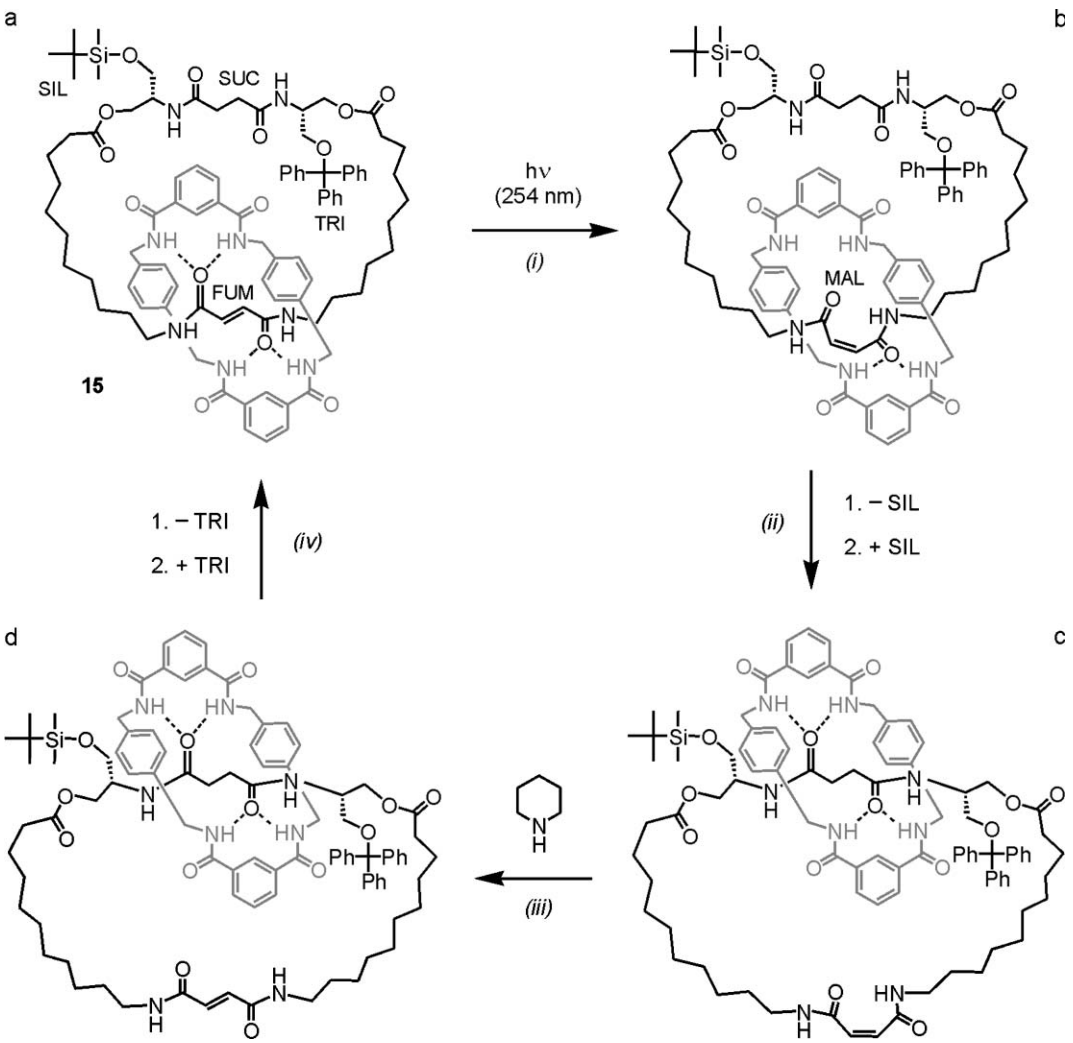

Fig. 14 Structural formula of catenane **15** and scheme for clockwise rotation of the smaller ring about the larger one by a sequence of photochemical and chemical reactions. Note that by exchanging the order of steps (ii) and (iv) the counterclockwise rotation of the small ring is obtained.

shuttles, and lifts. Oscillatory and even rotary movements have been obtained in several catenane structures. Most artificial molecular machines have so far been investigated only in solution; in some cases they have been employed to make engineered surfaces and even solid-state devices[40] that exhibit a function.

In general, artificial molecular machines must overcome energy barriers to operate by exploiting thermal fluctuations, as happens for natural nanomachines. When the energy input is large, as for instance in the case of photoexcitation, it can lead the system to energy levels well above the barriers associated to mechanical motion in the electronic ground state. In such a case, it is possible that the mechanical movement corresponds to a downhill process with no appreciable activation barriers.

The recent outstanding results achieved in this research field, some of which have been reviewed here, let us optimistically hope that useful devices based on artificial nanomachines will see the light in the not too distant future. Apart from applications, the study of motion at the molecular level and the extension of the concept of motor and machine to the nanoscale are indeed fascinating topics for basic research. They are important not only for the growth of nanoscience and the development nanotechnology, but also to convey new incitements to Chemistry as a scientific discipline.

Acknowledgements

Financial support from the European Union (STREP "Biomach" NMP2-CT-2003-505487), the Italian Ministero degli Affari Esteri (Direzione Generale per la Promozione e la Cooperazione Culturale) and the University of Bologna is gratefully acknowledged.

References

1 International Technology Roadmap for Semiconductors 2005; http://public.itrs.net.
2 R. P. Feynman, *Eng. Sci.*, 1960, **23**, 22. See also: http://www.feynmanonline.com.
3 *Molecular Motors*, ed. M. Schliwa, Wiley-VCH, Weinheim, 2003.
4 D. S. Goodsell, *Bionanotechnology – Lessons from Nature*, Wiley, Hoboken, 2004.
5 R. A. L. Jones, *Soft Machines – Nanotechnology and life*, OUP, Oxford, 2005.
6 V. Balzani, A. Credi, F. M. Raymo and J. F. Stoddart, *Angew. Chem., Int. Ed.*, 2000, **39**, 3348.
7 V. Balzani, A. Credi and M. Venturi, *Molecular Devices and Machines – A Journey into the Nano World*, Wiley-VCH, Weinheim, 2003.
8 A. H. Flood, R. J. A. Ramirez, W.-Q. Deng, R. P. Muller, W. A. Goddard, III and J. F. Stoddart, *Aust. J. Chem.*, 2004, **57**, 301.
9 J.-P. Sauvage, *Chem. Commun.*, 2005, 1507.
10 K. Kinbara and T. Aida, *Chem. Rev.*, 2005, **105**, 1377.
11 *Top. Curr. Chem.*, 2005, 262 (Special volume on molecular motors; ed. T. R. Kelly).
12 R. A. van Delden, M. K. J. ter Wiel, M. M. Pollard, J. Vicario, N. Koumura and B. L. Feringa, *Nature*, 2005, **437**, 1337.
13 R. D. Astumian and P. Hänggi, *Phys. Today*, 2002, **55**(11), 33.
14 R. D. Astumian, *J. Phys.: Condens. Matter*, 2005, **17**, S3753.
15 A. Credi, *Aust. J. Chem.*, 2006, **59**, 157.
16 M. Clemente-León, A. Credi, M.-V. Martínez-Díaz, C. Mingotaud and J. F. Stoddart, *Adv. Mater.*, 2006, **18**, 1291 and references therein.
17 F. C. Simmel and W. U. Dittmer, *Small*, 2005, **1**, 284.
18 *Catenanes, Rotaxanes and Knots*, ed. J.-P. Sauvage and C. Dietrich-Buchecker, Wiley-VCH, Weinheim, 1999.
19 C. A. Schalley, T. Weilandt, J. Bruggemann and F. Vögtle, *Top. Curr. Chem.*, 2004, **248**, 141.
20 P. Thordarson, R. J. M. Nolte and A. E. Rowan, *Aust. J. Chem.*, 2004, **57**, 323 and references therein.
21 D.-H. Qu, Q.-C. Wang, X. Ma and H. Tian, *Chem.–Eur. J.*, 2005, **11**, 5929.
22 D.-H. Qu, Q.-C. Wang and H. Tian, *Angew. Chem., Int. Ed.*, 2005, **44**, 5296.
23 P. R. Ashton, R. Ballardini, V. Balzani, A. Credi, R. Dress, E. Ishow, C. J. Kleverlaan, O. Kocian, J. A. Preece, N. Spencer, J. F. Stoddart, M. Venturi and S. Wenger, *Chem.–Eur. J.*, 2000, **6**, 3558.
24 V. Balzani, M. Clemente-León, A. Credi, B. Ferrer, M. Venturi, A. H. Flood and J. F. Stoddart, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 1178.
25 E. R. Kay and D. A. Leigh, *Nature*, 2006, **440**, 286.
26 M. N. Chatterjee, E. R. Kay and D. A. Leigh, *J. Am. Chem. Soc.*, 2006, **128**, 4058.
27 V. Balzani, M. Clemente-León, A. Credi, M. Semeraro, M. Venturi, H.-R. Tseng, S. Wenger, S. Saha and J. F. Stoddart, *Aust. J. Chem.*, 2006, **59**, 193.
28 J. Berná, D. A. Leigh, M. Lubomska, S. M. Mendoza, E. M. Pérez, P. Rudolf, G. Teobaldi and F. Zerbetto, *Nat. Mater.*, 2005, **4**, 704.
29 E. Katz, O. Lioubashevsky and I. Willner, *J. Am. Chem. Soc.*, 2004, **126**, 15520.
30 E. Katz, R. Baron, I. Willner, N. Richke and R. D. Levine, *ChemPhysChem*, 2005, **6**, 2179.
31 J. D. Badjic, V. Balzani, A. Credi, S. Silvi and J. F. Stoddart, *Science*, 2004, **303**, 1845.
32 J. D. Badjic, C. M. Ronconi, J. F. Stoddart, V. Balzani, S. Silvi and A. Credi, *J. Am. Chem. Soc.*, 2006, **128**, 1489.
33 Y. Liu, A. H. Flood, P. A. Bonvallett, S. A. Vignon, B. H. Northrop, H.-R. Tseng, J. O. Jeppesen, T. J. Huang, B. Brough, M. Baller, S. Magonov, S. D. Solares, W. A. Goddard, C. M. Ho and J. F. Stoddart, *J. Am. Chem. Soc.*, 2005, **127**, 9745.
34 P. Thordarson, E. J. A. Bijsterveld, A. E. Rowan and R. J. M. Nolte, *Nature*, 2003, **424**, 915.
35 U. Létinois-Halbes, D. Hanss, J. M. Beierle, J.-P. Collin and J.-P. Sauvage, *Org. Lett.*, 2005, **7**, 5753 and references therein.
36 A.-C. Laemmel, J.-P. Collin, J.-P. Sauvage, G. Accorsi and N. Armaroli, *Eur. J. Inorg. Chem.*, 2003, 467 and references therein.
37 P. Mobian, J.-M. Kern and J.-P. Sauvage, *Angew. Chem., Int. Ed.*, 2004, **43**, 2392.
38 J.-P. Collin, D. Jouvenot, M. Koizumi and J.-P. Sauvage, *Eur. J. Inorg. Chem.*, 2005, 1850.
39 J. V. Hernandez, E. R. Kay and D. A. Leigh, *Science*, 2004, **306**, 1532.
40 Y. Luo, C. P. Collier, J. O. Jeppesen, K. A. Nielsen, E. Delonno, G. Ho, J. Perkins, H. R. Tseng, T. Yamamoto, J. F. Stoddart and J. R. Heath, *ChemPhysChem*, 2002, **3**, 519.