# Nanoscience and nanotechnology: The bottom-up construction of molecular devices and machines*

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*Abstract*: The bottom-up approach to miniaturization, which starts from molecules to build up nanostructures, enables the extension of the macroscopic concepts of a device and a machine to molecular level. Molecular-level devices and machines operate via electronic and/or nuclear rearrangements and, like macroscopic devices and machines, need energy to operate and signals to communicate with the operator. Examples of molecular-level photonic wires, plug/socket systems, light-harvesting antennas, artificial muscles, molecular lifts, and light-powered linear and rotary motors are illustrated. The extension of the concepts of a device and a machine to the molecular level is of interest not only for basic research, but also for the growth of nanoscience and the development of nanotechnology.

*Keywords*: molecular devices; molecular machines; information processing; photophysics; miniaturization.

## INTRODUCTION

Nanotechnology [1–8] is a frequently used word both in the scientific literature and in the common language. It has become a favorite, and successful, term among America's most fraudulent stock promoters [9] and, in the venture capital world of start-up companies, is perceived as "the design of very tiny platforms upon which to raise enormous amounts of money" [1]. Indeed, nanotechnology is a word that stirs up enthusiasm or fear since it is expected, for the good or for the bad, to have a strong influence on the future of mankind. Everybody seems to know what nanotechnology is, but even within the scientific community the meaning of this word is not yet well established. In fact, nanotechnology has apparently different meanings in different fields of science, e.g., in physics and chemistry. Perhaps surprisingly, nanoscience, the sister word of nanotechnology, is much less commonly used, but it is, all the same, ill-defined.

I will start with a few comments on the meanings of the component words: science, technology, and nano [10].

## Science

Science can be defined in several ways. For example, a branch of knowledge requiring systematic study and method [11], the cumulative body of systematized knowledge gained by observation, experiment,

and reasoning [12], or the sum of universal knowledge [13]. My own definition is the following: Science is a human activity aimed at knowing the laws of Nature and then using such knowledge to change the world. This definition reflects the fact that science operates and develops along two routes: discoveries and inventions. On one hand, science aims at discovering what already exists, but is still unknown; for example, how sunlight is converted into chemical energy by green plants (natural photosynthetic process). On the other hand, science aims at inventing what did not exist before; for example, the way in which water can be split into hydrogen and oxygen by sunlight (artificial photosynthesis). Science is the most powerful means that mankind has to understand the working principles of the material world, as well as to change the world. In the early times of science, most scientists were engaged in discovering Nature. As time progresses, scientists move more and more from discovering to inventing.

### Technology

Technology has a quite different meaning from an apparently similar word, namely, technique. Technique is the method of doing or performing, with skill acquired by experience, something that has already been established. Technology can be defined as *the ability of taking advantage of the progress of science to create novel opportunities for practical applications*. Technology is the main driving force for the progress of mankind since it provides a wealth of novel materials, devices, and machines capable of improving the quality of life. Unfortunately, however, technology can also be exploited for bad purposes: violence, war, terrorism. As technology advances, mankind's welfare improves but, at the same time, the world becomes more fragile. Indeed, in the last few decades there has been a tremendous development of technology and, at the same time, we have realized that it is practically impossible to protect from terrorist attacks all the technological achievements: aircrafts, power plants, skyscrapers, hazardous biomaterials, etc. Since it is clear that war multiplies terrorism, nowadays peace is not only a moral command, but also a necessity for the survival of our highly technological society.

### "Nano"

Nano is a prefix, namely, a word placed in front of another word to add or change its meaning. Nano, like micro, pico, etc., is used in front of a macroscopic unit to change its value by orders of magnitude. Nano means one billionth. Thus, nanometer is one billionth of a meter. When placed in front of words like science and technology, however, the meaning of nano is not that obvious (nanoscience cannot be a billionth of science!). Since experimental science and technology deal with material objects, it seems fair to say that *nanoscience and nanotechnology are science and technology concerning objects of nanometer dimension*, which are atoms (tenths of nanometers) and molecules (nanometers). Since anything is made of atoms and molecules, in principle, nanoscience and nanotechnology could be thought to cover all the branches of science and technology. Another possibility is that of limiting these words to the branches of science and technology that are specifically related to the atomic and molecular structure of macroscopic matter. Both proposals, however, are unsatisfactory, and neither physicists nor chemists would agree on defining nanoscience and nanotechnology in this way.

A more satisfactory definition of nanoscience and nanotechnology can be achieved by focusing on the intrinsic properties of nanoscale objects as such, and on the possibility of using, manipulating, or organizing them into assemblies in order to perform specific functions. This concept can be better explained in the frame of a discussion on miniaturization.

### MINIATURIZATION

The progress of civilization has always been related to the construction of novel devices and machines. For example, the outstanding development of information technology in the last few decades has been strictly related to the progressive miniaturization of the components employed for making computers.

The first electronic computer occupied an entire room, weighed 30 tons, was made of 18 000 valves, and lasted an average of 5.6 hours between repairs [14]. Nowadays, a microprocessor can be placed on a small desk, weighs less than 2 kg, has more than 50 million transistors, and practically does not need any repair.

## Top-down approach

The miniaturization of components for the construction of useful devices and machines has been and still is pursued by the top-down approach. This approach, which leads physicists and engineers to manipulate progressively smaller pieces of matter by photolithography and related techniques, has operated in an outstanding way up until now. It is becoming increasingly apparent, for example, that miniaturization in computer technology, which relies on silicon-based chips, is rapidly approaching the upper limits of its capabilities [15,16]. In particular, photolithography is subjected to drastic technical and economical limitations for dimensions smaller than 100 nm. This size is very small by the standards of everyday experience (about one thousandth the width of a human hair), but it is very large on the scale of atoms and molecules. Therefore, "there is plenty of room at the bottom" for further miniaturization, as Richard P. Feynman [17] stated in a famous talk to the American Physical Society in 1959, but the top-down approach does not seem capable of exploiting such an opportunity.

## Bottom-up approach

An alternative and most promising strategy to exploit science and technology at the nanometer scale is offered by the bottom-up approach, which starts from nano- or subnano-scale objects (namely, atoms or molecules) to build up nanostructures. The bottom-up approach is largely the realm of nanoscience and nanotechnology. This is the reason why chemists, being able to manipulate atoms and molecules, are in the ideal position to contribute to the development of nanoscience and nanotechnology. In the bottom-up approach to miniaturization, one can distinguish two different, limiting cases [10].

### Case 1
The nanoscale "objects" are very simple from a chemical viewpoint and do not exhibit any specific intrinsic function (atoms, clusters of atoms, small molecules). Function arises from ensembles of such objects. I will only mention a couple of examples. (i) Atoms or very simple molecules can be used to write a word of nanoscale dimension on a surface. For example, the new millennium has been celebrated by writing 2000 with 47 CO molecules placed on a Cu(211) surface [18]. (ii) Metal nanoparticles can be used to cover a surface. Gold nanoparticles are made of gold atoms as are gold sheets, but in the nanoparticles most of the gold atoms are on or close to the surface, and, therefore, they are exposed to interactions with other species. Covering a macroscopic piece with gold sheets (technology) or with gold nanoparticles (nanotechnology) leads to materials characterized by quite different properties. This field of nanoscience and nanotechnology is of the greatest interest to physicists and engineers (nanoparticles, nanostructured materials, nanoporous materials, nanopigments, nanotubes, nanoimprinting, quantum dots, etc.), and has already originated many innovative applications, particularly in materials science [19–22]. For basic investigations, an important role is played by manipulation or imaging nanoscale techniques [23].

### Case 2
The nanoscale "objects" have complex chemical composition (supramolecular [24] or multicomponent [25] systems), exhibit characteristic structures, show peculiar properties, and perform specific functions. All the natural [26,27] and artificial [28,29] molecular-level devices and machines belong to this category. The artificial molecular devices and machines must be synthesized starting from simpler components. This is a particularly appealing field where "the marriage of chemical synthetic talent with a

direction provided by device-driven ingenuity coming from engineering" [30] can lead to outstanding results.

In the following section, I will only deal with case 2 of nanoscience and nanotechnology.

## THE CONCEPTS OF MOLECULAR DEVICES AND MACHINES

Generally speaking, devices and machines are assemblies of components designed to achieve a specific function. Each component of the assembly performs a simple act, while the entire assembly performs a more complex, useful function, characteristic of that particular device or machine. For example, the function performed by a hair dryer (production of hot wind) is the result of acts performed by a switch, a heater, and a fan, suitably connected by electric wires and assembled in an appropriate framework. The macroscopic concepts of a device and a machine can be extended to the molecular level (Fig. 1) [28,31]. A *molecular device* can be defined as an assembly of a discrete number of molecular components designed to achieve a specific function. Each molecular component performs a single act, while the entire supramolecular assembly performs a more complex function, which results from the cooperation of the various components. A *molecular machine* is a particular type of device in which the (molecular) component parts can display changes in their relative positions as a result of some external stimulus [32]. Molecular-level devices and machines operate via electronic and/or nuclear rearrangements and, like macroscopic devices and machines, they need energy to operate and signals to communicate with the operator. The extension of the concepts of a device and a machine to the molecular level is of interest not only for basic research, but also for the growth of nanoscience and the development of nanotechnology. Chemists working in the frame of the bottom-up approach to the construction of nanoscale devices can rightly be named molecular engineers.
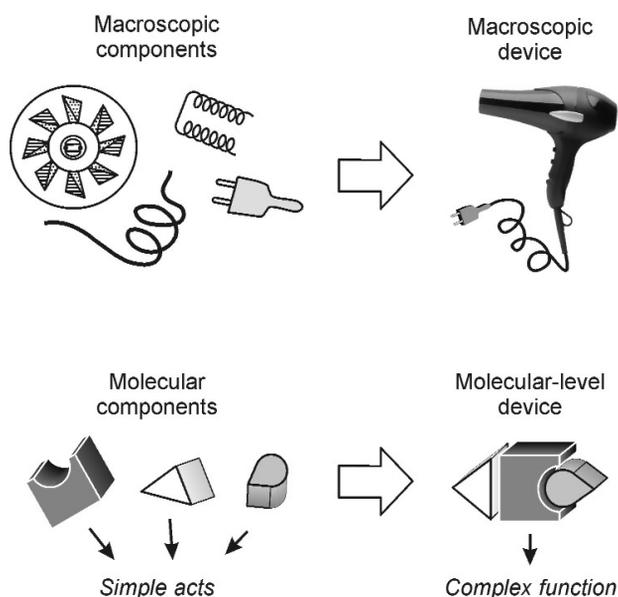


**Fig. 1** Extension of the macroscopic device concept to the molecular level.

It should be pointed out that nanoscale devices and machines cannot be considered merely as "shrunk" versions of macroscopic counterparts because physics is different at the nanoscale [27]. The most important differences arise because (i) molecules are in a state of constant random motion and are

subjected to continual collisions (Brownian motion), and (ii) in the nanoworld, things are somewhat floppy and stick strongly to each other because of electromagnetic interactions.

## BOTTOM-UP: ATOM-BY-ATOM OR MOLECULE-BY-MOLECULE?

The idea that atoms could be used to construct nanoscale devices and machines was first raised by R. P. Feynman in his previously mentioned address "There is plenty of room at the bottom" [17]. A key sentence of Feynman's talk is the following: "The principles of physics do not speak against the possibility of maneuvering things atom by atom". The possibility of constructing nanoscale devices "atom-by-atom" was depicted by K. E. Drexler in an exciting and visionary way in middle 1980s [33], and expanded in a more scientific (essentially theoretical) way later on [34–37]. This idea, however, which seems so much appealing to physicists, does not convince chemists [37–41]. By knowing the high reactivity of most atomic species, the subtle aspects of chemical bond, and the properties of molecules, they strongly believe that molecules are much more convenient building blocks than atoms to construct nanoscale devices and machines [42]. The main foundations of this idea are as follows: (i) molecules are stable species, whereas atoms are difficult to handle; (ii) Nature starts from molecules, not from atoms, to construct the great number and variety of nanodevices and nanomachines that sustain life (vide infra); (iii) most laboratory chemical processes are dealing with molecules, not with atoms; (iv) molecules are objects that already exhibit distinct shapes and carry device-related properties (e.g., properties that can be manipulated by photochemical and electrochemical inputs); (v) molecules can self-assemble or can be connected to make larger structures. Point v recalls the fundamental principle of supramolecular chemistry [24,25,28], whose rapid growth during the last two decades has shown that the "bottom-up" approach opens virtually unlimited possibilities concerning design and construction of artificial molecular-level devices and machines. A few examples will be described below. Furthermore, it has become more and more evident that such an approach can give invaluable contributions to better understanding the molecular-level aspects of the extremely complicated devices and machines that are responsible for the biological processes [26,27].

## ENERGY AND SIGNALS

Molecular devices and machines are chemical systems, and, therefore, they operate by means of chemical reactions that, broadly speaking, imply both electronic and nuclear rearrangements. In some cases, however, the function performed is essentially based on the transfer of electrons or electronic energy without substantial nuclear rearrangements. In other cases, the operation is based on the occurrence of extensive nuclear displacements.

The energy needed for the operation of a molecular device or machine can be supplied in the form of (i) a chemical reagent, (ii) an absorbed photon, or (iii) addition or subtraction of an electron. In view of the shortage of chemical fuels and increasing environmental problems [43], the ideal primary energy source is sunlight and the worthiest processes are those that do not form waste products.

In order to control and monitor the operation of a molecular device or machine, a suitable signal is needed. Since at least one molecular component of the system changes its state on performing the required function, any signal related to such a component can be used. Information on rate constants can be obtained by conventional or pulsed kinetic methods.

Since a device and a machine have to work by repeating cycles, an important requirement is reset. This means that any chemical reaction involved in the operation has to be reversible. This requirement is reasonably well met by energy-transfer, electron-transfer (redox), and proton-transfer (acid–base) processes, and by some types of photoisomerization and metal-ligand coordination reactions.

Molecular devices and machines are expected to find applications in several fields, including energy conversion and information transfer, storage, display, and processing; in the long run, they could lead to the construction of molecular-based (chemical) computers [28].

## MOLECULAR DEVICES

Photoinduced energy and electron transfer are basic processes for connecting light energy inputs with a variety of optical, electrical, and mechanical functions at the molecular level. Several devices can be designed for delivering electronic energy or electrons, in a controlled way, to predetermined components in a supramolecular system. For space reasons, only a few examples will be illustrated. A more exhausting discussion can be found elsewhere [28,29].

## Photonic wires

An important function at the molecular level is electronic energy transfer over long distances and/or along predetermined directions. This function can be obtained by linking donor and acceptor components by a rigid spacer. Most of the investigated systems based on coordination compounds contain oligopyridine metal complexes as donor and acceptor units. Usually, both the donor and the acceptor excited states are luminescent, so that the occurrence of energy transfer can be monitored by quenching and/or sensitization experiments with continuous and pulsed excitation techniques.

The most interesting systems are those in which the two chromophoric units are connected by rigid, modular spacers, as in the case of the $[Ru(bpy)_3]^{2+}$–$(ph)_n$–$[Os(bpy)_3]^{2+}$ (ph = 1,4–phenylene; $n$ = 2, 3, 4, 5) species (Fig. 2) [44]). The lowest energy level of the bridge decreases slightly as the number



$[Ru(bpy)_3]^{2+}$-$(ph)_n$-$[Os(bpy)_3]^{2+}$      $n$ = 2, 3, 4, 5



$k_{en.\ tr.}$ / $10^{10}$ $s^{-1}$: $n$=2, 25; $n$=3, 5.9; $n$=4, 0.41; $n$=5, 0.05
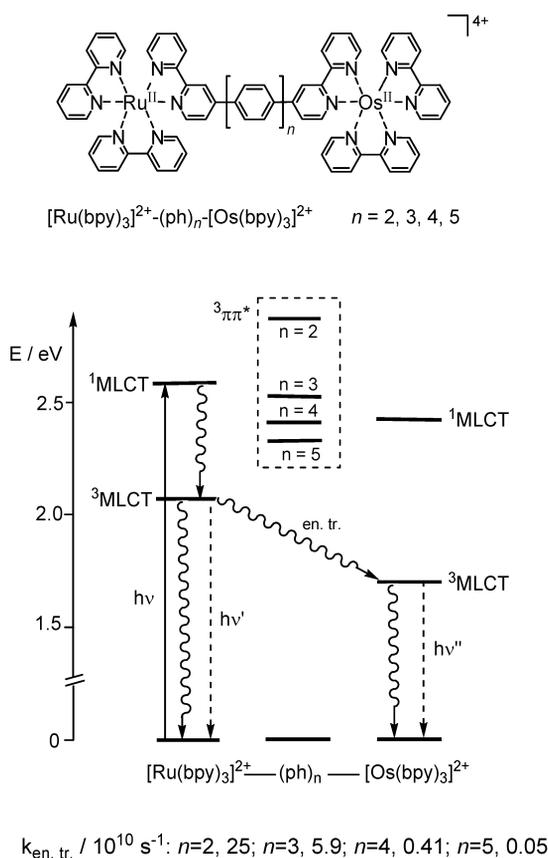
**Fig. 2** Structure of compounds $[Ru(bpy)_3]^{2+}$–$(ph)_n$–$[Os(bpy)_3]^{2+}$ and energy-level diagram for the energy-transfer process [44].

of phenylene units increases, but always lies above the donor and acceptor levels involved in energy transfer. A further decrease in the energy of the triplet excited state of the spacer would be expected to switch the energy-transfer mechanism from superexchange-mediated to hopping. In the series of compounds shown in Fig. 2 the energy-transfer rate decreases with increasing the length of the oligophenylene spacer. Such rate constants are much higher than those expected for a Förster-type mechanism, whereas they can be accounted for by a superexchange Dexter mechanism. The values obtained for the energy-transfer rate in the series of compounds $[Ru(bpy)_3]^{2+}–(ph)_nR_2–[Os(bpy)_3]^{2+}$ [45], in which the central phenylene unit carries two hexyl chains (R), are much lower than those found for the unsubstituted compounds, most likely because the bulky substituents increase the tilt angle between the phenyl units.

## Molecular plug/socket systems

Supramolecular species whose components are connected by means of noncovalent forces can be disassembled and reassembled [46] by modulating the interactions that keep the components together, thereby allowing switching of electron- or energy-transfer processes. Two-component systems of this type are reminiscent of plug/socket electrical devices and, to mimic their macroscopic counterparts, must be characterized by (i) the possibility of connecting/disconnecting the two components in a reversible way, and (ii) the occurrence of an electron or electronic energy flow from the socket to the plug when the two components are connected (Fig. 3a). Hydrogen-bonding interactions between ammonium ions and crown ethers are particularly convenient for constructing molecular-level plug/socket devices since they can be switched on and off quickly and reversibly by means of acid–base inputs. In the system illustrated in Fig. 3b, the plug-in function is related to the threading, driven by formation of strong $[N^+–H\cdots O]$ hydrogen bonds in nonpolar solvents, of (±)-binaphthocrown ether **1** by the dialkylammonium moiety of the wire-like compound $[\mathbf{2H}]^{3+}$, obtained by protonation of amine $\mathbf{2}^{2+}$ [47]. In the plugged-in pseudorotaxane structure, an electron-transfer process to the bipyridinium unit of $[\mathbf{2H}]^{3+}$ takes place upon light excitation of the binaphthyl unit of the macrocycle, causing quenching of the typical binaphthyl fluorescence. Addition of a stoichiometric amount of base, which deprotonates the ammonium ion, causes the recovery of the binaphthyl fluorescence, demonstrating that plug-out of the pseudorotaxane structure has occurred.

A similar plug/socket system, which deals with the transfer of electronic energy, is illustrated in Fig. 3c [48]. The absorption and fluorescence spectra of a $CH_2Cl_2$ solution containing equal amounts of (±)-binaphthocrown ether **3** and amine **4** indicate the absence of any interaction between the two compounds. Addition of a stoichiometric amount of acid causes profound changes in the fluorescence behavior of the solution, namely, (i) the fluorescence of **3** is quenched, and (ii) the fluorescence of $[\mathbf{4H}]^+$ is sensitized upon excitation with light absorbed exclusively by the crown ether. These observations are consistent with the formation of a pseudorotaxane-type adduct wherein very efficient energy transfer takes place from the binaphthyl unit of the crown ether to the anthracenyl group incorporated within the dialkylammonium ion. Such a pseudorotaxane can be disassembled by the subsequent addition of a stoichiometric amount of base, thereby interrupting the photoinduced energy flow, as indicated by the fact that the initial absorption and fluorescence spectra are restored. 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 **5**, is employed (Fig. 3c).

The plug/socket concept has recently been used to construct extended systems that mimic at the molecular level the function played by an extension cable [49,50].
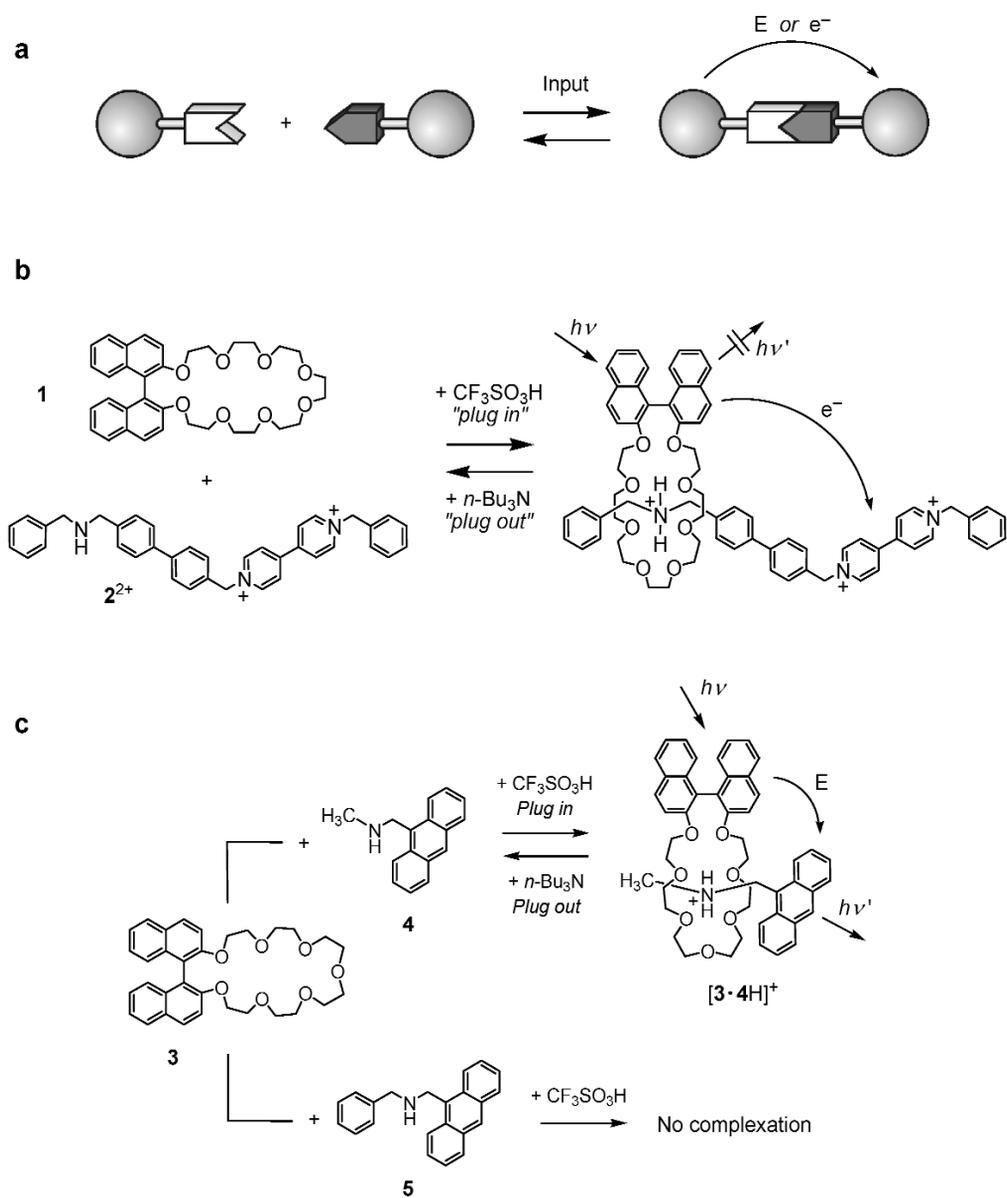
**Fig. 3** Schematic representation of a plug/socket system (a); switching of photoinduced electron (b) and energy (c) transfer by acid/based controlled plug in/plug out of suitable molecular components [47,48].

## Light-harvesting antennas

In suitably designed dendrimers, electronic energy transfer can be channeled toward a specific position of the array. Compounds of this kind play the role of antennas for light harvesting. Several light-harvesting dendrimers have been recently investigated [51]. An example is illustrated below.

The dendrimer shown in Fig. 4 consists of a hexaamine core surrounded by 8 dansyl-, 24 dimethoxybenzene-, and 32 naphthalene(NP)-type units [52]. In dichloromethane solution, this dendrimer exhibits the characteristic absorption bands of the component units and a strong dansyl-type fluorescence. Energy transfer from the peripheral dimethoxybenzene and NP units to the fluorescent

dansyl units occurs with >90 % efficiency. When the dendrimer hosts a molecule of the fluorescent eosin dye (Fig. 4), the dansyl fluorescence, in its turn, is quenched and sensitization of the fluorescence of the eosin guest can be observed. Quantitative measurements show that the encapsulated eosin molecule collects electronic energy from all of the 64 chomophoric units of the dendrimer with an efficiency >80 % (partial overlapping between dansyl and eosin emissions precludes a better precision). Both intramolecular (i.e., within dendrimer) and intermolecular (i.e., dendrimer host → eosin guest) energy-transfer processes occur very efficiently by a Förster-type mechanism because of the strong overlap between the emission and absorption spectra of the relevant donor/acceptor units. An advantage shown by such host–guest light-harvesting systems is that the wavelength of the resulting sensitized emission can be tuned by using the same dendrimer and different types of guests.

Lanthanide ions have also been incorporated into dendrimers containing chromophoric groups and amide units. In the case of $Nd^{3+}$, sensitization of the near infrared emission (1064 nm) of the lanthanide ion has been obtained [53].
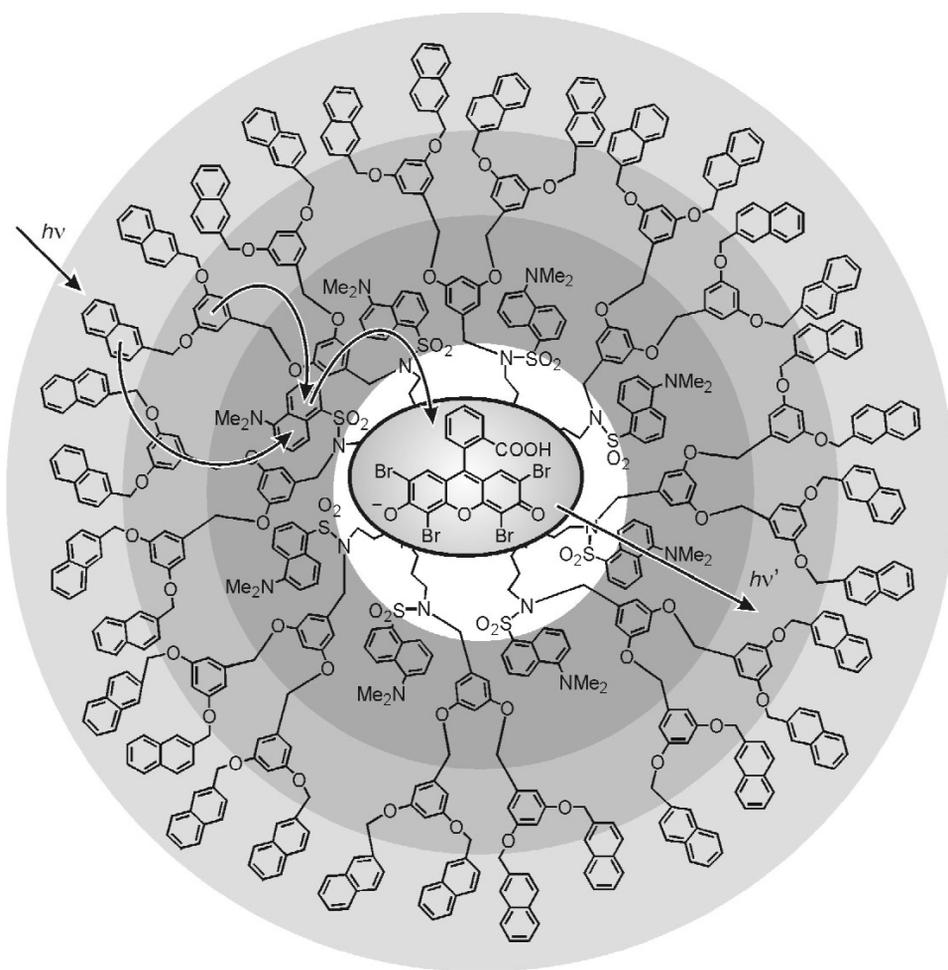


**Fig. 4** Schematic representation of the energy-transfer processes taking place in a dendrimer which contains three different types of light-harvesting chromophoric units and a hosted eosin molecule [52].

## MOLECULAR MACHINES

### Dethreading/rethreading of pseudorotaxanes

Dethreading/rethreading of the wire and ring components of a pseudorotaxane reminds the movement of a piston in a cylinder. A system in which dethreading/rethreading is exclusively governed by light energy without generation of any waste product is illustrated in Fig. 5 [54]. The thread-like species *trans*-**6**, which contains a π-electron-rich azobiphenoxy unit, and the electron-accepting host **7**$^{4+}$ self-assemble very efficiently ($K_{a,trans} = 1.5 \times 10^5$ L mol$^{-1}$ in MeCN at 298 K) to give a pseudorotaxane. In the pseudorotaxane structure, the characteristic fluorescence of free **7**$^{4+}$ is completely quenched by charge-transfer interactions. Irradiation with 365 nm light of a solution containing *trans*-**6** and **7**$^{4+}$ ($1 \times 10^{-4}$ mol L$^{-1}$, 80 % complexed species) causes photoisomerization of *trans*-**6** to *cis*-**6**. Since the cyclophane interaction with *cis*-**6** ($K_{a,cis} = 1 \times 10^4$ L mol$^{-1}$) is much weaker than that with *trans*-**6**, photoexcitation causes a dethreading process (Fig. 5), as indicated by the strong increase in the fluorescence intensity of **7**$^{4+}$. On irradiation at 436 nm or by warming the solution in the dark, the *trans*-isomer can be reformed and, as a result, it rethreads inside the cyclophane.
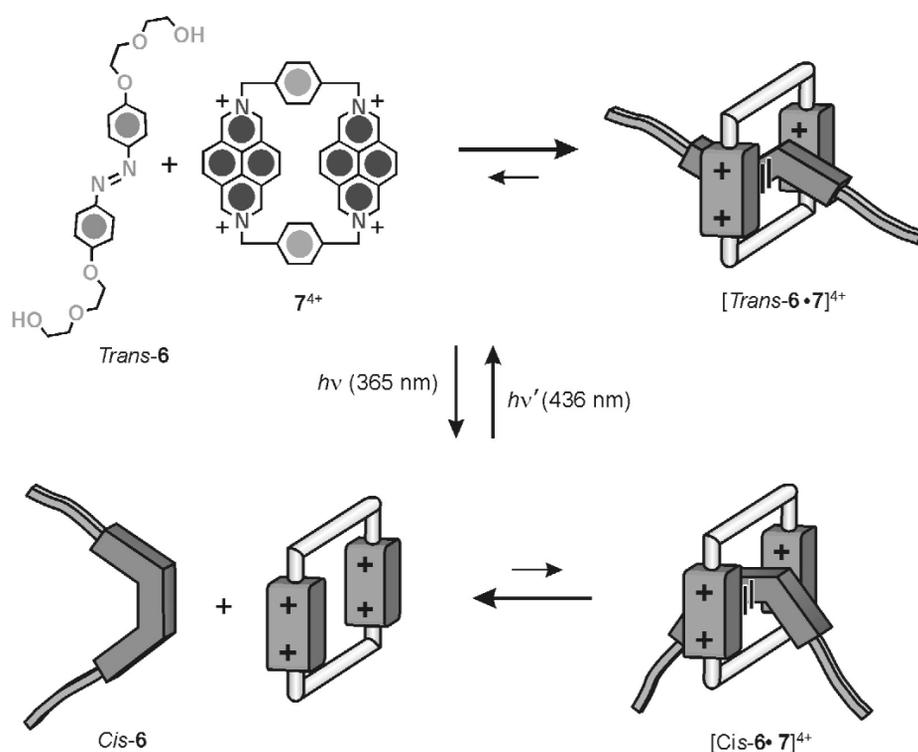


**Fig. 5** Controllable dethreading/rethreading of a pseudorotaxane based on *trans-cis* photoisomerization [54].

### Artificial molecular muscles

An exciting development in the field of molecular machines has been the construction of a rudimentary molecular-scale muscle [55] based on the topology of a rotaxane dimer which can undergo contraction and stretching movements (Fig. 6). The synthesized system contains two Cu(I) metal ions and two identical ring-and-string components. Each component consists of a ring containing a bidentate phenanthroline-type unit, and a string containing a bidentate phenanthroline, a terdentade terpyridine, and a

bulky stopper unit. Each of the two Cu(I) metal ions present in the rotaxane dimer is coordinated to two bidentate chelates, because Cu(I) prefers a four-coordination arrangement. Under these conditions, the system is "extended" (length 8.3 nm). On electrochemical oxidation of Cu(I), it was expected that the system would contract, because Cu(II) prefers a five-coordination arrangement and should, therefore, be surrounded by a bidentate and a terdentate ligand. This change in the coordination environment had, in fact, been previously observed for rotaxanes and catenanes of the same family [56]. In this case, however, electrochemical oxidation has apparently no effect. However, contraction (to about 6.5 nm) can be obtained by extraction of Cu(I) with a large excess of KCN) and successive remetalation with $Zn(NO_3)_2$ (Fig. 6). The back transformation of the contracted Zn species to the extended Cu species can be achieved by addition of $[Cu(CH_3CN)_4 \cdot PF_6]$.
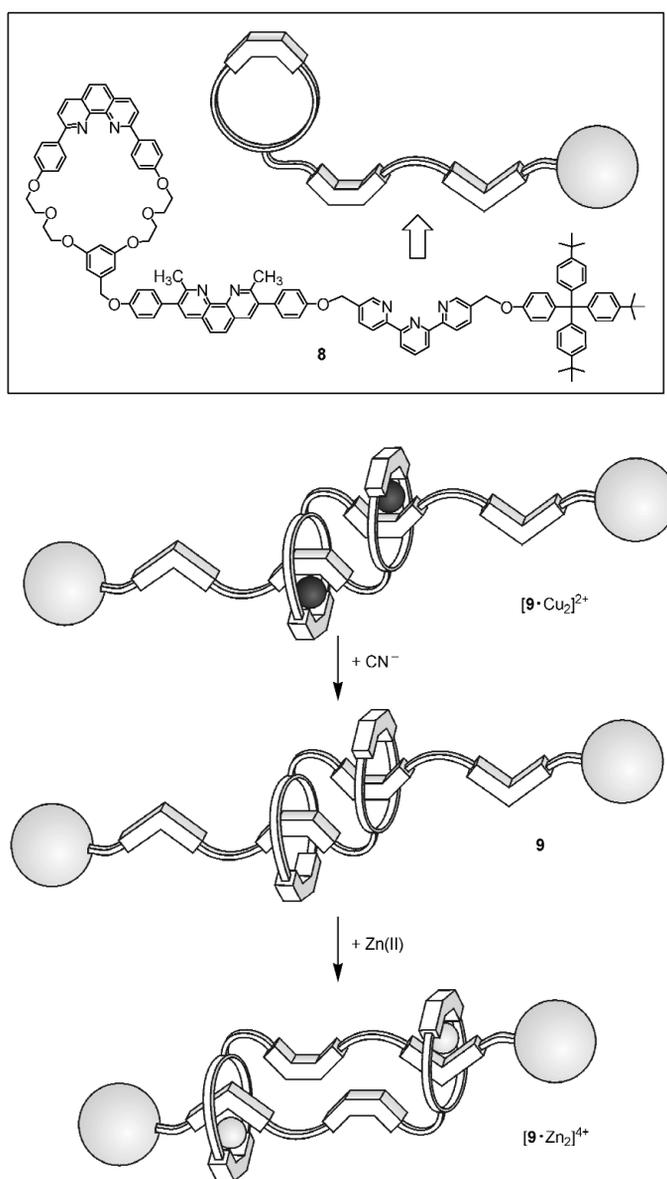


**Fig. 6** The prototype of an artificial molecular muscle based on a rotaxane dimer [55].

Recently, the molecular muscle concept has been implemented [57] by means of a self-assembled monolayer of a cleverly designed palindromic three-component rotaxane (Fig. 7), 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 NP stations, and to an inter-ring distance of 1.4 nm. Reduction of the TTF cationic units restores the original mechanical state. Owing to the disulfide tether covalently linked to each ring, a monolayer of the rotaxane could be assembled onto a gold surface. An array of flexible silicon micro-cantilever beams ($500 \times 100 \times 1$ µm), coated on one side with a monolayer of rotaxane molecules, was shown to undergo controllable and reversible bending up and down when exposed to the synchronous addition of an aqueous chemical oxidant [$Fe(ClO_4)_3$] and reductant (ascorbic acid) in a transparent fluid cell. These experiments suggest that the collective effect of billions of molecular machines in carefully engineered systems can be harnessed to do mechanical work on a larger scale.
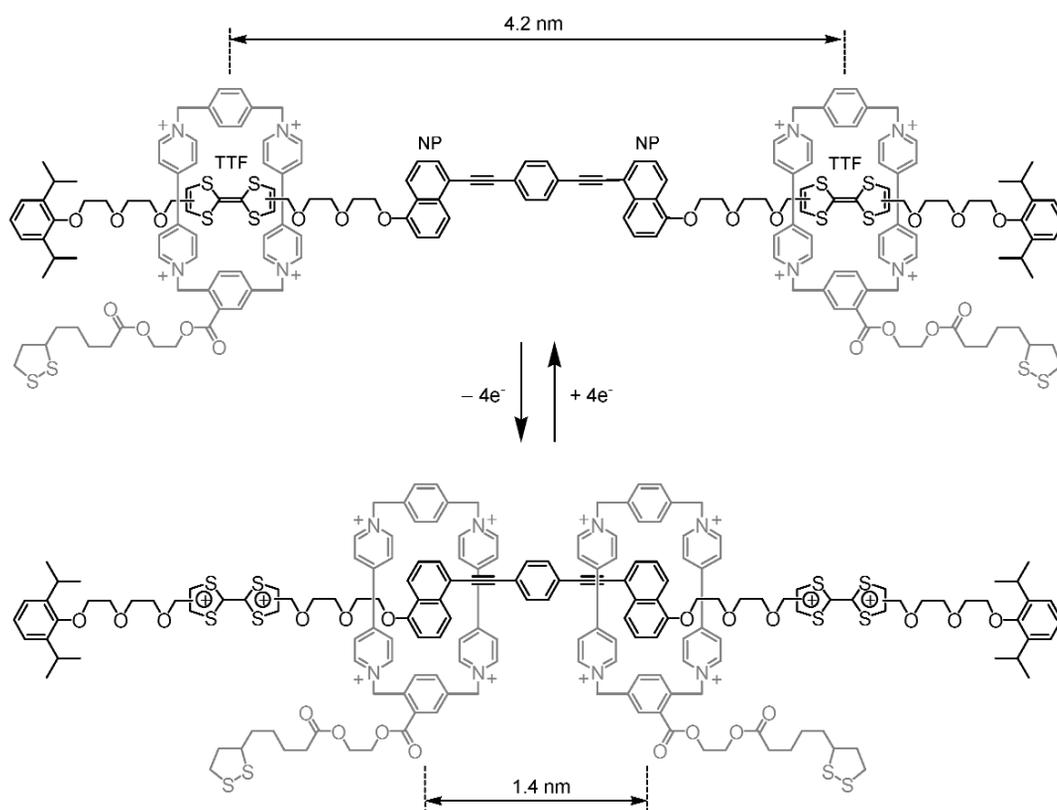


**Fig. 7** Chemical formula of a palindromic rotaxane and the redox-controlled switching between its contracted and extended forms [57].

## A molecular lift

The rotaxane shown in Fig. 8a incorporates a dialkylammonium and a bipyridinium recognition site in its dumbbell-shaped component [58]. The dibenzo[24]crown-8 macrocycle resides exclusively around the ammonium recognition site as a result of hydrogen bonds between the [$CH_2NH_2^+$] moiety of the dumbbell and the oxygen atoms of the macrocycle. On addition of a base, deprotonation of the ammonium recognition site occurs, the intercomponent hydrogen bonds are destroyed, and the macro-

cycle shuttles to the bipyridinium recognition site. The original conformation is restored by addition of acid.

Extending the above-reported idea of a two-station dumbbell to a trifurcated system enabled the preparation of the rotaxane shown in Fig. 8b which contains two stations in each of its three arms [59]. This compound is ~2.5 nm in height and has a diameter of ~3.5 nm. It consists of a tripod component containing two different notches—one ammonium center and one 4,4′-bipyridinium unit—at different levels in each of its three legs. Such legs are interlocked by the tritopic host, which plays the role of a platform that can be made to stop at the two different levels. Initially, the platform resides exclusively on the "upper" level, i.e., with the three rings surrounding the ammonium centers (Fig 8b, state 0). On addition of a base, deprotonation of the ammonium center occurs and, as a result, the platform moves to the "lower" level, i.e., with the three crown ether rings surrounding the bipyridinium units (Fig. 8b, state 1). The distance travelled by the platform is ~0.7 nm, and the potential force that can be generated is 200 pN, more than one order of magnitude larger than that generated by natural linear motors like kinesin. Subsequent addition of acid restores the ammonium centers, and the platform moves back to the upper level. The "up and down" elevator-like motion, which corresponds to a quantitative switching and can be repeated many times, can be monitored by ^{1}H NMR spectroscopy, electrochemistry, and absorption and fluorescence spectroscopy.
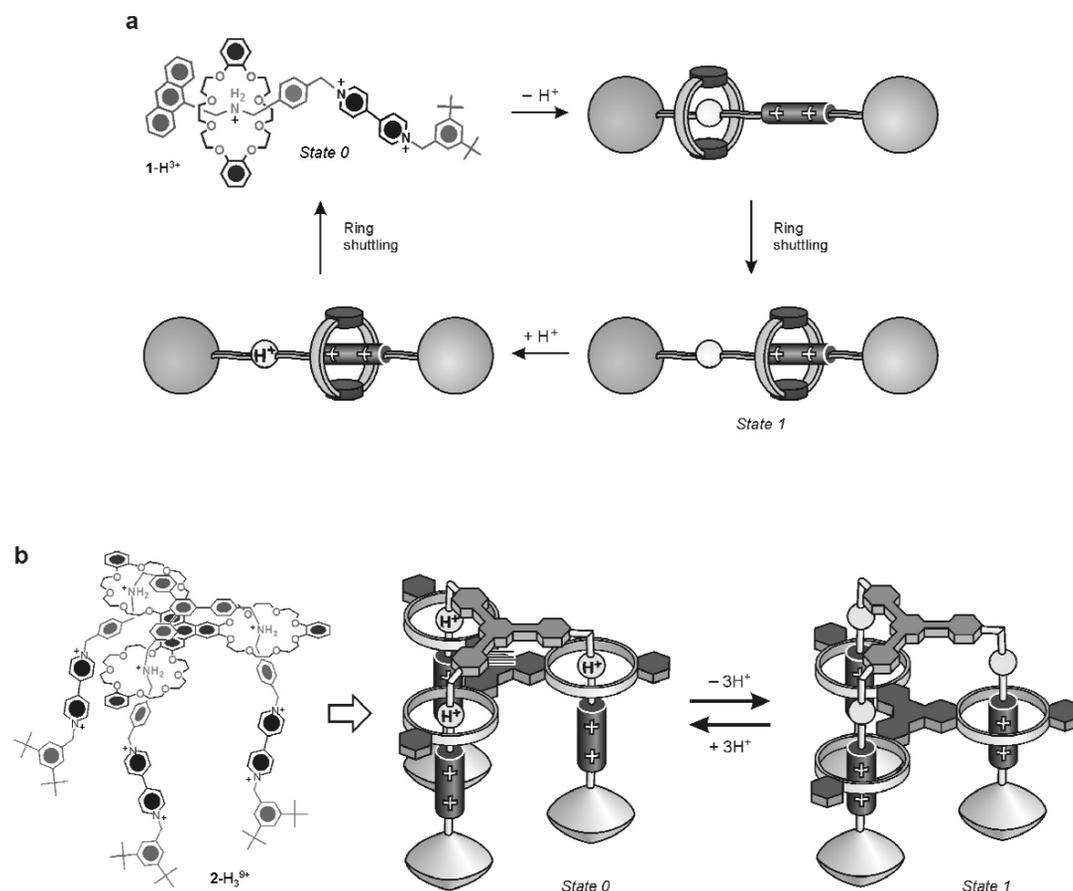


**Fig. 8** An acid/base-controllable molecular shuttle (a) [58], and a molecular lift (b) [59].

## A linear motor powered by sunlight

Photoinduced ring switching in a rotaxane containing two different recognition sites in the dumbbell-shaped component has been achieved with the compound shown in Fig. 9 [60]. This compound consists of six molecular components suitably chosen and assembled in order to achieve the devised function. It comprises a bis-$p$-phenylene-34-crown-10 electron donor macrocycle **R** (hereafter called the ring), and a dumbbell-shaped component which contains two electron acceptor recognition sites for the ring, namely, 4,4′-bipyridinium ($A_1$) and 3,3′-dimethyl-4,4′-bipyridinium ($A_2$) units, that can play the role of "stations" for the ring **R**. Furthermore, the dumbbell-shaped component incorporates a $[Ru(bpy)_3]^{2+}$-type (bpy = 2,2′-pyridine) electron-transfer photosensitizer **P** which is able to operate with visible light and also plays the role of a stopper, a $p$-terphenyl-type rigid spacer **S** which has the task of keeping the photosensitizer far from the electron acceptor units, and finally a tetraarylmethane group **T** as the second stopper. The stable translational isomer is the one in which the **R** component encircles the $A_1$ unit because this station is a better electron acceptor than the other one.
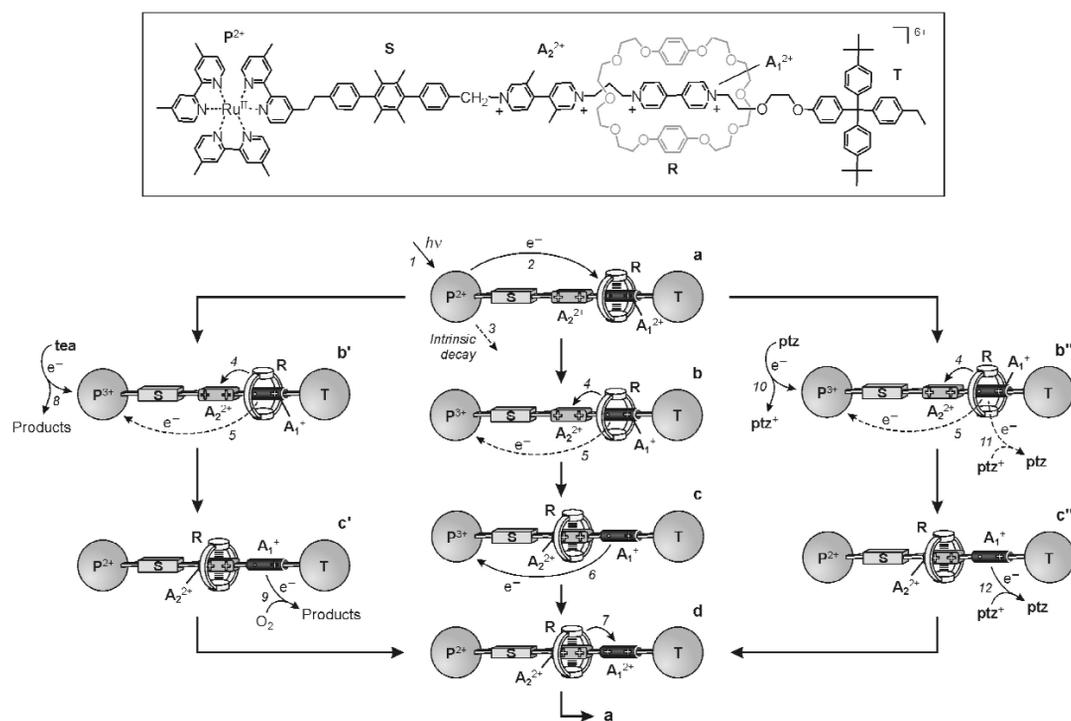


**Fig. 9** Schematic representation of the intramolecular (center) sacrificial (left) and relay (right) mechanisms for the photoinduced shuttling movement of macrocycle **R** between the two stations $A_1^{2+}$ and $A_2^{2+}$ [60].

The photoinduced shuttling is triggered by the $[Ru(bpy)_3]^{2+}$-type component which, on excitation with visible light, transfers an electron to the $A_1$. As schematized in Fig. 9, three shuttling mechanisms have been investigated [60]: (i) a mechanism involving an energetic contribution from low energy fuels (Fig. 9 left); (ii) a mechanism involving the kinetic assistance of an external electron relay (Fig. 9, right); and (iii) a purely intramolecular photochemical mechanism (Fig. 9, center). The quantum yield of ring displacement is 0.16, 0.12, and 0.02, respectively. When shuttling occurs via mechanisms (ii) and (iii), the rotaxane behaves as an autonomous "four-stroke" linear motor powered by sun light.

Several other examples of shuttling movement in rotaxanes have been reported [28,29].

## A photochemically driven rotary motor

A light-driven molecular motor has been designed and constructed by exploiting the *trans-cis* photo-isomerization around a carbon–carbon double bond in suitably designed alkene-type compounds containing chiral centers [61].

The first investigated system is that shown in Fig. 10. Both helical subunits of this compound can adopt a right-handed (*P*) or a left-handed (*M*) helicity. As a result, a total of four stereoisomers is possible. The *cis-trans* isomerizations are reversible and occur on irradiation at appropriate wavelengths. In contrast, the inversions of helicities, while maintaining a *cis* or a *trans* configuration, occur irreversibly under the influence of thermal energy. On irradiation (≥280 nm, 218 K) of a solution of (*P,P*)-*trans*, a mixture of (*P,P*)-*trans* and (*M,M*)-*cis* is obtained in a ratio of 5:95. When the solution is
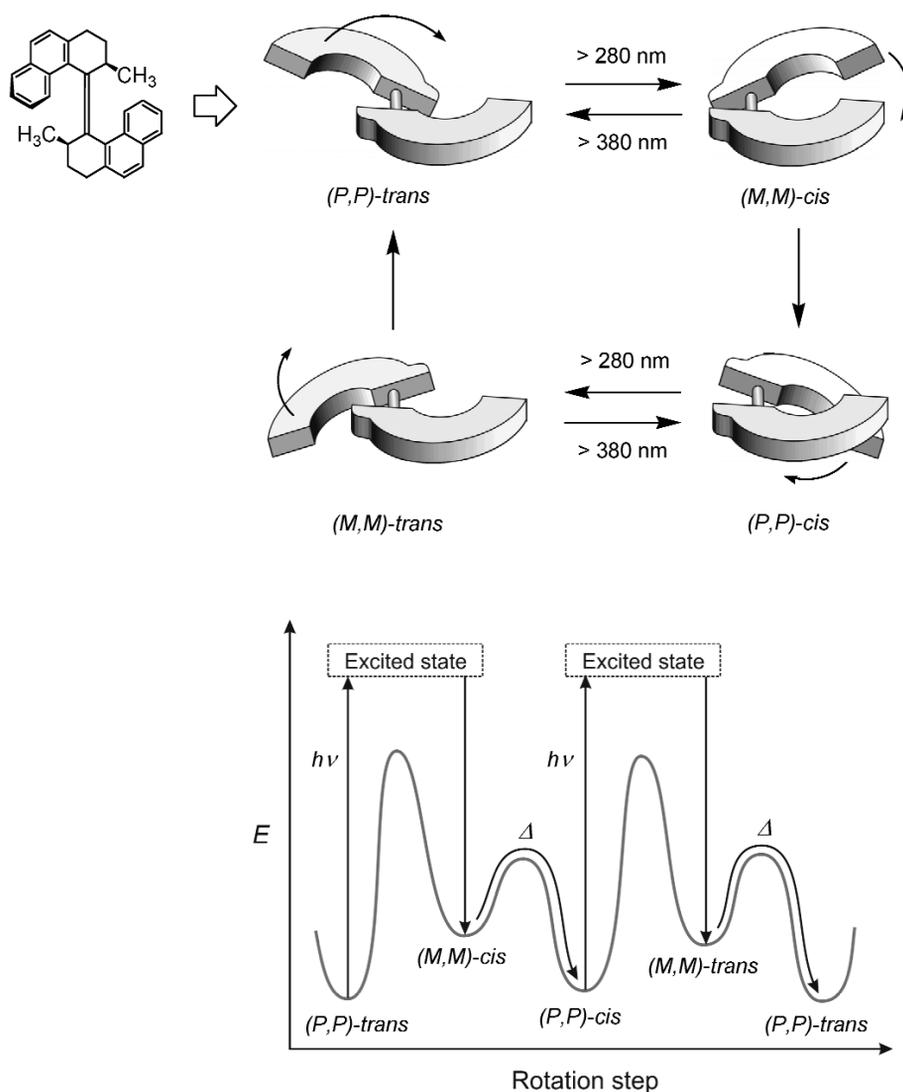


**Fig. 10** Unidirectional rotation around a carbon–carbon double bond in a suitably designed alkene-type compound containing chiral centers. Each light-driven, energetically uphill process is followed by a thermal, energetically downhill process [61].

warmed to 293 K (*M,M*)-*cis* is converted irreversibly to (*P,P*)-*cis*. Subsequent irradiation (≥280 nm) of the solution produces a mixture of (*P,P*)-*cis* and (*M,M*)-*trans* in a ratio of 10:90. When the temperature is increased further (333 K), (*M,M*)-*trans* is converted irreversibly to the original isomer (*P,P*)-*trans*. Thus, a sequence of light- and temperature-induced isomerizations can be exploited to move this molecular rotor in one direction only (Fig. 10). Indeed, when (*P,P*)-*trans* is irradiated (≥280 nm) at 293 K a clockwise 360-degree rotation occurs spontaneously. The unidirectional motion in this system is dictated by the stereogenic centers associated with the two methyl substituents. As a result of *trans-cis* isomerization, the axial methyl substituents of (*P,P*)-*trans* are forced to adopt a less favorable equatorial orientation in (*M,M*)-*cis*. The strain associated with the equatorial methyl susbstituents is, however, released on thermal conversion of (*M,M*)-*cis* to the more stable isomer (*P,P*)-*cis*. The subsequent *cis-trans* isomerization forces the methyl groups to adopt, once again, equatorial orientations in the isomer (*M,M*)-*trans*. Finally, the thermal conversion of (*M,M*)-*trans* to the original isomer (*P,P*)-*trans* is accompanied by a change from equatorial to the more stable axial orientations for the methyl substituents. More recently, several modifications have been made to improve the performance of the rotary motor and to connect it with other molecules, nanoparticles, or surfaces [62–65].

## CONCLUSION

Nanoscience and nanotechnology are still in their infancy. At present, new exciting results and, sometimes, disappointing checks alternate on the scene, as it always happens in fields that have not yet reached maturity. In his famous address to the American Physical Society, R. P. Feynman [17] concluded his reflection on the idea of constructing molecular-level machines as follows: "What would be the utility of such machines? Who knows? I cannot see exactly what would happen, but I can hardly doubt that when we have some control of the rearrangement of things on a molecular scale we will get an enormously greater range of possible properties that substances can have, and of different things we can do". For sure, these new properties will lead to a wide variety of applications which we cannot even envisage today.

As science expands and technology develops, the world becomes more fragile. Development of nanotechnology presents, indeed, many problems that are currently discussed by the scientific community, as reviewed, for example, in the book *The Nanotech Pioneers* [1]. First, there is a need for a rational, informed, and transparent dialogue between scientists and citizens on the risks and benefits of nanotechnology. Some of the fears raised, such as an environmental disaster due to self-replication of artificial nanorobots or nanoorganisms and creation of machines that are smarter than human beings, belong to science fiction. Dread related to military applications (e.g., weapons of mass destruction, cyborg soldiers) are, unfortunately, real and urge all nations to maintain control of civilian institutions over the military establishment. Other fears concern the toxic potential of materials at the nanolevel [66], a problem that hopefully can be controlled by principles and test procedures capable of ensuring safe manufacture and use of nanomaterials in the marketplace [67].

In a book entitled *Our Final Hour* [68], Martin Rees describes in detail the great number of risks of our age related to bad or incautious use of the most recent developments of science and technology. In his opinion, there is a 50 % chance that our civilization will self-destroy before the end of this century. Many scientists object that Rees overemphasizes the negative potential of science. I agree, but I also believe that he has neglected more important facets of the fragility problem.

We live in a fragile world, indeed. But we are in danger not so much because of the development of science that cannot be avoided and, as already happened in the past, can help solving mankind problems. Rather, we are in danger because we do not realize that Earth is a spaceship with limited resources that carries 6.5 billion people. Risks derive from two main features [43]: (i) too much consumption, as shown by the fact that, in global ha/person, Earth's biocapacity is 1.8, whereas the average footprint is 2.2 [69,70]; (ii) too much disparity, so much so that if all the world's inhabitants were to live at current North American ecological standards, we should look around for another three Earths to accommodate

them [70]. History shows that scientific research usually benefits the rich only. Therefore, concern should also be raised over the potential for nanotechnologies to increase the gap between the rich and the poor, adding a "nanodivide" to the already large number of factors that cause disparity.

In affluent countries, the tacit assumption is that there is never enough, without realizing that an unlimited economic growth on a finite planet is not possible. Apparently, we have forgotten that the economic growth is not an end, but a means toward a sustainable and friendly present and future of *all* humanity. Living on the Earth believing that there is no need of the concepts of "enough" and of "equity" is already quite risky and will clearly become impossible in a few decades. Learning to say enough is a necessary condition for a sustainable world. Establishing equity is not only a moral duty, but also a basic need for creating a peaceful world.

Scientists should become aware that science and technology alone will not take us where we need to be in a few decades. Responsible scientists, while creating, with the greatest moral care, new science and technology, should also play an important role as authoritative, informed, and concerned citizens of the planet Earth. As pointed out by Richard R. Ernst [71], "When we set out, by our research activity in the laboratory, to incrementally influence the course of history, we are also requested to contemplate the desired long term global development. Who else, if not the scientists, is responsible for setting guidelines for defining progress and for protecting the interests of future generations?"

Scientists, regardless of their specialization, should clearly explain the limits of our "spaceship" Earth to all citizens and especially to economists and policy makers. Science must indeed be rooted in a profound understanding of people, organizations, nations, and cultures [72]. As Albert Einstein said, "Concern for man himself and his fate must always constitute the chief objective of all technological endeavours; never forget this in the midst of your diagrams and equations" [73].

## ACKNOWLEDGMENTS

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