

Light-powered molecular-scale machines*

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Abstract: The macroscopic concepts of a machine can be extended to the molecular level. Molecular-level machines are constructed by the molecule-by-molecule bottom-up approach following the guidelines of supramolecular chemistry. Like macroscopic machines, molecular machines are characterized by (i) the kind of energy supplied to make them work, (ii) the kind of movement performed by their components, (iii) the way in which their operation can be controlled and monitored, (iv) the possibility to repeat the operation, (v) the time needed to complete a cycle of operation, and (vi) the function performed. The most convenient way to supply energy to a molecular machine is through photochemical energy inputs. Photochemical techniques offer, indeed, several advantages: (i) photons can make a machine work without formation of waste products, (ii) light can be switched on/off easily and rapidly, (iii) lasers provide the opportunity of working in very small space and very short time domains, (iv) photons can be used to “read” the state of the system and to monitor the operation of the machine. The extension of the concepts of 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.

INTRODUCTION

At the root of our existence lies movement at the molecular level [1–3]. Nature provides living systems with complex molecules called motor proteins which work inside a cell like ordinary machines built for everyday needs. Because of these biological engines, we can walk, talk, and even think.

Mankind’s progress has always been related to the construction of novel machines. Depending on the purpose of its use, a machine can be very big or very small. In the last 50 years, progressive miniaturization of the components employed for the construction of machines has resulted in outstanding technological achievements. A common prediction is that further progress in miniaturization will not only decrease the size and increase the power of computers, but also open the way to new technologies in the fields of medicine, the environment, energy, and materials.

Until now, miniaturization has been pursued by a large downward (top-down) approach, which is reaching the limits of its physical capabilities (hundreds of nanometers). Miniaturization, however, can be pushed further on (Fig. 1) because “there is plenty of room at the bottom”, as Richard P. Feynman stated in a famous talk to the American Physical Society in 1959 [4]. In the last 10 years, chemists who have always been working “at the bottom”, have taken up Feynman’s challenge. Starting from molecules, the smallest entities of matter that have distinct shapes and properties, chemists have developed a “bottom-up” approach to construct molecular-level machines of nanometer size.

Natural molecular-level machines are extremely complex systems. Their structures and detailed working mechanisms have been elucidated only in a few cases, and any attempt to construct systems of

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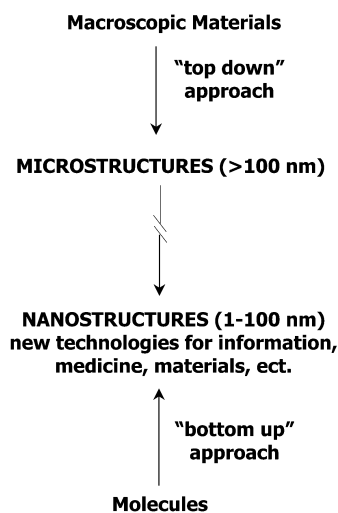


Fig. 1 Top-down and bottom-up approaches to miniaturization.

such a complexity by using the bottom-up molecular approach would be hopeless. Therefore, chemists are trying to construct much simpler molecular-level machines, without mimicking the complexity of the biological structures. In the last few years, synthetic talent, which has always been the most distinctive feature of chemists, combined with a device-driven ingenuity evolved from chemists' attention to functions and reactivity, have led to the design and construction of a great number of very interesting molecular-level machines.

The concepts underlying the bottom-up approach to molecular machines, and, more generally, to nanotechnology, are those of supramolecular chemistry [5]. The potentialities, limitations, and hopes connected with the bottom-up approach have been anticipated and beautifully described by a great Italian chemist and writer, Primo Levi, in his book *The Monkey's Wrench* [6].

"...it is reasonable to proceed a bit at a time, first attaching two pieces, then adding a third, and so on. ...We don't have those tweezers we often dream of at night, the way a thirsty man dreams of springs, that would allow us to pick up a segment, hold it firm and straight, and paste it in the right direction on the segment that has already been assembled. If we had those tweezers (and it's possible that, one day, we will), we would have managed to create some lovely things that so far only the Almighty has made, for example, to assemble—perhaps not a frog or a dragonfly—but at least a microbe or the spore of a mould".

CONCEPT OF A MOLECULAR MACHINE

A macroscopic machine is any combination of mechanisms for utilizing, modifying, applying, or transmitting energy [7]. The movements of the mobile parts of a macroscopic machine can be described by Newton's equation of motions, which determines the coordinates and speed of each part of the machine relative to a given origin. Going down to very small dimensions, the question arises [8–10], whether the macroscopic concept of movement can be maintained. The concept of movement, in fact, is not intuitive in the quantum mechanical language because the Schrödinger equation of motions only gives a correspondence between forces and quantum eigenstates. These problems, however, do not seem to be relevant for nanoscale-size molecular machines, as shown by the fact that the structure and even the

movement of single molecules with diameter of about 1 nm can clearly be seen by using modern techniques [11].

Molecular-level machines operate via nuclear movements caused by chemical reactions. Any kind of chemical reaction involves, of course, some nuclear displacement. The term “molecular machine”, however, is used only for chemical systems performing reactions that can cause large-amplitude motions, leading to real translocation of some component parts of the system. Particularly interesting nuclear motions from the viewpoint of artificial molecular machines are those related to (i) isomerization reactions involving $-N=N-$, $-C=N-$, and $-C=C-$ double bonds in covalent supramolecular structures, (ii) metal-ligand reactions causing the formation or disruption of coordination bonds, and (iii) acid-base or redox reactions causing making/breaking of intermolecular bonds (including hydrogen bonds).

Molecular-level machines must contain a motor, which in principle consists of a mobile and a stationary part. An external operator should be able, by means of a given input, to induce the displacement of the movable component from the stationary one. When the system is investigated in solution, where both components are in motion, the bulkiest one is considered motionless and the other one is said to move with respect to it. Besides a motor, macroscopic machines contain a great variety of auxiliary components such as fasteners, bearings, drive shafts, gears, brakes, rotors, etc. The concepts of machine components can also be extended to the molecular scale. For example, the role of molecular-level fasteners can be played by covalent bonds linking distinct subunits of the system, or by strong intermolecular interactions like those originating from multiple hydrogen bonds; star-shaped molecules can play the role of gears; steric crowding caused by a substituent placed in a selected position of a moving subunit can play the role of a brake. Examples of chemical systems capable of performing the above reported functions can be found in chapters 11 and 13 of a recent monograph [12].

Like macroscopic machines, molecular-level machines are characterized by (i) the kind of energy supplied to make them work, (ii) the kind of movement performed by their components, (iii) the way in which their operation can be controlled and monitored, (iv) the possibility to repeat the operation at will, (v) the time scale needed to complete a cycle of operation, and (vi) the function performed.

ENERGY SUPPLY

In order to make a molecular machine work, energy must be supplied to its motor. The most obvious way to supply energy to a chemical system is by using some kind of fuel capable of causing a chemical reaction. In his famous address “There is Plenty of Room at the Bottom”, R. P. Feynman discussed the possibility of constructing molecular-level machines and observed [4]: “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 nature, where chemical energy is used to power the biological machines that sustain life.

Consider, for example, what happens in plants, where energy is supplied by degradation of adenosine triphosphate (ATP) [13,14]. The energy (about 12 kT) is stored in a phosphate bond and is released when this bond is broken to form adenosine diphosphate (ADP), and inorganic phosphate (P_i). The natural motors continuously “break” ATP molecules in a never-ending cycle, somewhat like a machine gun “breaking” bullets [13]. Although the chemical reactions are reversible, the cycle goes one way because the photosynthetic process makes use of the solar energy flux to supply fresh new ATP, while all the used ADPs and P_i s are removed.

In the same way, if an artificial molecular-level machine has to work by inputs of chemical energy, it will need addition of fresh reactants (“fuel”) at any step of its working cycle, with the concomitant formation of waste products. Accumulation of waste products will inevitably compromise the operation of the machine, unless they are removed from the system, as it happens both in the natural machines and in the macroscopic internal combustion engines.

The need to remove waste products introduces noticeable limitations in the design and construction of artificial molecular-level machines based on “chemical fuel” inputs. There is, however, an alternative, more convenient way to power artificial molecular machines.

Light energy

In green plants, the energy needed to sustain the machinery of life is provided by sunlight [15], but light energy is not used as such to produce mechanical movements; rather, it is used to produce a chemical fuel, ATP. Light energy, however, can directly cause photochemical reactions involving large nuclear movements. A simple example is a photoinduced isomerization from the lower energy *trans* to the higher-energy *cis* form of a molecule containing $-C=C-$ or $-N=N-$ double bonds, which is followed by a spontaneous or light-induced back reaction [16,17]. Such photoisomerization reactions have indeed been used to design molecular machines driven by light energy inputs [18]. In supramolecular species, photoinduced electron-transfer reactions can often cause large displacement of molecular components [12]. Indeed, working with suitable systems, an endless sequence of cyclic molecular-level movements can in principle be performed making use of light energy inputs without generating waste products.

Compared to chemical energy inputs, photochemical energy inputs offer other advantages, besides the fundamental one of not generating waste products: (i) light can be switched on/off easily and rapidly; (ii) lasers provide the opportunity of working in very small space and very short time domains; (iii) photons, besides supplying the energy needed to make a machine work, can also be useful to “read” the state of the system and thus to control and monitor the operation of the machine.

Several light-powered molecular machines have been recently reported. For space reason, only an example will be illustrated below. An exhaustive treatment of artificial molecular-level machines powered by light energy, electrical energy, or chemical energy can be found in chapters 12–16 of a recent monograph [12].

“Four-stroke” cyclic linear motor powered by light

In order to achieve photoinduced ring switching in rotaxanes containing two different recognition sites in the dumbbell-shaped component, the thoroughly designed compound $\mathbf{1}^{6+}$ shown in Fig. 2 was synthesized [19]. This compound consists of the electron-donor macrocycle R, and a dumbbell-shaped component that contains (i) $[\text{Ru}(\text{bpy})_3]^{2+}$ (P) as one of its stoppers, (ii) a *p*-terphenyl-type ring system as a rigid spacer (S), (iii) a 4,4'-bipyridinium unit (A_1) and a 3,3'-dimethyl-4,4'-bipyridinium unit (A_2) as electron-accepting stations, and (iv) a tetraarylmethane group as the second stopper (T). The structure of rotaxane $\mathbf{1}^{6+}$ was characterized by mass spectrometry and NMR spectroscopy, which also established, along with cyclic voltammetry, that the stable translational isomer is the one in which the R component encircles the A_1 unit, in keeping with the fact that this station is a better electron acceptor than the other one. The electrochemical, photophysical, and photochemical (under continuous and pulsed excitation) properties of the rotaxane, its dumbbell-shaped component, and some model compounds have then been investigated, and two strategies have been devised in order to obtain the photoinduced abacus-like movement of the R macrocycle between the two stations A_1 and A_2 : one is fully based on processes involving only the rotaxane components (intramolecular mechanism), while the other one requires the help of external reactants (sacrificial mechanism).

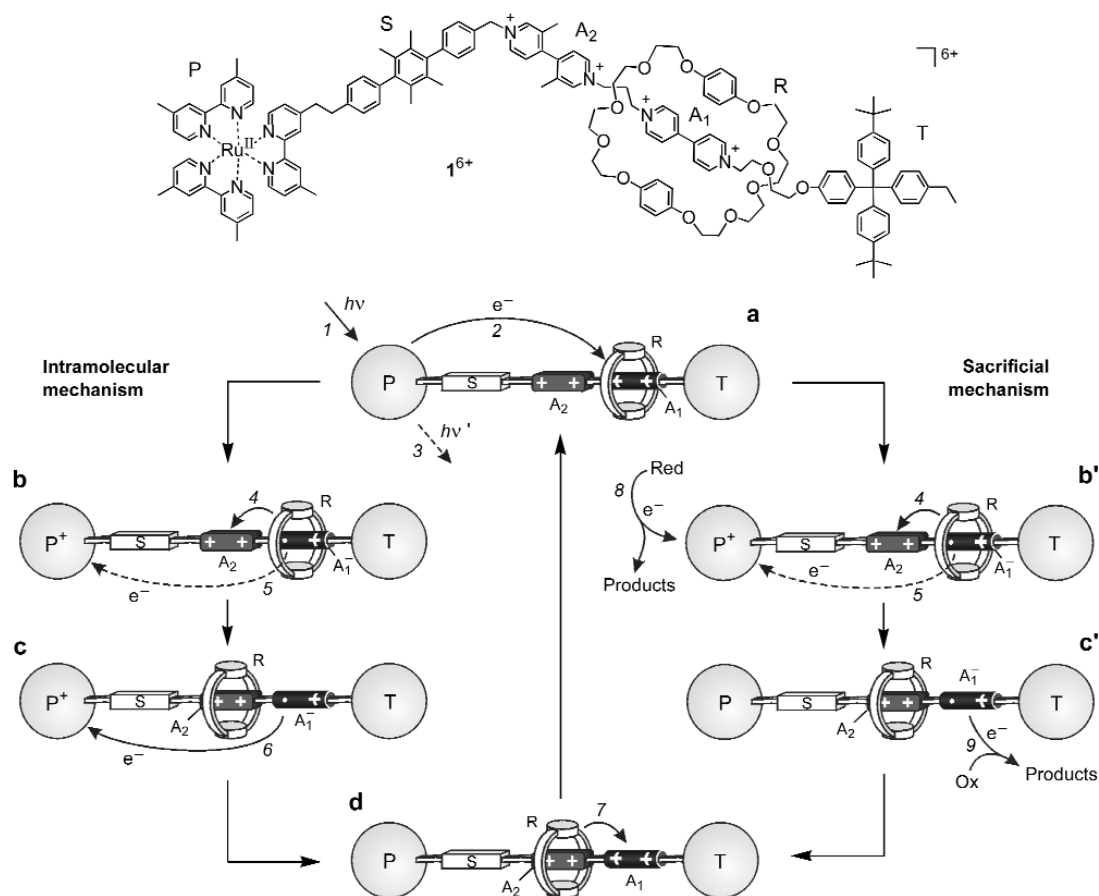


Fig. 2 Rotaxane 1^{6+} and schematic representation of the intramolecular (left) and sacrificial (right) mechanisms for the photoinduced shuttling movement of macrocycle R between the two stations A_1 and A_2 [19].

The intramolecular mechanism, illustrated in the left-hand side of Fig. 2, is based on the following four operations [19]:

- Destabilization of the stable translational isomer:* Light excitation of the photoactive unit P (step 1) is followed by the transfer of an electron from the excited state to the A_1 station, which is encircled by the ring R (step 2), with the consequent "deactivation" of this station; such a photoinduced electron-transfer process has to compete with the intrinsic decay of the excited state of P (step 3).
- Ring displacement:* The ring moves from the reduced station A_1^- to A_2 (step 4), a step that has to compete with the back electron-transfer process from A_1^- (still encircled by R) to the oxidized photoactive unit P^+ (step 5). This is the most difficult requirement to meet in the intramolecular mechanism.
- Electronic reset:* A back electron-transfer process from the "free" reduced station A_1^- to P^+ (step 6) restores the electron-acceptor power to the A_1 station.
- Nuclear reset:* As a consequence of the electronic reset, back movement of the ring from A_2 to A_1 takes place (step 7).

The results obtained seem to indicate that electronic reset of the system after light excitation (step 5; $k = 2.4 \times 10^5 \text{ s}^{-1}$) is faster than the ring displacement (step 4). It is worthwhile noticing that, in a system that behaves according to the intramolecular mechanism shown in the left-hand side of Fig. 2, each light input causes the occurrence of a forward and back ring movement (i.e., a full cycle) without generation of any waste product. In some way, it can be considered as a “four-stroke” cyclic linear motor powered by light.

The alternative, less demanding sacrificial mechanism is based on the use of external redox reactants (a reductant like triethanolamine, and an oxidant such as dioxygen) that operate as illustrated in the right-hand side of Fig. 2 [19]:

- (a) *Destabilization of the stable translational isomer*: as in the previous mechanism.
- (b') *Ring displacement after scavenging of the oxidized photoactive unit*: since the solution contains a suitable reductant, a fast reaction of such species with P^+ (step 8) competes successfully with the back electron-transfer reaction (step 5); therefore, the originally occupied station remains in its reduced state A_1^- , and the displacement of the ring R to A_2 (step 4), even if it is slow, does take place.
- (c') *Electronic reset*: after an appropriate time, restoration of the electron-acceptor power of the A_1 station is obtained by oxidizing A_1^- with a suitable oxidant such as dioxygen (step 9).
- (d) *Nuclear reset*: as in the previous mechanism (step 7).

The results obtained show that such a sacrificial mechanism is fully successful. Of course, this mechanism is less appealing than the intramolecular one because it causes the formation of waste products. However, instead of using a sacrificial reductant, i.e., an electron-donor molecule that undergoes a fast decomposition reaction after electron transfer has taken place, an external “reversible” reductant (electron relay), giving rise to a stable oxidized form, may be successfully employed, provided that the back electron-transfer process can be slowed down by a wise choice of the partners.

It should also be stressed that the mechanical movement of the cyclic component between the two stations and the related changes in the spectroscopic and electrochemical properties obey the binary logic and can therefore be taken as a basis for information processing [20].

Another example of light-driven molecular shuttle is described [21].

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