Rotaxane- and catenane-based molecular machines and motors

Alberto Credi,[a]* Roberto Ballardini,[b] Vincenzo Balzani,[a] Belén Ferrer,[a]
Maria Teresa Gandolfi,[a] Serena Silvi,[a] Margherita Venturi[a]

[a]Dipartimento di Chimica "G. Ciamician", Università di Bologna, Via Selmi 2, 40126 Bologna, Italy. [b]Istituto ISOF-CNR, via Gobetti 101, 40129 Bologna, Italy
E-mail: alberto.credi@unibo.it

The concept of (macroscopic) machine can be extended to the molecular level. A *molecular machine* can be defined as an assembly of a discrete number of molecular components (i.e., a supramolecular system) in which the component parts can display changes in their relative positions as a result of some external stimulus. Rotaxanes and catenanes are promising systems for the construction of artificial molecular machines. The design, synthesis and investigation of chemical systems able to function as molecular machines and motors is of interest not only for basic research, but also for the growth of nanoscience and the development of nanotechnology. A few examples of molecular machines taken from our own research will be illustrated.

1 Introduction

1.1 Extreme miniaturization: the bottom-up approach

A *device* is something invented and constructed for a special purpose, and a *machine* is a particular type of device in which the component parts display changes in their relative positions as a result of some external stimulus. Progress of mankind has always been related to the construction of novel devices. Depending on the purpose of its use, a device can be very big or very small. In the last fifty years, progressive miniaturization of the components employed for the construction of devices and machines has resulted in outstanding technological achievements, particularly in the field of information processing. A common prediction is that further progress in miniaturization 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.

Until now miniaturization has been pursued by a large-downward (top-down) approach, which is reaching practical and fundamental limits (presumably ca. 50 nanometers) [1]. Miniaturization, however, can be pushed further on since "there is plenty of room at the bottom", as Richard P. Feynman stated in a famous talk to the American Physical Society in 1959 [2].

The key sentence of Feynman's talk was the following: *"The principle of physics do not speak against the possibility of manoeuvring things atom by atom".* The idea of the "atom-by-atom" bottom-up approach to the construction of nanoscale devices and machines, however, which was so much appealing to some physicists [3] did not convince chemists who are well aware of the high reactivity of most atomic species and of the subtle aspects of chemical bond. Chemists know [4] that atoms are not simple spheres that can be moved from a place to another place at will. Atoms do not stay isolated; they bond strongly to their neighbours and it is difficult to imagine that the atoms can be taken from a starting material and transferred to another material.

In the late 1970s a new branch of chemistry, called *supramolecular chemistry*, emerged and expanded very rapidly, consecrated by the award of the Nobel Prize in Chemistry to C.J. Pedersen [5], D.J. Cram [6], and J.-M. Lehn [7] in 1987. In the frame of research on supramolecular chemistry, the idea began to arise in a few laboratories [8,9,10] that molecules are much more convenient building blocks than atoms to construct nanoscale devices and machines. The main reasons at the basis of this idea are: (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; (iii) most of the laboratory chemical processes deal with molecules, not with atoms; (iv) molecules are objects that 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. In the same period, research on molecular electronic devices began to flourish [11].

In the following years supramolecular chemistry grew very rapidly [12] and it became clear that the "bottom-up" approach based on molecules opens virtually unlimited possibilities concerning design and construction of artificial molecular-level devices and machines. Recently the concept of molecules as nanoscale objects exhibiting their own shape, size and properties has been confirmed by new, very powerful techniques, such as single-molecule fluorescence spectroscopy and the various types of probe microscopies, capable of "seeing" [13] or "manipulating" [14] single molecules, and even to investigate bimolecular chemical reactions at the single molecule level [15].

Much of the inspiration to construct molecular-level devices and machines comes from the outstanding progress of molecular biology that has begun to reveal the secrets of the natural molecular-level devices and machines which constitute the material base of life. Bottom-up construction of devices and machines as complex as those present in Nature is, of course, an impossible task [16]. Therefore chemists have tried to construct much simpler systems, without mimicking the complexity of the biological structures. In the last few years, synthetic talent, that 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 outstanding achievements in this field [17,18,19,20].

1.2 Characteristics of molecular machines and motors

The words *motor* and *machine* are often used interchangeably when referred to molecular systems. It should be recalled, however, that a motor converts energy into mechanical work, while a machine is a device, usually containing a motor component, designed to accomplish a function. Molecular machines and motors operate via electronic and/or nuclear rearrangements and, like the macroscopic ones, are characterized by *(i)* the kind of energy input supplied to make them work, *(ii)* the type of motion (linear, rotatory, oscillatory, ...) performed by their components, *(iii)* the way in which their operation can be monitored, *(iv)* the possibility to repeat the operation at will (cyclic process), and *(v)* the time scale needed to complete a cycle. According to the view described above, an additional and very important distinctive feature of a molecular machine with respect to a molecular motor is *(vi)* the function performed [18].

As far as point *(i)* is concerned, a chemical reaction can be used, at least in principle, as an energy input. In such a case, however, if the machine has to work cyclically [point *(iv)*], it will need addition of reactants at any step of the working cycle, and the accumulation of by–products resulting from the repeated addition of matter can compromise the operation of the device. On the basis of this consideration, the best energy inputs to make a molecular device work are photons [21] and electrons [22]. It is indeed possible to design very interesting molecular devices based on appropriately chosen photochemically and electrochemically driven reactions [20].

In order to control and monitor the device operation [point *(iii)*], the electronic and/or nuclear rearrangements of the component parts should cause readable changes in some chemical or physical property of the system. In this regard, photochemical and electrochemical techniques are very useful since both photons and electrons can play the dual role of "writing" (i. e., causing a change in the system) and "reading" (i. e., reporting the state of the system).

The operation time scale of molecular devices [point *(v)*] can range from less than picoseconds to seconds, depending on the type of rearrangement (electronic or nuclear) and the nature of the components involved.

Finally, as far as point *(vi)* is concerned, the functions that can be performed by exploiting the movements of the component parts in molecular machines are various and, to a large extent, still unpredictable. It is worth to note that the mechanical movements taking place in molecular-level machines, and the related changes in the spectroscopic and electrochemical properties, usually obey binary logic and can thus be taken as a basis for information processing at the molecular level. Artificial molecular machines capable of performing logic operations have been reported [23].

1.3 Rotaxanes and catenanes as artificial molecular machines

Most of the recently designed artificial molecular machines and motors are based on rotaxanes and catenanes [20]. The names of these compounds derive from the Latin words *rota* and *axis* for wheel and axle, and *catena* for chain. Rotaxanes [24] are minimally composed (Figure 1a) of an axle-like molecule surrounded by a macrocyclic compound and terminated by bulky groups (stopper) that prevent disassembly; catenanes [24] are made of (at least) two interlocked macrocycles or "rings" (Figure 1b). Rotaxanes and catenanes are appealing systems for the construction of molecular machines because motions of their molecular components can be easily imagined (Figure 2).

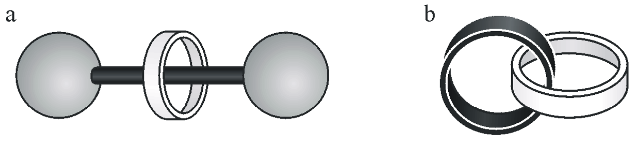


Figure 1. Schematic representation of a rotaxane (a) and a catenane (b)

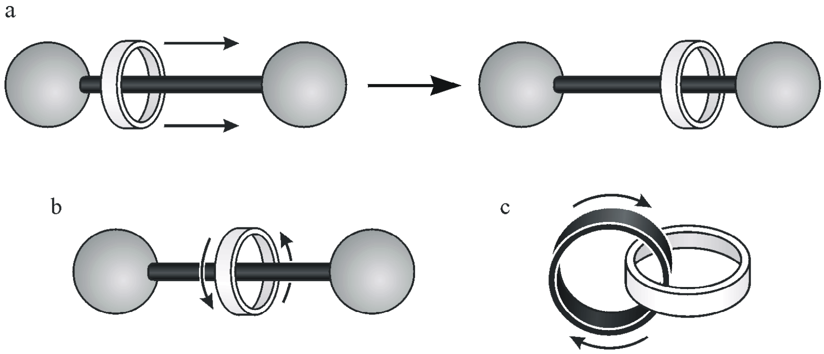


Figure 2. Schematic representation of some of the intercomponent motions that can be obtained with rotaxanes and catenanes: shuttling (a) and ring rotation (b, c)

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 of rotaxanes and catenanes, involve electron-donor/acceptor ability, hydrogen bonding, hydrophobic/hydrophylic character, π-π stacking, coulombic forces and, on the side of the strong interaction limit, metal-ligand bonding.

In the next sections, a few examples of artificial molecular machines based on rotaxanes and catenanes taken from our research will be illustrated.

2 An acid-base controlled molecular shuttle

In rotaxanes containing two different recognition sites in the dumbbell-shaped component, it is possible to switch the position of the ring between the two 'stations' by an external stimulus. A system which behaves as a chemically controllable molecular shuttle is compound $\mathbf{1}^{3+}$ shown in Figure 3 [25]. It is made of a dibenzo[24]crown-8 (DB24C8) macrocycle and a dumbbell-shaped component containing a dialkylammonium center and a 4,4'-bipyridinium unit. An anthracene moiety is used as a stopper because its absorption, luminescence, and redox properties are useful to monitor the state of the system. Since the N^+–H···O hydrogen bonding interactions between the DB24C8 macrocycle and the ammonium center are much stronger than the electron donor-acceptor interactions of the macrocycle with the bipyridinium unit, the rotaxane exists as only one of the two possible translational isomers. Deprotonation of the ammonium center with a base (a tertiary amine) causes 100% displacement of the macrocycle to the bipyridinium unit; reprotonation directs the macrocycle back onto the ammonium center (Figure 3). Such a switching process has been investigated in solution by ^{1}H NMR spectroscopy and by electrochemical and photophysical measurements [25]. The full chemical reversibility of the energy supplying acid/base reactions guarantees the reversibility of the mechanical movement, in spite of the formation of waste products. Notice that this system could be useful for information processing since it exhibits a binary logic behavior. It should also be noted that, in the deprotonated rotaxane, it is possible to displace the crown ring from the bipyridinium station by destroying the donor-acceptor interaction through reduction of the bipyridinium station or oxidation of the dioxybenzene units of the macrocyclic ring. Therefore, in this system, mechanical movements can be induced by two different types of stimuli (acid-base and electron-hole).

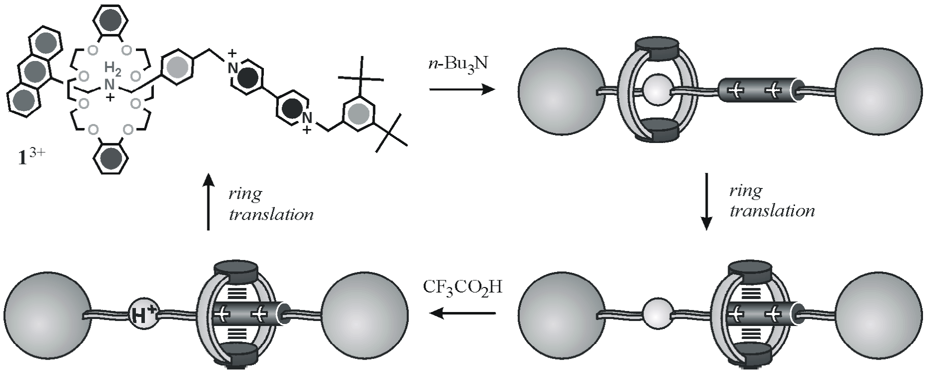

1^{3+}

Figure 3. A chemically controllable molecular shuttle. The macrocyclic ring can be switched between the two stations of the dumbbell-shaped component by acid-base inputs

3 A light-driven molecular shuttle

For a number of reasons, light is the most convenient form of energy to make artificial molecular machines work [21]. In order to achieve photoinduced ring shuttling in rotaxanes containing two different recognition sites in the dumbbell-shaped component, the thoroughly designed compound $\mathbf{2}^{6+}$ (Figure 4) was synthesized [26]. This compound is made of the electron-donor macrocycle R, and a dumbbell-shaped component which contains (i) $[Ru(bpy)_3]^{2+}$ (P) as one of its stoppers, (ii) a 4,4'-bipyridinium unit (A_1) and a 3,3'-dimethyl-4,4'-bipyridinium unit (A_2) as electron accepting stations, (iii) a *p*-terphenyl-type ring system as a rigid spacer (S), and (iv) a tetraarylmethane group as the second stopper (T). The structure of rotaxane $\mathbf{2}^{6+}$ was characterized by mass spectrometry and ^{1}H 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 was based on processes involving only the rotaxane components (intramolecular mechanism), while the other one required the help of external reactants (sacrificial mechanism).

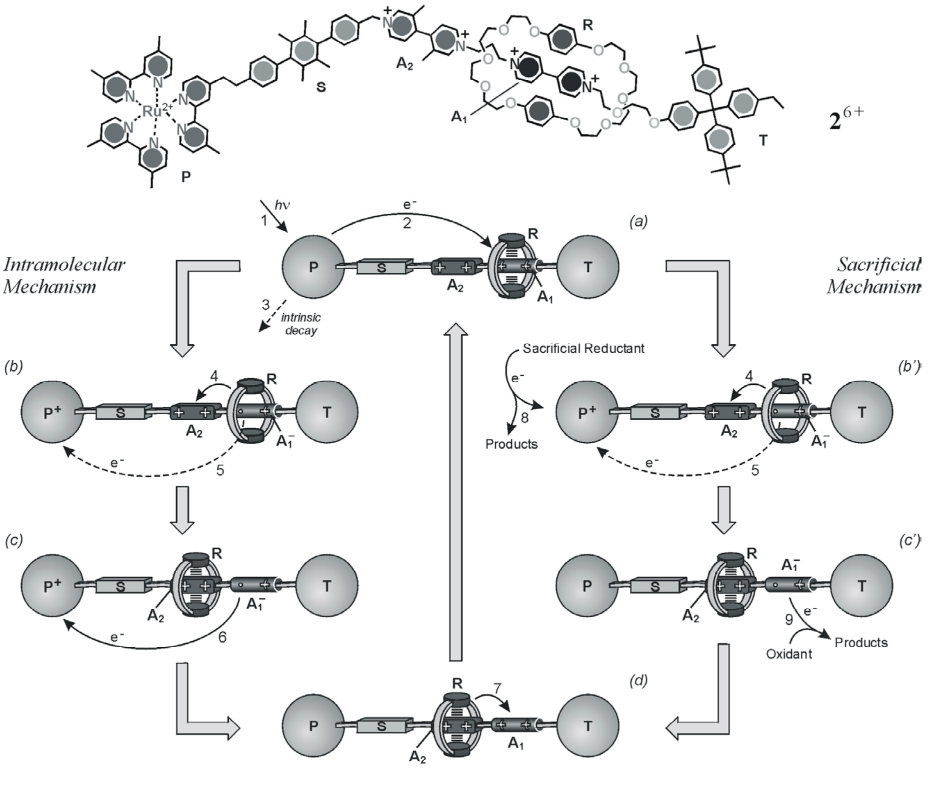


Figure 4. Structural formula of the rotaxane $\mathbf{2}^{6+}$ and schematic representation of the intramolecular (left) and sacrificial (right) mechanisms for the photoinduced shuttling movement of macrocycle R between the two stations A_1 and A_2

The intramolecular mechanism, illustrated in the left part of Figure 4, is based on the following four operations [26]:

(a) *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 P* (Step 3).

(b) *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.

(c) *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.

(d) *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 [26] do not indicate cleary whether the ring displacement (Step 4) is faster than the electronic reset of the system after light excitation (Step 5; $k= 2.4\times10^5\ s^{-1}$). More detailed laser flash photolysis studies suggest that these two processes could occur on the same time scale [27].

It is worthwhile noticing that in a system which behaves according to the intramolecular mechanism shown in Figure 4 (left) 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.

A less demanding mechanism is based on the use of external sacrificial reactants (a reductant like triethanolamine and an oxidant like dioxygen) that operate as illustrated in the right part of Figure 4:

(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 sacrificial reductant, a fast reaction of such species with P^+ (Step 8) competes successfully with the back electron-tranfer 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 O_2 (Step 9).

(d) *Nuclear reset*, as in the previous mechanism (Step 7).

The results obtained [26] 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. An alternative strategy is to use a non-sacrificial (reversible) reductant species that is regenerated after the back electron-transfer process [28].

4 Controlled ring rotation in catenanes

In a catenane, structural changes caused by rotation of one ring with respect to the other can be clearly evidenced when one of the two rings contains two non-equivalent units. In the catenane **3^{4+}** shown in Figure 5, the electron-acceptor tetracationic cyclophane is 'symmetric', whereas the other ring contains two different electron–

donor units, namely, a tetrathiafulvalene (TTF) and a 1,5-dioxynaphthalene (DON) unit [29].

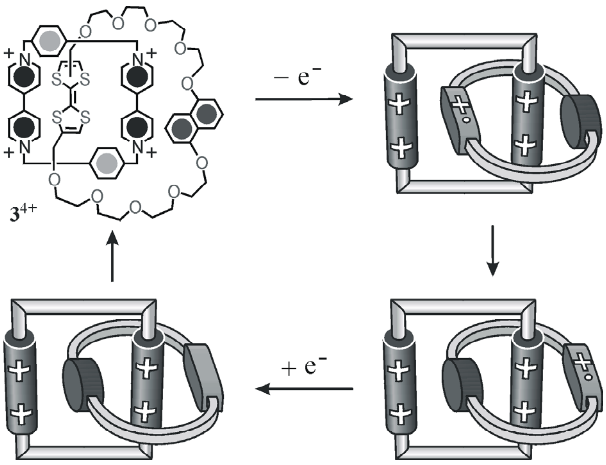
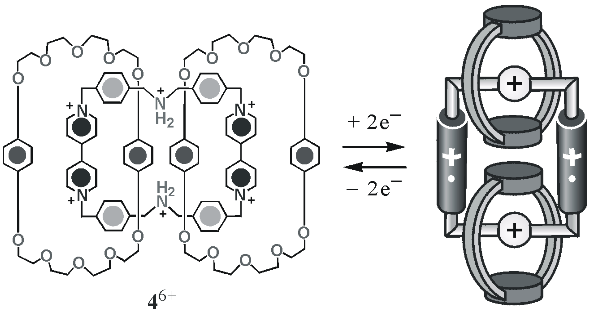


Figure 5. Redox controlled ring rotation in a catenane containing a non-symmetric ring

In a catenane structure, the electron donor located inside the cavity of the electron-acceptor ring experiences the effect of two electron-acceptor units, whereas the alongside electron donor experiences the effect of only one electron acceptor. Therefore, the better electron donor (i. e., TTF) enters the acceptor ring and the less good one (i.e., DON) remains alongside. On electrochemical oxidation, the first observed process concerns TTF, which thus loses its electron donating properties. Furthermore, an electrostatic repulsion arises between TTF^+ and the tetracationic macrocycle. These effects cause rotation of one ring to yield the translational isomer with the DON moiety positioned inside the acceptor ring. Upon reduction of TTF^+, the initial configuration is restored. However, this may happen without the occurrence of a *full* rotation, because it is equally probable that the reset caused by reduction of TTF^+ occurs by a reverse rotation compared to that occurred in the forward switching caused by TTF oxidation. In order to obtain a full rotation, i.e., a molecular-level rotary motor, the direction of each switching movement should be controllable. This goal can likely be reached by introducing appropriate functions in one of the two macrocycles [20,21]. When this goal is reached, it will be possible to convert alternate electrical potential energy into a molecular-level mechanical rotation.

Controlled rotation of the molecular rings has been achieved also in a catenane composed of three interlocked macrocycles ($\mathbf{4}^{6+}$, Figure 6) [30]. Upon addition of one electron in each of the bipyridinium units, the two macrocycles move on the ammonium stations, and move back to the original position when the bipyridinium units are reoxidized. Unidirectional ring rotation has recently been obtained [31] in a peptide-based catenane having the same topology as $\mathbf{4}^{6+}$.



4^{6+}

Figure 6. Redox controlled movements of the ring components upon reduction-oxidation of the bipyridinium units in a catenane composed of three interlocked macrocycles

5 Conclusion and perspectives

In the last few years, several examples of molecular machines and motors have been designed and constructed [17–20]. It should be noted, however, that the molecular-level machines described in this chapter operate in solution, that is, in an incoherent fashion. Although the solution studies of chemical systems as complex as molecular machines are of fundamental importance, it seems reasonable that, before functional supramolecular assemblies can find applications as machines at the molecular level, they have to be interfaced with the macroscopic world by ordering them in some way. The next generation of molecular machines and motors will need to be organized at interfaces [32], deposited on surfaces [33], or immobilized into membranes [16a,34] or porous materials [35] so that they can behave coherently. Indeed, the preparation of modified electrodes [22,36] represent one of the most promising ways to achieve this goal. Solid-state electronic devices based on functional rotaxanes and catenanes have already been developed [37]. Furthermore, addressing a single molecular-scale device by instruments working at the nanometer level is no longer a dream [13–15,38].

Apart from more or less futuristic applications, the extension of the concept of a machine to the molecular level is of interest not only for the development of nanotechnology, but also for the growth of basic research. Looking at supramolecular chemistry from the viewpoint of functions with references to devices of the macroscopic world is indeed a very interesting exercise which introduces novel concepts into Chemistry as a scientific discipline.

Acknowledgments

We would like to thank Prof. J. F. Stoddart and his group for a long lasting and most profitable collaboration. Financial support from EU (RT Network HPRN-CT-2000-00029 and STREP NMP2-CT-2003-505487), MIUR (Supramolecular Devices project and FIRB RBNE019H9K), and the University of Bologna (Funds for Selected Research Topics) is gratefully acknowledged.

References

1 (a) Keyes, R.W. Proc. IEEE 2001, 89, 227. (b) International Technology Roadmap for Semiconductors (ITRS), 2003 Edition, available at http://public.itrs.net

2 (a) Feynman, R.P. *Eng. Sci.* **1960**, *23*, 22. (b) Feynman, R.P. *Saturday Rev.* **1960**, *43*, 45. See also: http://www.its.caltech.edu/˜feynman

3 (a) Drexler, K.E. *Engines of Creation*, *The Coming Era of Nanotechnology*, Anchor Press, New York, 1986. (b) Drexler, K.E. *Nanosystems. Molecular Machinery, Manufacturing, and Computation*, Wiley, New York, 1992.

4 Smalley, R.E. *Sci. Am.* **2001**, *285*, 76.

5 Pedersen, C.J. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1021.

6 Cram, D.J. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1009.

7 Lehn, J.-M. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 89.

8 Joachim, C.; Launay, J.-P. *Nouv. J. Chem*. **1984**, *8*, 723.

9 Balzani, V.; Moggi, L.; Scandola, F. in *Supramolecular Photochemistry*, (Ed.: Balzani, V.), Reidel, Dordrecth, 1987, p. 1.

10 Lehn, J.-M. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1304.

11 (a) Aviram, A.; Ratner, M.A. *Chem. Phys. Lett.* **1974**, *29*, 277. (b) *Molecular Electronic Devices* (Ed.: Carter, F.L.), Dekker, New York, 1982. (c) *Molecular Electronic Devices II* (Ed.: Carter, F.L.), Dekker, New York, 1987. (d) *Molecular Electronic Devices* (Eds: Carter, F.L.; Siatkowski, R.E.; Wohltjen, H.), Elsevier, Amsterdam, 1988. (e) *Molecular Electronics - Science and Technology* (Ed.: Aviram, A.), Engeneering Foundation, New York, 1989. (f) Miller, J.S. *Adv. Mater.* **1990**, *2*, 378. (g) Miller, J.S. *Adv. Mater.* **1990**, *2*, 495. (h) Miller, J.S. *Adv. Mater.* **1990**, *2*, 603. (i) Metzger, R.M.; Panetta, C.A. *New J. Chem.* **1991**, *15*, 209. (j) Mirkin, C.A.; Ratner, M.A. *Annu. Rev. Phys. Chem.* **1992**, *43*, 719.

12 (a) Vögtle, F. *Supramolecular Chemistry. An Introduction*, Wiley, Chichester, 1991. (b) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*, Horwood, Chichester, 1991. (c) Lehn, J.-M. *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995.

13 (a) *Single Molecule Spectroscopy* (Eds.: Rigler, R.; Orrit, M.; Talence, I.; Basché, T.), Springer-Verlag, Berlin, 2001. (b) Moerner, W.E. *J. Phys. Chem. B* **2002**, *106*, 910. (c) *Single Molecule Detection in Solution* (Eds.: Zander, Ch.; Enderlein, J.; Keller, R.A.), Wiley-VCH, Weinheim, 2002.

14 (a) Gimzewski, J.K.; Joachim, C. *Science* **1999**, *283*, 1683. (b) Hla, S.-W.; Meyer, G.; Rieder, K.-H. *ChemPhysChem* **2001**, *2*, 361.

15 See, e.g.: Christ, T.; Kulzer, F.; Bordat, P.; Basché, T. *Angew. Chem. Int. Ed.* **2001**, *40*, 4192.

16 Structural and functional integration of motor proteins within artificial nanodevices has been obtained. For impressive examples, see: (a) Steinberg-Yfrach, G.; Rigaud, J.-L.; Durantini, E.N.; Moore, A.L.; Gust, D.; Moore, T.A. *Nature* **1998**, *392*, 479. (b) Soong, R.K.; Bachand, G.D.; Neves, H.P.; Olkhovets, A.G.; Craighead, H.G.; Montemagno, C.D. *Science* **2002**, *290*, 1555.

17 Balzani, V.; Credi, A.; Raymo, F.M.; Stoddart, J.F. *Angew. Chem. Int. Ed.* **2000**, *39*, 3348.

18 *Acc. Chem. Res.* **2001**, *34*, n. 6 (Special Issue on Molecular Machines; Guest Editor: Stoddart, J.F.).

19 *Struct. Bond.* **2001**, *99* (Special Volume on Molecular Machines and Motors; Guest Editor: Sauvage, J.-P.).

20 Balzani, V.; Credi, A.; Venturi, M. *Molecular Devices and Machines – A Journey into the Nano World*, Wiley-VCH, Weinheim, 2003.

21 (a) Ballardini, R.; Balzani, V.; Credi, A.; Gandolfi, M.T.; Venturi, M. *Acc. Chem. Res.* **2001**, *34*, 445. (b) Ballardini, R.; Balzani, V.; Credi, A.; Gandolfi, M.T.; Venturi, M. *Int. J. Photoenergy* **2001**, *3*, 63.

22 Kaifer, A.E.; Gómez-Kaifer, M. *Supramolecular Electrochemistry*, Wiley-VCH, Weinheim, 1999.

23 Balzani, V.; Credi, A.; Venturi, M. *ChemPhysChem* **2003**, *4*, 49.

24 *Molecular Catenanes, Rotaxanes and Knots* (Eds.: Sauvage, J.-P.; Dietrich-Buchecker, C.), Wiley-VCH, Weinheim, Germany, 1999.

25 Ashton, P.R.; Ballardini, R.; Balzani, V.; Baxter, I.; Credi, A.; Fyfe, M.C.T.; Gandolfi, M.T.; Gomez-Lopez, M.; Martinez-Diaz, M.V.; Piersanti, A.; Spencer, N.; Stoddart, J.F.; Venturi, M.; White, A.J.P.; Williams, D.J. *J. Am. Chem. Soc.* **1998**, *120*, 11932.

26 Ashton, P.R.; Ballardini, R.; Balzani, V.; Credi, A.; Dress, K.R.; Ishow, E.; Kleverlaan, C.J.; Kocian, O.; Preece, J.A.; Spencer, N.; Stoddart, J.F.; Venturi, M.; Wenger, S. *Chem. Eur. J.* **2000**, *6*, 3558.

27 Balzani, V.; Credi, A.; Ferrer, B.; Stoddart, J.F., unpublished results.

28 Brouwer, A.M.; Frochot, C.; Gatti, F.G.; Leigh, D.A.; Mottier, L.; Paolucci, F.; Roffia, S.; Wurpel, G.W.H. *Science* **2001**, *291*, 2124.

29 (a) Asakawa, M.; Ashton, P.R.; Balzani, V.; Credi, A.; Hamers, C.; Mattersteig, G.; Montalti, M.; Shipway, A.N.; Spencer, N.; Stoddart, J.F.; Tolley, M.S.; Venturi, M.; White, A.J.P.; Williams, D.J. *Angew. Chem. Int. Ed.* **1998**, *37*, 333. (b) Balzani, V.; Credi, A.; Mattersteig, G.; Matthews, O.A.; Raymo, F.M.; Stoddart, J.F.; Venturi, M.; White, A.J.P.; Williams, D.J *J. Org. Chem.* **2000**, *65*, 1924.

30 Ashton, P.R.; Baldoni, V.; Balzani, V.; Credi, A.; Hoffmann, H.D.A.; Martinez-Diaz, M.V.; Raymo, F.M.; Stoddart, J.F.; Venturi, M. *Chem. Eur. J.* **2001**, *7*, 3482.

31 Leigh, D.A.; Wong, J.K.Y.; Dehez, F.; Zerbetto, F. *Nature* **2003**, *424*, 174.

32 Recent examples: (a) Lynch, D.E.; Hamilton, D.G.; Calos, N.J.; Wood, B.; Sanders, J.K.M. *Langmuir* **1999**, *15*, 5600. (b) Brown, C.L.; Jonas, U.; Preece, J.A.; Ringsdorf, H.; Seitz, M.; Stoddart, J.F. *Langmuir* **2000**, *16*, 1924. (c) Asakawa, M.; Higuchi, M.; Mattersteig, G.; Nakamura, T.; Pease, A.R.; Raymo, F.M.; Shimizu, T.; Stoddart, J.F. *Adv. Mater.* **2000**, *12*, 1099. (d) Gonzalez-Gaitano, G.; Guerrero-Martinez, A.; Ortega, F.; Tardajos, G. *Langmuir* **2001**, *17*, 1392.

33 Recent examples: (a) Buey, J.; Swager, T.M. *Angew. Chem. Int. Ed.* **2000**, *39*, 608. (b) Kleverlaan, C.J.; Indelli, M.T.; Bignozzi, C.A.; Pavanin, L.; Scandola, F.; Hasselman, G.M.; Meyer, G.J. *J. Am. Chem. Soc.* **2000**, *122*, 2840. (c) Shipway, A. N.; Willner, I. *Acc. Chem. Res.* **2001**, *34*, 421. (d) Cavallini, M.; Lazzaroni, R.; Zamboni, R.; Biscarini, F.; Timpel, D.; Zerbetto, F.; Clarkson, G.J.; Leigh, D.A. *J. Phys. Chem. B* **2001**, *105*, 10826. (e) Samorì, P.; Jackel, F.; Unsal, O.; Godt, A.; Rabe, J.P. *ChemPhysChem* **2001**, *2*, 461. (f) Auletta, T.; van Veggel, F.C.J.M.; Reinhoudt, D.N. *Langmuir* **2002**, *18*, 1288. (f) Cavallini, M.; Biscarini, F.; Leon, S.; Zerbetto, F.; Bottari, G.; Leigh, D.A. *Science* **2003**, *299*, 531. (g) Long, B.; Nikitin, K.; Fitzmaurice, D. *J. Am. Chem. Soc.* **2003**, *125*, 5152.

34 (a) Steinberg-Yfrach, G.; Liddell, P.A.; Hung, S.-C.; Moore, A.L.; Gust, D.; Moore, T.A. *Nature* **1997**, *385*, 239. (b) Gust, D.; Moore, T.A.; Moore, A.L. *Acc. Chem. Res.* **2001**, *34*, 40. (c) Bennett, I.M.; Farfano, H.M.V.; Bogani, F.; Primak, A.; Liddell, P.A.; Otero, L.; Sereno, L.; Silber, J.J.; Moore, A.L.; Moore T.A.; Gust, D. *Nature* **2002**, *420*, 398.

35 (a) Chia, S.; Cao, J.; Stoddart, J.F.; Zink, J.I. *Angew. Chem. Int. Ed.* **2001**, *40*, 2447. (b) Álvaro, M.; Ferrer, B.; García, H.; Palomares, E.J.; Balzani, V.; Credi, A.; Venturi, M.; Stoddart, J. F.; Wenger, S. *J. Phys. Chem. B* **2003**, *107*, 14319.

36 Recent examples of threaded and interlocked molecular systems supported on solid electrodes: (a) Willner, I.; Pardo-Yissar, V.; Katz, E.; Ranjit, K.T. *J. Electroanal. Chem.* **2001**, *497*, 172. (b) Herranz, M.A.; Colonna, B.; Echegoyen, L. *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 5040. (c) Raehm, L.; Kern, J.-M.; Sauvage, J.-P.; Hamann, C.; Palacin, S.; Bourgoin, J.-P. *Chem. Eur. J.* **2002**, *8*, 2153. (d) Bryce, M.R.; Cooke, G.; Duclairoir, F.M.A.; John, P.; Perepichka, D.F.; Polwart, N.; Rotello, V.M.; Stoddart, J.F.; Tseng, H.-R. *J. Mater. Chem.* **2003**, *13*, 2111.

37 (a) Collier, C.P.; Wong, E.W.; Belohradsky, M.; Raymo, F.M.; Stoddart, J.F.; Kuekes, P.J.; Williams, R.S.; Heath, J.R. *Science* **1999**, *285*, 391. (b) Collier, C.P.; Mattersteig, G.; Wong, E.W.; Luo, Y.; Beverly, K.; Sampaio, J.; Raymo, F.M.; Stoddart, J.F.; Heath, J.R. *Science* **2000**, *289*, 1172. (c) Luo, Y.; Collier, C.P.; Jeppesen, J.O.; Nielsen, K.A.; DeIonno, E.; Ho, G.; Perkins, J.; Tseng, H.-R.; Yamamoto, T.; Stoddart, J.F.; Heath, J.R. *ChemPhysChem* **2002**, *3*, 519. (h) Diehl, M.R.; Steuerman, D.W.; Tseng, H.-R.; Vignon, S.A.; Star, A.; Celestre, P.C.; Stoddart, J.F.; Heath, J.R. *ChemPhysChem* **2003**, *4*, 1335.

38 Metzger, R.M. *Chem. Rev.* **2003**, *103*, 3803.