



MATERIALE	AL 2024	HS/EP	HS/EP + 5% CN
MODULO DI YOUNG [Pa]	70E9	12E10	16E10
MASSA [Kg]	206.3	84.1	69.7

Tab.6.1. massa della struttura al variare del materiale

Il passaggio dalla lega di alluminio al composito Hs/Ep fornisce una notevole riduzione della massa M. L'uso dei carbon nanotubes permette, almeno dal punto di vista numerico, di ridurre ulteriormente il peso. Successivamente è stato realizzato un prototipo piano (fig. 6.2) in composito utile per studiare i processi di fabbricazione di elementi anisogrid con dimensioni maggiori e geometrie più complesse.

Il composito è costituito da:

- resina epossidica
- indurente
- fibre di vetro
- polvere nanometrica contenente carbon nanotubes

Il dimostratore ha evidenziato un ottimo comportamento alle sollecitazioni meccaniche.

Per rendere il processo più industriale e migliorare le caratteristiche dell'elemento stesso, è necessario realizzare uno stampo che sia flessibile, facilmente estraibile e riutilizzabile. La tecnica impiegata è quella della prototipazione rapida con la quale costruire il contro stampo da cui si ricava lo stampo in silicone (fig. 6.3).

Sono stati realizzati anche degli stampi a geometria lattice anisogrid cilindrica che opportunamente dimensionata può trovare utile applicazione in molti settori dell'aerospazio.

## 7. Conclusioni

Con il presente lavoro sono state descritte le attività di ricerca riguardanti la sintesi, la purificazione e la caratterizzazione morfologica dei nanotubi in carbonio e come disperderli in una matrice polimerica. Inoltre, è stato dimostrato come l'uso di CN permetta, almeno dal punto di vista teorico, di ridurre la massa di una struttura aerospaziale. Le nanotecnologie e i materiali compositi possono avere un profondo sviluppo e applicazione in molti settori dell'Ingegneria. È necessario implementare tutti i processi in modo da rendere questo tipo di tecnologia competitiva in termini tecnico/economici.

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# Artificial molecular machines and motors

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## Foreword

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 [xviii].

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 [xx].

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 machines [point (v)] can range from microseconds to seconds, depending on the type of rearrangement and the nature of the components involved.

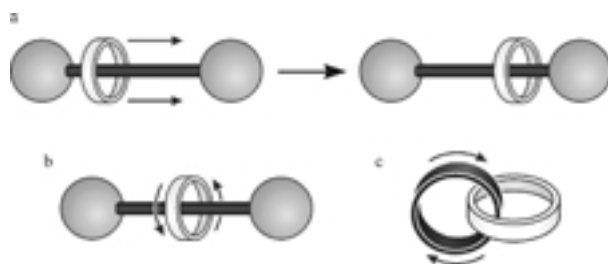
Finally, as far as point (vi) is concerned, the functions that can be performed by exploiting the movements of the component parts in molecular machines are various and, to a large extent, still unpredictable. It is worth to note that the mechanical movements taking place in molecular-level machines, 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 [xx]. 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 [xxiv] 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)



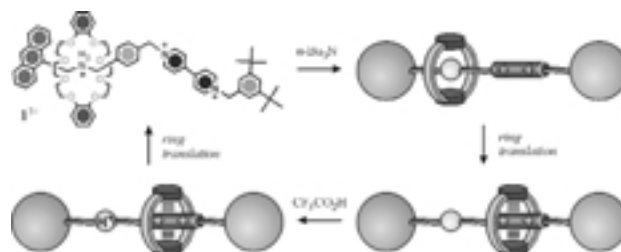
**Figure 2.** Schematic representation of some of the intercomponent motions that can be obtained with rotaxanes and catenanes: shuttling (a) and ring rotation (b, c)

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/hydrophilic character, p-p 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 **1<sup>3+</sup>** 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<sup>+</sup>-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 <sup>1</sup>H nuclear magnetic resonance (NMR) spectroscopy and by electrochemical and photophysical measurements [xxv]. 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 in-

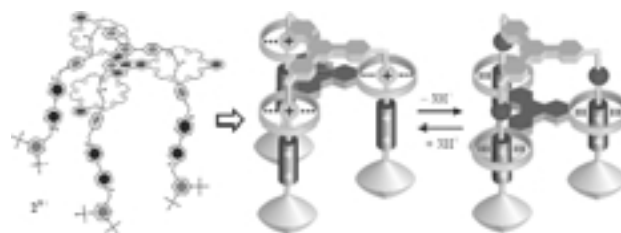
duced by two different types of stimuli (acid-base and electron-hole).



**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 molecular elevator

By incorporating the architectural features of the acid-base switchable rotaxane **1<sup>3+</sup>** (Figure 3) [xxv] into those of a recently investigated triply threaded two-component supramolecular bundle [26], we came up with the design of the molecular elevator **2<sup>3+</sup>** shown in Figure 4 [27]. This nanoactuator, which is ca. 2.5 nm in height and has a diameter of ca. 3.5 nm, consists of a trifurcated rig-like component containing two different notches – one ammonium center and one bipyridinium unit – at different levels in each of its three legs. The latter are interlocked by a tritopic host made up of three DB24C8-type macrocycles fused trigonally to a central aromatic floor; such a platform can be made to stop at the two different levels. The three legs of the rig carry bulky feet that prevent the loss of the platform. Compound **2<sup>3+</sup>** was synthesized using a template-directed protocol from a trifurcated guest and the tritopic host which form a 1:1 adduct (superbundle) that can be converted into a mechanically interlocked elevator by functionalization of the ends of each leg with bulky 3,5-di-*tert*-butylbenzyl groups.



**Figure 4.** Chemical formula and operation scheme of the molecular elevator **29<sup>+</sup>**

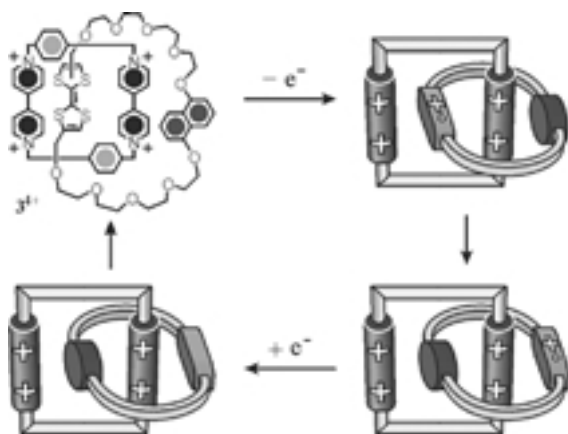
Initially, the platform resides exclusively on the “upper” level, i.e., with the three macrocycles surrounding the ammonium centers. This preference results from strong N<sup>+</sup>-H...O hydrogen bonding and weak stabilizing p-p stacking forces between the aromatic cores of the platform and rig components. Upon addition of a strong, non-nucleophilic phosphazene base to an acetonitrile solution of **2<sup>3+</sup>**, deprotonation of the ammonium center occurs and, as a result, the platform moves to the “lower” level, that is, with the

three macrocycles surrounding the bipyridinium units (Figure 4). This structure is stabilized by electron donor-acceptor interactions between the electron-rich aromatic units of the platform and the electron-deficient bipyridinium units of the rig component. Subsequent addition of acid restores the ammonium centers, and the platform moves back to the "upper" level (Figure 4). The elevator motion, which can be followed by  $^1\text{H}$  NMR spectroscopy, electrochemistry, and absorption and fluorescence spectroscopy, is quantitative and can be repeated many times on the same solution [xxvii]. The distance travelled by the platform is about 0.7 nm, and from thermodynamic considerations we estimate that the elevator movement from the upper to lower level can potentially generate a force of up to 200 pN – one order of magnitude higher than that developed by natural linear motors such as myosin and kinesin [28].

It should be noted that the acid-base controlled mechanical motion in  $2^{3+}$  can lead to other interesting functions, e.g., the opening and closing of a large cavity, and the control of the positions and properties of the bipyridinium legs. These findings confirm that, by employing an incremental design strategy and a bottom-up template-directed synthetic protocol, it is possible to produce multivalent compounds capable of performing non-trivial mechanical movements and exercising a variety of different functions upon external stimulation.

#### 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].

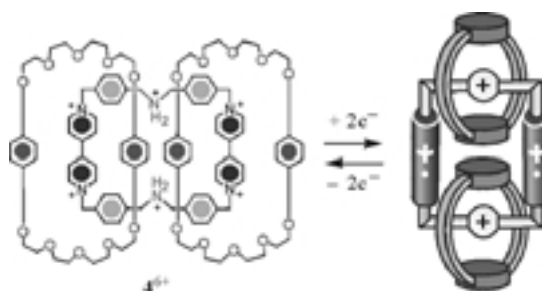


**Figure 5.** Redox controlled ring rotation in a catenane containing a non-symmetric ring

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 bet-

ter 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  $\text{TTF}^+$  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  $\text{TTF}^+$ , 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  $\text{TTF}^+$  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 [xx,xxi]. 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 ( $4^{6+}$ , 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  $4^{6+}$ .



**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 [xvii–xx]. 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 [xviii,34] or porous materials [35] so that they can behave coherently. Indeed, the preparation of



modified electrodes [xxii,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 [xiii-xv,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.

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