

Bottom-up approach to Nanotechnology

"Crowned"
Fe porphyrin



Metal
chelate



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 mold

Primo Levi

Lariat ether



Cryptate



Sculptures by Vizi Béla

The Bottom-Up Approach to Molecular-Level Devices and Machines

Vincenzo Balzani,* Alberto Credi, and Margherita Venturi^[a]

Abstract: The macroscopic concepts of a device and a machine can be extended to the molecular level. Molecular-level devices and machines are constructed by a bottom-up approach. The atom-by-atom bottom-up approach is unrealistic from the chemical viewpoint. The bottom-up approach molecule-by-molecule following the guidelines of supramolecular (multicomponent) chemistry has proved to be successful. 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: chemistry and art • miniaturization • molecular devices • molecular machines • nanotechnology • supramolecular chemistry

“Ma siamo sempre dei ciechi, anche nel caso migliore, cioè che la struttura sia semplice e stabile: ciechi, e non abbiamo quelle pinzette che sovente ci capita di sognare di notte, come uno che ha sete sogna le sorgenti, e che ci permetterebbero di prendere un segmento, di tenerlo ben stretto e diritto, e di incollarlo nel verso giusto sul segmento che è già montato. Se quelle pinzette le avessimo (e non è detto che un giorno non le avremo) saremmo già riusciti a fare delle cose graziose che fin adesso le ha fatte solo il Padreterno, per esempio a montare non dico un ranocchietto o una libellula, ma almeno un microbo o il semino di una muffa”.

P. Levi, *La Chiave a Stella*, Einaudi, Torino, 1978, p. 151

“But we are still blind, even in the best circumstances, that is, with structures that are simple and stable. Blind, and 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 mold”.

P. Levi, *The Monkey's Wrench*, Penguin Books, New York, 1995, p. 144.

Introduction

A device is something invented and constructed for a special purpose and a machine is any combination of mechanisms for utilizing, modifying, applying, or transmitting energy, whether simple or complex.^[1] In everyday life we make extensive use of macroscopic 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 hairdryer (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 straightforwardly extended to the molecular level.^[2] A *molecular-level device* can be defined as an assembly of a discrete number of molecular components (i.e., a supramolecular structure, vide infra) 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-level machine* is a particular type of molecular-level device in which the component parts can display changes in their relative positions as a result of some external stimulus.^[3] Molecular-level devices and machines operate through 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.^[3–8]

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The Race towards Miniaturization

The progress of civilization has always been related to the construction of novel devices and machines. In the last fifty years, a great variety of new devices and machines for collecting, processing, displaying, and storing information have come into use. The outstanding development of information technology has been strictly related to the progressive miniaturization of the components employed for the construction of such devices and machines. The first electronic computer was made of 18 000 valves, weighed 30 tons, occupied an entire room, and lasted an average of 5.6 hours between repairs.^[9] A state-of-the-art microprocessor today has more than 40 million transistors, a number that is destined to increase in the future. One can wonder whether we do really need to keep on making things smaller. The answer is that further miniaturization will not only decrease the size and increase the power of computers, but is also expected to open the way to new technologies capable of revolutionizing medicine, producing a wealth of new materials providing renewable energy sources, and solving the problem of environmental pollution.^[8]

Large-Downward (Top-Down) Approach

The miniaturization of components for the construction of useful devices and machines is currently pursued by the large-downward (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. In 1965 G. E. Moore^[10] predicted that every three years 1) device size would reduce by 33 %, 2) chip size would increase by 50 %, and 3) the number of components on a chip would quadruple. Such a prediction has been fulfilled until now and the potentiality of laser techniques in the top-down approach to miniaturization has also been exploited for construction of microelectromechanical systems (MEMS).^[11] An example of the definition that can be reached by the top-down approach is given by the fine features of the bull shown in Figure 1, which was crafted by two-photon photopolymerization.^[12] It is becoming increasingly apparent, however, that today's computer technology, which relies on silicon-based chips, is rapidly approaching the limits of its physical capabilities.^[13, 14] In particular, photolithography is subjected to drastic limitations for dimensions smaller than 100 nanometers. 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 (tenths of nanometers) and molecules (nanometers). Therefore, "there is plenty of room at the bottom" for further miniaturization, as Richard P. Feynman^[15] 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. To proceed towards further miniaturization, science and technology will have to find new ways.

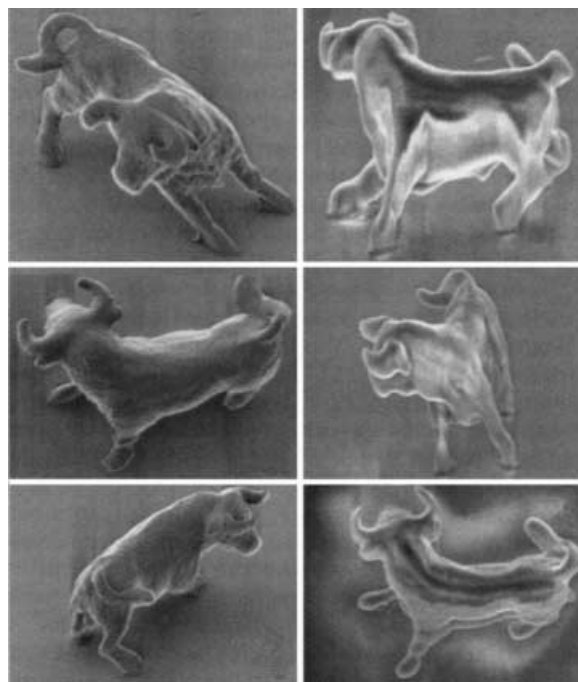


Figure 1. Scanning electron micrographs of bull sculptures crafted on a resin by two-photon photopolymerization, showing the definition reached by top-down miniaturization. These sculptures are 10 μm long and 7 μm high, and are about the size of a red blood cell. Reproduced by permission from Reference [12].

Small-Upward (Bottom-Up) Approach

An alternative and promising strategy towards technology at the nanometer scale is offered by the small-upward (bottom-up) approach, which starts from atom or molecules and builds up to nanostructures. Chemists, by the nature of their discipline, are already at the bottom, since they are able to manipulate atoms and molecules. Therefore they are in the ideal position to develop bottom-up strategies for the construction of nanoscale devices and machines.

The bottom-up approach to nanotechnology is relatively new. Until a few decades ago, in fact, nanotechnology was not considered an obtainable objective by physicists.^[7] The dominant idea, derived from quantum theory,^[16] was that atoms are fuzzy entities that "must no longer be regarded as identifiable individuals",^[17] and "form a world of potentialities or possibilities rather than one of things or facts".^[18] From the point of view of quantum theory, molecular structure is not an intrinsic property,^[19] but a metaphor.^[20] Such ideas, of course, were never shared by chemists who had long before established^[21] that atoms are material and reliable building blocks for constructing molecules and that molecules have well-defined sizes and shapes.^[22] This concept has been beautifully presented by a great chemist and writer, Primo Levi, in his book "La Chiave a Stella":^[23] "*Il mio mestiere vero, quello che ho studiato a scuola e che mi ha dato da vivere fino ad oggi, è il mestiere del chimico. Non so se lei ne ha un'idea chiara, ma assomiglia un poco al suo: solo che noi montiamo e smontiamo delle costruzioni molto piccole. Ci dividiamo in due rami principali, quelli che montano e quelli che smontano,*

e gli uni e gli altri siamo come dei ciechi con le dita sensibili. Dico come dei ciechi, perché appunto, le cose che noi manipoliamo sono troppo piccole per essere viste, anche coi microscopi più potenti; e allora abbiamo inventato diversi trucchi intelligenti per riconoscerle senza vederle.” “Quelli che smontano, cioè i chimici analisti, devono essere capaci di smontare una struttura pezzo per pezzo senza danneggiarla, o almeno senza danneggiarla troppo; di allineare i pezzi smontati sul bancone, sempre senza vederli, di riconoscerli uno per uno, e poi di dire in che ordine erano attaccati insieme.”

The idea that atoms could be used to construct nanoscale machines was first raised by R. P. Feynman, in the previously mentioned address “There is Plenty of Room at the Bottom” to the American Physical Society in 1959.^[15] The key sentence of Feynman’s talk is the following: “The principle of physics do not speak against the possibility of maneuvering things atom by atom”. As we will see below, however, chemists do not believe to the possibility of realizing an atom-by-atom approach to nanostructures.

Bottom-up atom-by-atom: The idea of constructing nanoscale devices “atom-by-atom” was depicted in an exciting and visionary way in middle eighties by K. E. Drexler.^[24] Later on he exposed his ideas on nanosystems and molecular manufacturing in a more scientific (essentially theoretical) way.^[25, 26] He proposed, and still maintains,^[27] the possibility of constructing a general-purpose building nanodevice, nicknamed as an *assembler*. Such a nanorobot could, in principle, build almost anything, including copies of itself, by atomic-scale “pick-and-place”: a set of nanoscale pincers would pick individual atoms from their environment and place them where they would serve as a part of some active or structural component. Such a technology would revolutionize manufacturing, allowing, for example, the low-cost, pollution-free construction of lightweight and extremely strong materials that, in their turn, would revolutionize transportation (in particular, space transportation). Even more exciting, medical nanorobots (e.g., nanoscale submarines capable of navigating through the blood) have been envisioned that would be able to repair the human body by destroying viruses and cancer cells, reconstructing damaged structures, removing accumulated waste from the brain, and bringing the body back to a state of youthful health.^[28] According to Drexler,^[24, 27] the potential of nanotechnology has also a dark side that should already be taken into serious consideration by responsible governments. The outstanding potentiality of nanotechnology could, in fact, be exploited by aggressive nations, terrorist groups, or even individuals for bad purposes, with much more danger than that caused by chemical and biological weapons. Furthermore, the prospect has been raised that the potential for self-replication of the assemblers could escape human control leading to myriads of copies of themselves that, at the end, would ravage the earth. An even more frightening possibility would be that such self-replicating nanorobots would, by design or random mutation, develop the ability to communicate with one another and evolve, step by step, until they become “alive” and create an artificial society that, at best, would not need us.

The fascinating but, admittedly, abstract ideas of Drexler^[24–28] about the construction, futuristic use, and frightening potential of nanomachines have been skeptically and ironically commented by a large part of the scientific community.^[29–32] In particular, the concept of an assembler, that is, of a nanorobot that can manipulate and build things atom by atom, is considered unrealistic for at least two well-grounded reasons:^[31, 32] 1) the fingers of a hypothetical manipulator arm should themselves be made out of atoms, which implies that they would be too fat to have control of the chemistry in the nanometer region; 2) such fingers would also be too sticky: the atoms of the manipulator hands will adhere to the atom that is being moved, so that it will be impossible to place it in the desired position. In more general terms, the idea of the “atom-by-atom” bottom-up approach to nanotechnology, which seems so appealing to physicists, does 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 that atoms are not simple balls that can be moved from a place to another place at will. Atoms do not stay isolated; they bond strongly to their neighbors, and it is difficult to imagine that the atoms constituting the nanomanipulator fingers could take an atom from a starting material and transfer it to another material. Thinking that such assemblers can really work is tantamount to ignore the complexity and subtlety of bond-breaking and bond-making processes.

It should be recognized, however, that Drexler’s visionary ideas have had at least the merit to draw the attention of people on science and to influence genuine scientists to direct their research projects towards the fascinating world of nanotechnology.

Bottom-up molecule-by-molecule: In the late 1970’s 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,^[33] D. J. Cram,^[34] and J.-M. Lehn^[35] in 1987. In the same period, research on molecular electronic devices began to flourish.^[36] In the frame of research on supramolecular chemistry, the idea began to arise in a few laboratories^[35, 37–39] 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 as follows: 1) molecules are stable species, whereas atoms are difficult to handle; 2) nature starts from molecules, not from atoms, to construct the great number and variety of nanodevices and nanomachines that sustain life; 3) most of the laboratory chemical processes deal with molecules, not with atoms; 4) 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); and 5) molecules can self-assemble or can be connected to make larger structures.

In the following years supramolecular chemistry grew very rapidly,^[40–44] and it became clear that the supramolecular “bottom-up” approach opens virtually unlimited possibilities concerning design and construction of artificial molecular-level devices and machines. Furthermore, it became more and

more evident that such an approach can give invaluable contributions to better understand the molecular-level aspects of the extremely complicated devices and machines that are responsible for the biological processes.^[45]

It should not be forgotten that the development of the supramolecular bottom-up approach towards the construction of nanodevices and nanomachines was made possible by the high degree of knowledge reached in other fields of chemistry. Particularly important, in this regard, have been the contributions given by organic synthesis, which supplied a variety of building blocks, and of photochemistry,^[38, 41, 46] which offered the way to investigate the early examples of molecular-level devices and machines (e.g., light-controlled molecular-level tweezers,^[47] triads for vectorial charge separation,^[48] and light-harvesting antennae^[49]).

It should also be recalled that in the last few years 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”^[50] or “manipulating”^[51] single molecules. It has been possible, for example, to make ordered arrays of molecules (e.g., to write words^[52] and numbers^[51] by aligning single molecules in the desired pattern) and even to investigate bimolecular chemical reactions at the single molecule level.^[53]

Supramolecular (Multicomponent) Chemistry

Supramolecular chemistry is a highly interdisciplinary field that has developed at an astonishingly fast rate during the last two decades.^[40–44, 54] In a historical perspective, as pointed out by J.-M. Lehn,^[55] supramolecular chemistry originated from Paul Ehrlich’s receptor idea, Alfred Werner’s coordination chemistry, and Emil Fischer’s lock-and-key image. It was only in the 1970’s, however, that some fundamental concepts such as molecular recognition, preorganization, self-assembly, etc., were introduced and supramolecular chemistry began to emerge as a discipline.

The most authoritative and widely accepted definition of supramolecular chemistry is that given by J.-M. Lehn, namely “the chemistry beyond the molecule, bearing on organized entities of higher complexity that result from the association of two or more chemical species held together by intermolecular forces”.^[35, 40] As it is often the case, however, problems arise as soon as a definition is established; for example^[54] the definition of organometallic chemistry as “the chemistry of compounds with metal-to-carbon bonds” rules out Wilkinson’s compound, $[\text{RhCl}(\text{PPh}_3)_3]$, which is perhaps the most important catalyst for organometallic reactions.

A first problem presented by the above-mentioned classical definition of supramolecular chemistry concerns whether or not metal–ligand bonds can be considered intermolecular forces. If yes, complexes like $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy = 2,2'-bipyridine), that are usually considered molecules,^[56] should be defined as supramolecular species; if not, systems like the $[\text{Eu} \subset \text{bpy}.\text{bpy}.\text{bpy}]^{3+}$ cryptate, that are usually considered

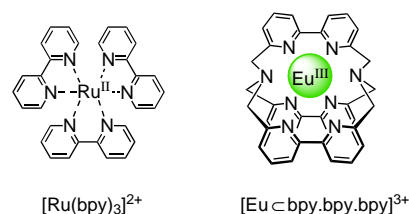


Figure 2. $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Eu} \subset \text{bpy}.\text{bpy}.\text{bpy}]^{3+}$: molecular or supramolecular species?

supramolecular antenna devices,^[57] should, in fact, be defined as molecules (Figure 2).

There is, however, a more general problem. Broadly speaking, one can say that with supramolecular chemistry there has been a change in focus from molecules to molecular assemblies or multicomponent systems. According to the original definition when the components of a chemical system are linked by covalent bonds, the system should not be considered a supramolecular species, but a molecule. This point is particularly important in dealing with molecular-level devices and machines, that are usually multicomponent systems in which the components can be linked by chemical bonds of various nature.

Consider, for example, the three systems^[58] shown in Figure 3 that play the role of molecular-level charge-separation devices. In each of them, two components, a Zn^{II} –porphyrin and a Fe^{III} –porphyrin, can be immediately singled out. In **1**, these two components are linked by a hydrogen-bonded bridge, that is, by intermolecular forces, whereas in **2** and **3** they are linked by covalent bonds. According to the above-reported classical definition of supramolecular chemistry, **1** is a supramolecular species, whereas **2** and **3** are (large) molecules. In each of the three systems, the two components substantially maintain their intrinsic properties and, upon

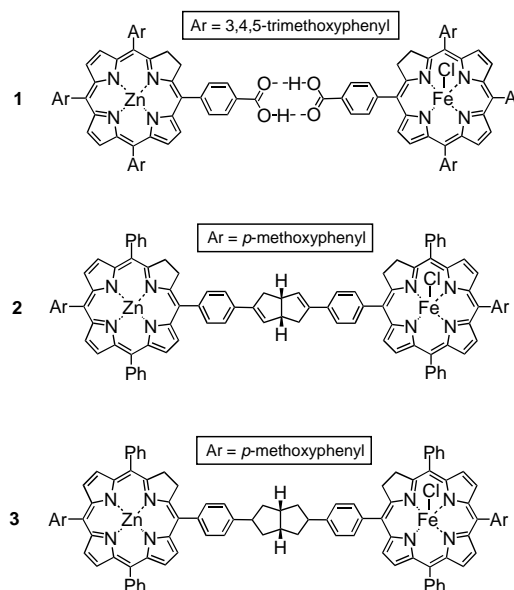


Figure 3. Three dyads that possess Zn^{II} –porphyrin and Fe^{III} –porphyrin units linked by an H-bonded bridge (**1**), a partially unsaturated bridge (**2**), and a saturated bridge (**3**):^[58] molecular or supramolecular species?

light excitation, electron transfer takes place from the Zn^{II} -porphyrin unit to the Fe^{III} -porphyrin one. The values of the rate constants for photoinduced electron transfer ($k_{\text{et}} = 8.1 \times 10^9$, 8.8×10^9 , and $4.3 \times 10^9 \text{ s}^{-1}$ for **1**, **2**, and **3**, respectively) show that the electronic interaction between the two components in **1** is comparable to that in **2**, and is even stronger than that in **3**. Clearly, as far as photoinduced electron transfer is concerned, it would sound strange to say that **1** is a supramolecular species, and **2** and **3** are molecules.

Another example of difficulty in applying the original definition of supramolecular chemistry is encountered with pseudorotaxanes and rotaxanes (Figure 4).^[59] A pseudorotaxane, for example, **4**⁴⁺, as any other type of adduct, can be clearly defined a supramolecular species, whereas a rotaxane, for example, **5**⁴⁺ (and even a catenane, e.g., **6**⁴⁺), in spite of the fact that they are more complex species than pseudorotaxanes, should be called molecules according to the classical definition.

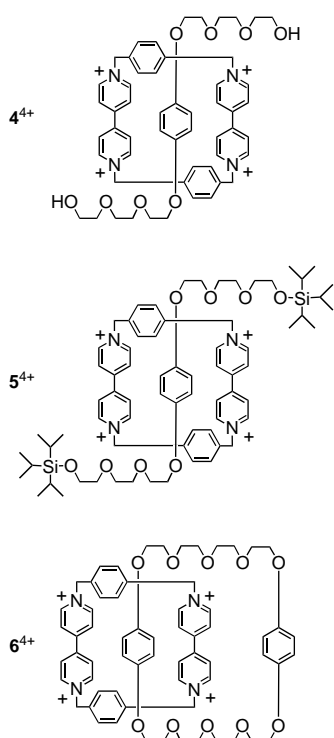


Figure 4. Pseudorotaxane (**4**⁴⁺), rotaxane (**5**⁴⁺), and catenane (**6**⁴⁺):^[59] molecular or supramolecular species?

We conclude that the classical definition of supramolecular chemistry as “the chemistry beyond the molecule” is quite useful, but, from the functional viewpoint, the distinction between what is molecular and what is supramolecular should be better based on other grounds, rather than on the nature of the bonds that link the components.

Large molecules versus supramolecular (multicomponent) systems: It has been proposed,^[41, 60, 61] and is now widely accepted,^[54i,j, 62–64] that, in the case of chemical systems which are investigated from the viewpoint of the effects caused by external stimulations, the definition of supramolecular species

can be based on the degree of intercomponent electronic interactions. This concept is illustrated, for example, in Figure 5. In the case of a photochemical stimulation, a system $A \sim B$, consisting of two units (\sim indicates any type of “bond”

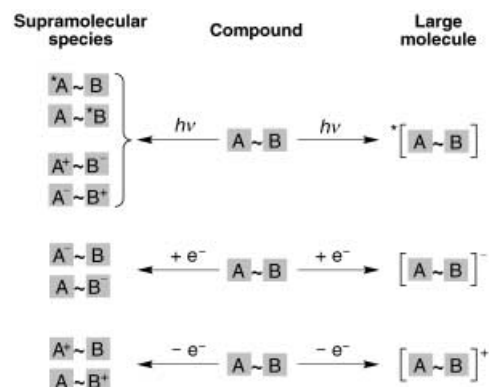


Figure 5. Schematic representation of the difference between a supramolecular system and a large molecule based on the effects caused by a photon or an electron input.^[61]

that keeps the units together), can be defined a supramolecular species if light absorption leads to excited states that are substantially localized on either A or B, or causes an electron transfer from A to B (or vice versa). By contrast, when the excited states are substantially delocalized on the entire system, the species can be better considered as a large molecule. Similarly (Figure 5),^[61] oxidation and reduction of a supramolecular species can substantially be described as oxidation and reduction of specific units, whereas oxidation and reduction of a large molecule leads to species in which the hole or the electron are delocalized on the entire system. In more general terms, when the interaction energy between units is small compared to the other relevant energy parameters, a system can be considered a supramolecular species, regardless of the nature of the bonds that link the units. Therefore, species made of covalently-linked (but weakly interacting) components, such as **2** and **3** shown in Figure 3, and **5**⁴⁺ and **6**⁴⁺ in Figure 4, can be taken as belonging to the supramolecular domain when they are stimulated by photons or electrons. It can be noted that the properties of each component of a supramolecular species, that is, of an assembly of weakly interacting molecular components, can be known from the study of the isolated components or of suitable model molecules.

Self-organization and covalent synthetic design: Self-assembly and self-organization^[40, 65] are dominant processes in the chemistry of living biological systems.^[45] For example, light-harvesting antennae of bacterial photosynthesis are formed by self-assembling and self-organization of a great number of molecular components.^[66] It is indeed amazing how nature is capable of mastering weak intermolecular forces to construct supramolecular devices and machines.^[45, 66–68] Construction of *artificial* supramolecular structures by self-organization needs suitably programmed^[40, 43, 44, 54m] molecular components and

full control of all the weak intermolecular forces (including solute–solvent interactions) involved in the thermodynamically driven formation of the desired system. This difficult task can be successfully fulfilled by careful chemical design of the molecular components. Several supramolecular structures (e.g., helicates,^[69] grids,^[70] capsules,^[71] molecular polyedra^[72]) have indeed been obtained by self-association and self-organization of artificial molecular components. The construction of artificial supramolecular devices and machines by self-assembling and self-organization, however, is a much more difficult task, since the various molecular components have to be programmed not only for their self-assembling into a structurally organized system, but also for their functional integration, as required by the operation that the device or the machine is expected to perform. Furthermore, supramolecular systems based on weak interactions are fragile, since they can be easily disassembled by external perturbations (e.g., change of solvent, change of pH); although this property can be exploited for obtaining particular functions,^[73] in most cases the device or machine should not undergo disassembly. Therefore, artificial devices and machines are often constructed by following a design based on covalent interconnecting bonds by using the powerful strategies and techniques of modern synthetic chemistry.^[74]

Supramolecular chemistry, art, and nanotechnology: As mentioned above, the chemical, molecule-by-molecule “bottom-up” approach opens virtually unlimited possibilities concerning design and construction of supramolecular species of nanoscale dimensions. Leonardo da Vinci did not know chemistry; nevertheless, his comment^[75] “... dove la Natura finisce di produrre le sue spezie, l'uomo quivi comincia con le cose naturali, con l'aiutorio di essa Natura, a creare infinite spezie ...” is quite appropriate for the outstanding development of artificial supramolecular chemistry.^[40]

In several cases, supramolecular species have fascinating shapes^[76] that recall those of macroscopic objects and structures encountered in everyday life. Some examples of aesthetically appealing supramolecular species are shown in Figures 6 and 7.^[77] As Primo Levi noticed,^[78] “*Infatti, accade anche in chimica, come in architettura, che gli edifici, 'belli' e cioè simmetrici e semplici, siano anche i più saldi: avviene insomma per le molecole come per le cupole delle cattedrali o per le arcate dei ponti.*” Interestingly, while chemists build up supramolecular systems that mimic macroscopic works of art (Figure 8),^[79] artists begin to take supramolecular compounds as models for creating beautiful sculptures (Figure 9).^[80]

The concepts of supramolecular (multicomponent) chemistry can be profitably used to design and construct a great variety of artificial compounds capable of performing potentially useful functions, namely 1) compounds for transfer, transport, and collection of electrons or electronic energy; 2) multistate/multifunctional systems; and 3) compounds capable of performing mechanical movements (machines). Looking at supramolecular chemistry from the viewpoint of functions with references to devices and machines of the macroscopic world is indeed a very interesting exercise that introduces novel concepts, injects daring ideas, and stimulates creativity in the fields of chemistry and nanotechnology.^[81]

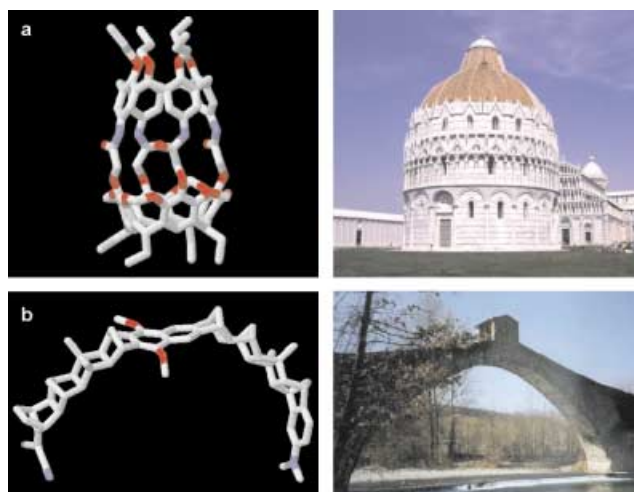


Figure 6. Molecular architecture: two fascinating nanometer-scale supramolecular species and the corresponding macroscopic counterparts. a) A resorcarene-calixarene carcerand^[77a] and the Battistero of Pisa (Italy); b) a norbornylogous-type compound^[77b] and the Olina medieval bridge, Modena (Italy). The geometries of the molecules are constructed by molecular mechanics calculations.

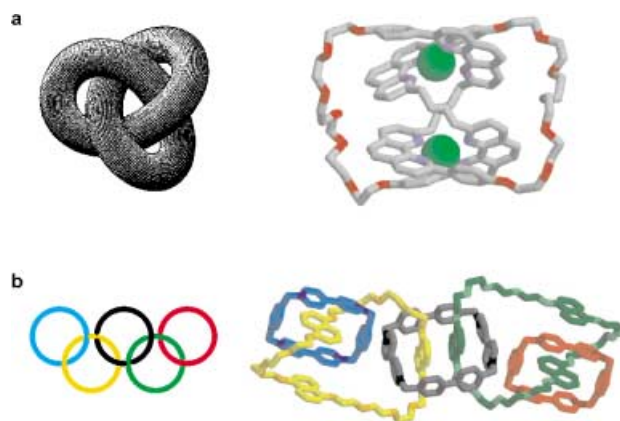


Figure 7. a) A trefoil knot, represented by the artist M. C. Escher, and a molecular trefoil knot;^[77c] b) the Olympic Committee symbol along with its molecular version, a catenane constituted of five interlocked macrocycles.^[77d] Crystal structures courtesy of a) Professor Jean-Pierre Sauvage, University of Strasbourg, France, and b) Professor David J. Williams, Imperial College, London, UK.

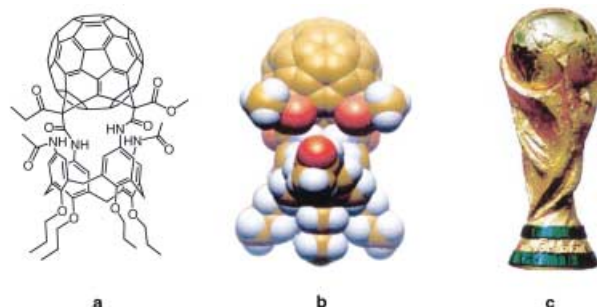


Figure 8. A supramolecular system consisting of a fullerene covalently linked to a calixarene:^[79] a) a classical chemical representation, b) a PM3-calculated space filling model showing the shape relationship of this supramolecular structure with the football World Cup (c). Reproduced by permission of The Royal Society of Chemistry (RSC) and the Centre National de la Recherche Scientifique (CNRS).



Figure 9. Sculptures by Vizi Béla^[80] representing two classical supramolecular systems: a) a cryptate, b) a lariat ether.

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