Molecular Devices and Machines – A Journey into the Nano World

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To Carla, Daniela and Sergio

Preface

Discoveries consist in seeing what everybody has seen and thinking what nobody has thought
A. Szent-Gyorgyi

The progress of mankind has always been related to the construction of novel devices and machines. Depending on its purpose a device or a machine 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 reduce 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 top-down (large-downward) approach which is reaching the limits of its physical capabilities (hundreds of nanometers). Miniaturization can, however, be pushed further, 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. In the last ten 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 the construction of molecular-level devices and machines of nanometer size.

The concept underlying the chemical, bottom-up, approach to nanotechnology was beautifully anticipated by Primo Levi, a great Italian chemist and writer: *''... è più ragionevole arrivarci a poco per volta, montando prima due pezzi soli, poi il terzo e così via. 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 solo fatte il Padreterno, per esempio a montare non dico un ranocchio o una libellula, ma almeno un microbo o il semino di una muffa.''* (P. Levi, La Chiave a Stella, Einaudi, Torino, 1978, p. 151) [1].

Much of the inspiration to construct artificial molecular-level devices and machines comes from the outstanding progress made in molecular biology that

has begun to reveal the secrets of the natural molecular-level devices and machines which constitute the material basis of life. Bottom-up construction of devices and machines as complex as those present in Nature is, of course, an impossible task. Chemists are therefore trying to construct much simpler molecular-level devices and machines, without mimicking the complexity of biological structures. In the last few years talent in synthesis, always the most distinctive feature of chemists, combined with device-driven ingenuity evolved from chemists' attention to functions and reactivity, have led to the design and construction of many very interesting molecular-level devices and machines.

Most of these artificial systems have been investigated in solution, where incoherence often remains a major impediment to performing useful functions, although demonstration that the concept of device and machine can be extended to the molecular level is of the greatest importance *per se*. No doubt, this concept will be (sometimes, it has already been) used to create systems of great practical interest. As we move further into the new century the bottom-up approach to nanotechnology seems indeed to offer almost unlimited promise and opportunity for science and society.

In view of the rapidly growing interest of the scientific community in molecular-level devices and machines we felt that a monograph was needed to cover the introductory features underlying this field and to present a unifying, critical, and stimulating overview of this new frontier of chemical research. Throughout the book emphasis is placed on concepts that are then illustrated with examples of the various kinds of artificial device or machine, taken from recent literature. Selected examples of natural and biomimetic molecular-level systems are also presented, not so much for the purpose of comparison with artificial systems, but rather to give the reader a flavor of the beauty and complexity of the chemical mechanisms responsible for the material aspects of life. Artificial devices and machines based on heterogeneous or solid-state systems are mentioned only briefly, not only because space is limited, but also because we believe this field to be largely empirical and not yet fully mature scientifically, although it seems so close to important applications.

The book contains several introductory chapters and sections that illustrate the fundamental principles underlying the achievements described. We have tried to cover advanced scientific research rigorously, making use of friendly language and many schemes, diagrams, and other figures to illustrate the topic dealt with as clearly as possible. An appendix with a glossary and a list of abbreviations will help readers not familiar with chemistry.

The systems discussed in this book belong to traditionally different areas of chemistry. For example, host–guest species are usually considered a topic of organic chemistry, polynuclear metal complexes are almost exclusively dealt with in inorganic chemistry books and journals, and electrochemistry and flash photolysis belong to the realm of physical chemistry. A non-negligible merit of the topic dealt with in this book is that of urging the average chemist to overcome the fences in which he or she has been traditionally confined and to promote collaboration with apparently unrelated (in fact, complementary) research groups.

We feel that the book can be useful not only for scientists engaged in research in the fields of chemistry, physics, biology, and nanotechnology, but also as a basic text or a complementary reading source for graduate and postgraduate courses dealing with, for example, supramolecular chemistry, physical organic chemistry, photochemistry, electrochemistry, and energy- and electron-transfer processes. We also believe that in a few years courses focussing on molecular-level devices and machine will become a requirement in all major universities.

No book can be written in isolation, and this book has, indeed, benefited from discussions with many colleagues. First of all we would like to thank all the members of our research group for their scientific support and, even more, for their friendship. We particularly are grateful to Roberto Ballardini, Maria Teresa Gandolfi, and Mauro Maestri, who are deeply involved in some of the topics covered by this book, for valuable collaboration and stimulating discussion. We would also like to thank warmly Professor J. Fraser Stoddart and his group for long-lasting, profitable, and friendly collaboration in the field of molecular machines.

Special thanks go to Paola Ceroni of our research group, and to Nicola Armaroli (ISOF-CNR, Bologna), Sebastiano Campagna (Università di Messina), Fernando Pina (Universidade Nova de Lisboa), and Franco Scandola (Università di Ferrara) for suggestions and critical reading of some chapters of the book. We thank Filippo Marchioni for preparing many drawings and for his help, with Serena Silvi, in gathering documentation, and Mara Monari for her contribution in preparing the subject index. We are grateful to our colleagues from all over the world who kindly sent us reprints and preprints of their papers, and the editors of a variety of scientific journals for their permission to reproduce figures.

Before closing, we would like to express our hope that the progress of research in the field dealt with in this book, and more generally the progress of science, will help mankind to create opportunities for peace and for reducing the gap between rich and poor countries.

Vincenzo Balzani, Alberto Credi, Margherita Venturi
Bologna, July 2002

Reference

1 English version: *"... 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 mold"* (P. Levi, The Monkey's Wrench, Penguin Books, New York, 1995, p. 144).

Contents

1
General Concepts

1.1
Devices and Machines at the Molecular Level

A device is something invented and constructed for a special purpose [1] 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 extended in a straightforward manner to the molecular level (Fig. 1.1) [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 perform 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 relative positions of the component parts can change as a result of some external stimulus [3]. Molecular-level devices and machines operate via electronic and/or nuclear rearrangements and, like macroscopic devices and machines, need energy to operate and signals to communicate with the operator.

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, 4].

1.2
Miniaturization of Devices and Machines

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

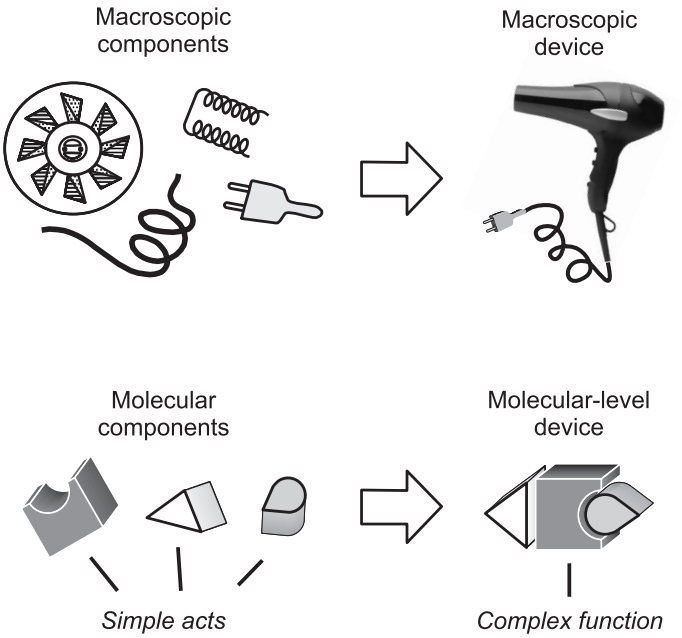


Fig. 1.1. Extension of the concept of the macroscopic device to the molecular level.

machines has come into use for collecting, processing, displaying, and storing information. The outstanding development of information technology has been closely 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 h between repairs [5]. A state-of-the-art microprocessor today has more than 40 million transistors, a number that is destined to increase in the future [6]. One might wonder whether we really do need to keep making things smaller. The answer is that further miniaturization will not only reduce the size and increase the power of computers, but is also expected to open the way to new technologies [7–10] capable of revolutionizing medicine, producing a wealth of new materials providing renewable energy sources, and solving the problem of environmental pollution.

1.3 Top-down (Large-downward) Approach

The miniaturization of components for the construction of useful devices and machines is currently pursued by the top-down (large-downward) approach. This approach, which leads physicists and engineers to manipulate progressively smaller pieces of matter by photolithography and related techniques, has operated outstandingly until now. In 1965 G.E. Moore [11] predicted that every three

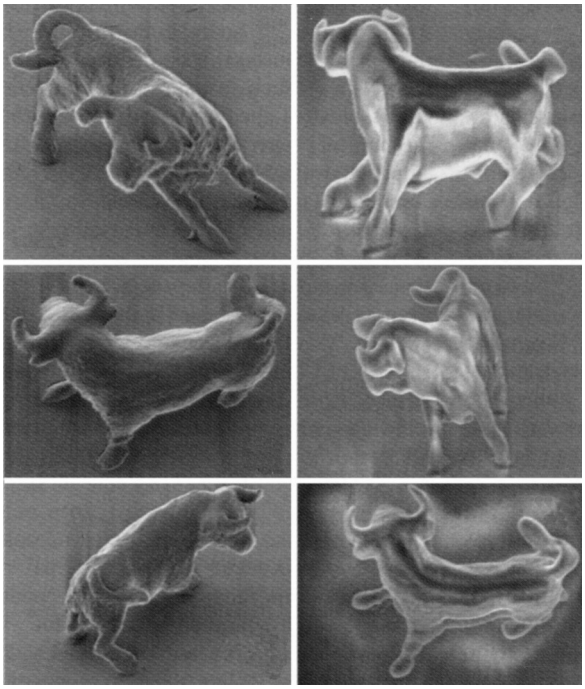


Fig. 1.2. Scanning electron micrographs of bull sculptures crafted on a resin by two-photon photopolymerization, showing the definition reached by top-down miniaturization. These sculptures are 10 μm long and 7 μm high, and are approximately the size of a red blood cell. Reproduced, with permission, from Ref. [13].

years (i) device size would reduce by 33 %, (ii) chip size would increase by 50 %, and (iii) the number of components on a chip would quadruple. This prediction has been fulfilled so far and the potential of laser techniques in the top-down approach to miniaturization has also been exploited for construction of micro-electromechanical systems (MEMS) [12]. 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 Fig. 1.2, that has been crafted by two-photon photopolymerization [13]. It is becoming increasingly apparent, however, that modern computer technology, which relies on silicon-based chips, is rapidly approaching the limits of its physical capabilities [14, 15]. In particular, photolithography is subject to drastic limitations for dimensions smaller than 100 nm. This size is very small by the standards of everyday experience (approximately one thousandth the width of a human hair) but 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 [16] stated in a famous talk to the American Physical Society in 1959, but the top-down approach does not seem capable of exploiting such opportunity. To proceed towards further miniaturization, science and technology will have to find new ways.

1.4
Bottom-up (Small-upward) Approach

An alternative and promising strategy towards technology on the nanometer scale is offered by the bottom-up (small-upward) approach, which starts from atom or molecules and builds up to nanostructures. Chemists, by the nature of their discipline, are already at the bottom, because they can manipulate atoms and molecules. They are, therefore, 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 [4b]. The dominant idea, derived from quantum theory [17], was that atoms are fuzzy entities that "must no longer be regarded as identifiable individuals" [18], and "form a world of potentialities or possibilities rather than one of things or facts" [19]. From the point of view of quantum theory, molecular structure is not an intrinsic property [20], but a metaphor [21]. Such ideas, of course, were never shared by chemists who long before had established [22] that atoms are material and reliable building blocks for constructing molecules and that molecules have well defined sizes and shapes [23]. This concept has been beautifully presented by a great chemist and writer, Primo Levi, in his book "La Chiave a Stella" [24]: *"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" [16]. The key sentence of Feynman's talk was: *"The principles of physics do not speak against the possibility of maneuvering things atom by atom"*. As we will see below, however, chemists do not believe in the possibility of realizing an atom-by-atom approach to nanostructures.

1.4.1
Bottom-up Atom-by-atom

The idea of constructing nanoscale devices "atom-by-atom" was depicted in an exciting and visionary way in mid-eighties by K.E. Drexler [25]. Later he espoused his ideas on nanosystems and molecular manufacturing in a more scientific

(essentially theoretical) way [26, 27]. He proposed, and still maintains [28], the possibility of constructing a general-purpose building nanodevice, nicknamed 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 technology would revolutionize manufacture, enabling, e.g., the low-cost, pollution-free construction of lightweight and extremely strong materials that, in their turn, would revolutionize transport (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 wastes from the brain and bringing the body back to a state of youthful health [29]. According to Drexler [25, 28], the potential of nanotechnology has also a dark side that should already be taken into serious consideration by responsible governments. The outstanding potential of nanotechnology could, in fact, be exploited by aggressive nations, terrorist groups, or even individuals for evil purposes, with much more danger than that caused by chemical and biological weapons. The prospect has also been raised that the potential for self-replication of the assemblers could escape human control, leading to myriads of copies of themselves that would, in the end, 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 [25–29] about the construction, futuristic use, and frightening potential of nanomachines have been skeptically and ironically commented upon by a large part of the scientific community [30–33]. In particular, the concept of an assembler, i.e. a nanorobot, that can manipulate and build things atom by atom, is considered unrealistic for at least two well grounded reasons [31, 32]: (i) the fingers of a hypothetical manipulator arm should themselves be constructed from atoms, which implies they would be too bulky to have control of chemistry in the nanometer region; (ii) such fingers would also be too sticky – the atoms of the manipulator hands would adhere to the atom being moved, so that it would 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 much 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 at least had the merit of drawing the attention of people to science and influencing many scientists to direct their research projects towards the fascinating world of nanotechnology.

1.4.2 Bottom-up Molecule-by-molecule

In the late nineteen-seventies a new branch of chemistry, *supramolecular chemistry* (Section 1.5) emerged and expanded very rapidly, consecrated by the award of the Nobel Prize in Chemistry to C.J. Pedersen [34], D.J. Cram [35], and J.-M. Lehn [36] in 1987. In the same period, research on molecular electronic devices begun to flourish [37]. In the framework of research on supramolecular chemistry the idea began to arise in a few laboratories [36, 38–40] that molecules are much more convenient building blocks than atoms for construction of nanoscale devices and machines. The main foundations of this idea were: (i) molecules are stable species, whereas atoms are difficult to handle; (ii) Nature starts from molecules, not from atoms, to construct the great number and variety of nanodevices and nanomachines that sustain life (*vide infra*); (iii) most laboratory chemical processes deal with molecules, not with atoms; (iv) molecules are objects that already have distinct shapes and carry device-related properties (e.g. properties that can be manipulated by photochemical and electrochemical inputs); and (v) molecules can self-assemble or can be connected to make larger structures.

In the following years supramolecular chemistry grew very rapidly [41–45] 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. It also became increasingly evident that such an approach can make an invaluable contribution to better understanding of molecular-level aspects of the extremely complicated devices and machines that are responsible for biological processes [46].

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 large amount of knowledge gained in other fields of chemistry. Particularly important in this regard have been the contributions made by organic synthesis, which supplied a variety of building blocks, and by photochemistry [39, 42, 47], which afforded a means of investigating the early examples of molecular-level devices and machines (e.g. light-controlled molecular-level tweezers [48], triads for vectorial charge separation [49], and light-harvesting antennae [50]).

It should also be recalled that in the last few years the concept of molecules as nanoscale objects with 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 microscopy, capable of "seeing" [51] or "manipulating" [52] single molecules. It has been possible, for example, to make ordered arrays of molecules (e.g. to write words [53] and numbers [52] by aligning single

molecules in the desired pattern) and even to investigate bimolecular chemical reactions at the single molecule level [54].

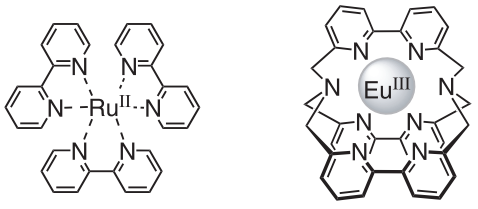
1.5
Supramolecular (Multicomponent) Chemistry

Supramolecular chemistry is a highly interdisciplinary field that has developed astonishingly rapidly in the last two decades [41–45, 55]. From a historical perspective, as pointed out by J.-M. Lehn [56], 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 after 1970, however, that 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" [36, 41]. As often occurs, however, problems arise as soon as a definition is established; for example [55j], the definition of organometallic chemistry as "the chemistry of compounds with metal-to-carbon bonds" rules out Wilkinson's compound, $RhCl(PPh_3)_3$, 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 such as $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine), usually regarded as molecules [57], should be defined as supramolecular species; if not, systems like the $[Eu \subset bpy.bpy.bpy]^{3+}$ cryptate, usually considered to be supramolecular antenna devices [58], should, in fact, be defined as molecules (Fig. 1.3).

There is, however, a more general problem. Broadly speaking, one can say that in supramolecular chemistry there has been a change in focus from molecules to molecular assemblies or multicomponent systems. According to the original defi-



$[Ru(bpy)_3]^{2+}$ $[Eu \subset bpy.bpy.bpy]^{3+}$

Fig. 1.3. $[Ru(bpy)_3]^{2+}$ and $[Eu \subset bpy.bpy.bpy]^{3+}$: molecular or supramolecular species?

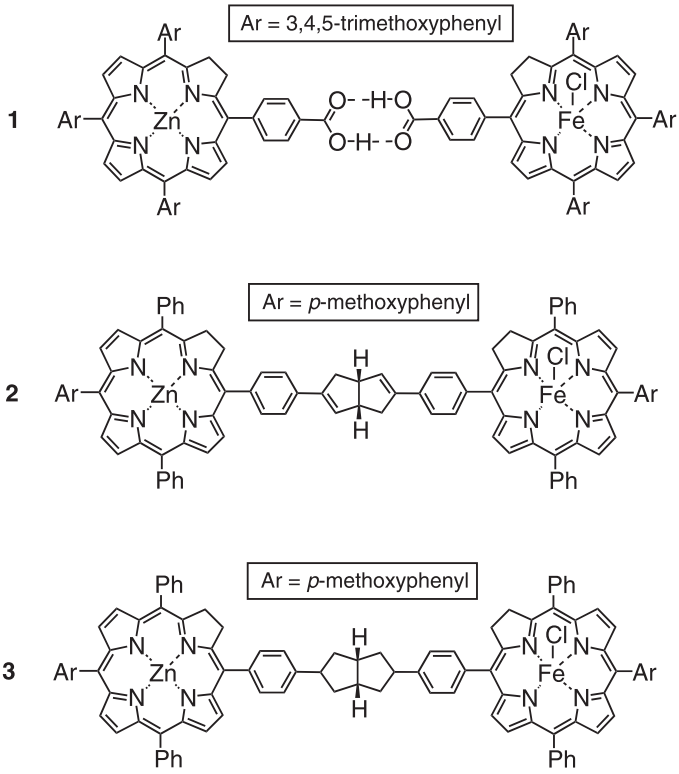


Fig. 1.4. Three dyads with Zn(II) porphyrin and Fe(III) porphyrin units linked by an H-bonded bridge (**1**), a partially unsaturated bridge (**2**), and a saturated bridge (**3**) [59]: molecular or supramolecular species?

nition, however, 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, which are usually multicomponent systems in which the components can be linked by chemical bonds of different nature.

Consider, for example, the three systems [59] shown in Fig. 1.4, which play the role of molecular-level charge-separation devices (Section 6.3.2). In each of these, 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, i.e. by intermolecular forces, whereas in **2** and **3** they are linked by covalent bonds. According to the classical definition of supramolecular chemistry reported above, **1** is a supramolecular species whereas **2** and **3** are (large) molecules. In each of these three systems the two components substantially maintain their intrinsic properties and, on excitation with light, electron transfer occurs from the Zn(II) porphyrin unit to the Fe(III) porphyrin unit. The values of the rate constants for photo-

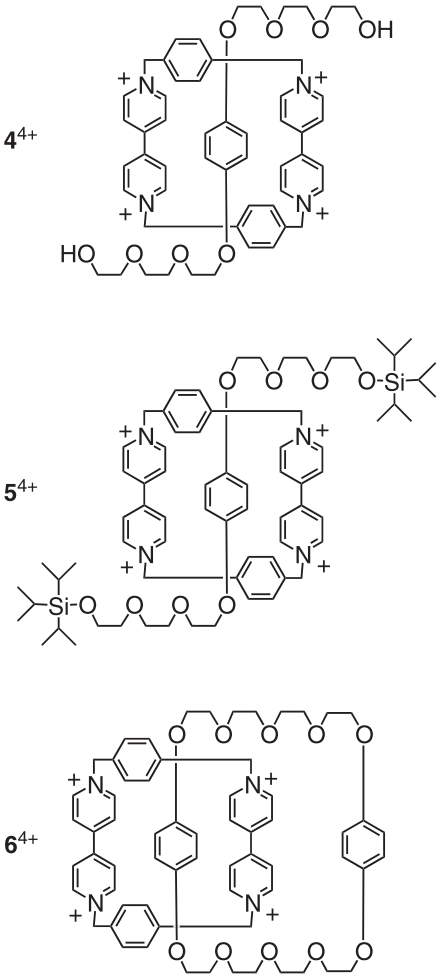


Fig. 1.5. Pseudorotaxane ($\mathbf{4}^{4+}$), rotaxane ($\mathbf{5}^{4+}$), and catenane ($\mathbf{6}^{4+}$) [60]: molecular or supramolecular species?

induced electron-transfer ($k_{el} = 8.1 \times 10^9$, 8.8×10^9, and 4.3×10^9 s^{-1} for **1**, **2**, and **3**, respectively) show that the electronic interaction between the two components in **1** is comparable with that in **2**, and even stronger than that in **3**. With regard to photoinduced electron transfer it would clearly be 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 (Fig. 1.5) [60]. A pseudorotaxane, e.g. $\mathbf{4}^{4+}$, can, in the same way as any other type of adduct, be clearly defined as a supramolecular species, whereas rotaxanes, e.g. $\mathbf{5}^{4+}$ (and even catenanes, e.g. $\mathbf{6}^{4+}$), despite being more complex than pseudorotaxanes, should be called molecules, in accordance with the classical definition.

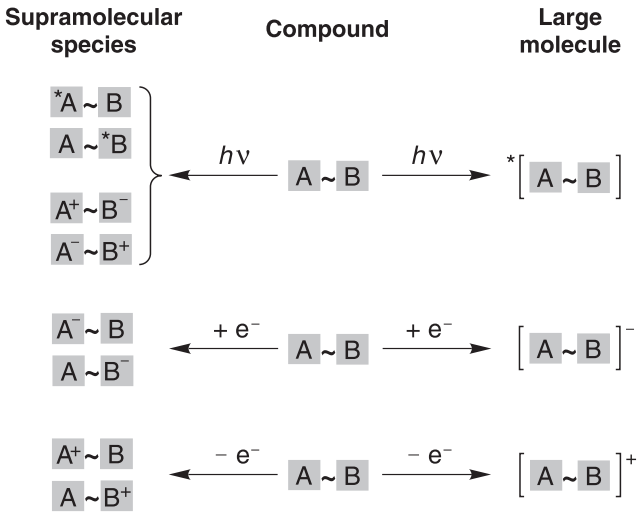


Fig. 1.6. Schematic representation of the difference between a supramolecular system and a large molecule based on the effects caused by a photon or an electron input.

Although we conclude that the classical definition of supramolecular chemistry as "the chemistry beyond the molecule" is quite useful, functionally 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.

1.5.1 Comparison of Large Molecules with Supramolecular (Multicomponent) Systems

It has been proposed [42, 61, 62], and is now widely accepted [55i, j, 63–65], that for chemical systems investigated from the viewpoint of the effects caused by external stimulation, the definition of supramolecular species can be based on the degree of intercomponent electronic interactions. This concept is illustrated, for example, in Fig. 1.6 [62]. On photochemical stimulation a system A∼B consisting of two units (∼ indicates any type of "bond" that keeps the units together) can be defined as a supramolecular species if light absorption leads to excited states that are substantially localized on either A or B, or causes electron transfer from A to B (or *vice versa*). In contrast, when the excited states are substantially delocalized on the entire system the species are better regarded as a large molecule. Similarly (Fig. 1.6), 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 over the entire system. In more general terms, when the interaction energy between units is small compared with the other relevant energy parameters, a system can be regarded as a supramolecular species, irrespective of the nature of the bonds that link the units. Species made of covalently-linked (but weakly