

I

General Concepts

1

Introduction

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]. The progress of human civilization 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 past 50 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 leading 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 [2]. A state-of-the-art microprocessor today has more than 500 million transistors [3], a number that is destined to increase in the future [4]. We can wonder whether we 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 [5–9] capable of revolutionizing medicine, producing a wealth of new materials, providing renewable energy sources, and solving the problem of environmental pollution.

Generally, 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 to the molecular level (Figure 1.1) [10]. A *molecular device* can be defined as an assembly of a discrete number of molecular components 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

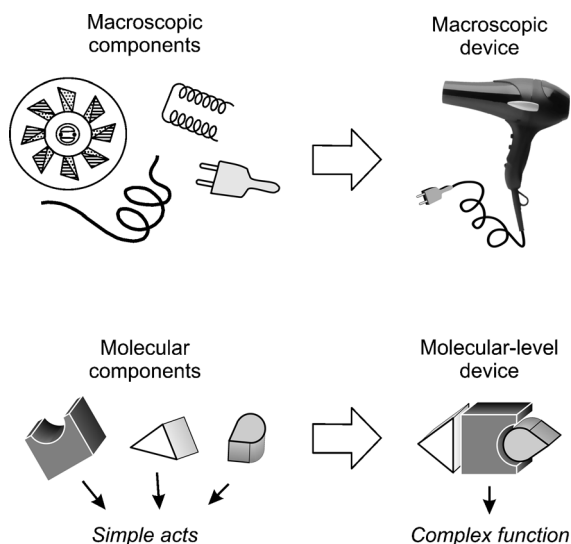


Figure 1.1 Extension of the macroscopic device concept to the molecular level.

the cooperation of the various components. A *molecular machine* is a particular type of device in which the (molecular) component parts can display changes in their relative positions as a result of some external stimulus [11–13]. Molecular-level devices and machines operate via electronic and/or nuclear rearrangements and, like macroscopic devices and machines, they also 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.

It should be pointed out that nanoscale devices and machines cannot be considered merely as “shrunk” versions of their macroscopic counterparts because physics is different at the nanoscale [14]. Some phenomena at the nanoscale are governed by the laws of quantum mechanics, and, most important, some intrinsic properties of molecular-level entities are quite different from those of macroscopic objects:

- molecules are in a state of constant random motion and are subjected to continual collisions (Brownian motion);
- in the nanoworld, things are somewhat floppy and stick strongly to each other because of electromagnetic interactions;
- the dimensions of molecules are much smaller than the wavelengths of the light used to supply energy or to obtain information;
- interference of electron waves may occur;
- in nanoscopic structures, properties may be affected by confinement of electron waves (quantum dots).

Since a variety of molecular devices and machines are already present, and work very well, in Nature, design and construction of artificial molecular devices and machines can greatly benefit from the knowledge of the working principles of

natural ones rather than from attempts to apply the macroscopic engineering principles at the nanoscale.

1.2

Nanoscience and Nanotechnology

Nanotechnology is a frequently used word both in the scientific literature and in the common language [15]. This word stirs up enthusiasm and fear because nanotechnology is expected, for the good and for the bad, to have a strong influence on the future of mankind [8]. Everybody seems to know what is nanotechnology, but even within the scientific community, the meaning of this word is not yet well established [16–18]. In fact, nanotechnology has apparently different meanings in different fields of science, for example, in physics and chemistry. Perhaps surprisingly, nanoscience, the sister word of nanotechnology, is much less commonly used, but it is all the same ill defined.

Nano, like micro, pico, and so on, is used in front of a macroscopic unit to reduce its value by orders of magnitude. Nano means one billionth. Thus, a nanometer is one billionth of a meter. When placed in front of words like science and technology, however, the meaning of nano is not that obvious. Since experimental science and technology deal with material objects, it seems fair to say that *nanoscience and nanotechnology are science and technology concerning objects of nanometer dimension*.

What really are nanoscience and nanotechnology can be better understood by focusing on the intrinsic properties of the nanoscale objects and on the possibility of using, manipulating, or organizing them into assemblies in order to perform specific functions [6–8,19–22]. These concepts can be explained by two limiting cases [23].

Case 1

The nanoscale “objects” are very simple from a chemical viewpoint and do not exhibit any specific intrinsic function (atoms, clusters of atoms, and small molecules). Functions arise from ensembles of such objects. A couple of examples can be mentioned:

- Atoms or very simple molecules can be used to write a word of nanoscale dimension on a surface. Figure 1.2 shows that the new millennium has been celebrated by writing 2000 with 47 CO molecules placed on Cu(211) [24].
- Metal nanoparticles can be used to cover a surface. A metal nanoparticle is made of metal atoms as is a metal leaf, but in the nanoparticle most of the atoms, whether on or close to the surface, are exposed to interactions with other species. Covering a macroscopic piece with metal leaves (technology) or with metal nanoparticles (nanotechnology) leads to materials characterized by quite different properties.

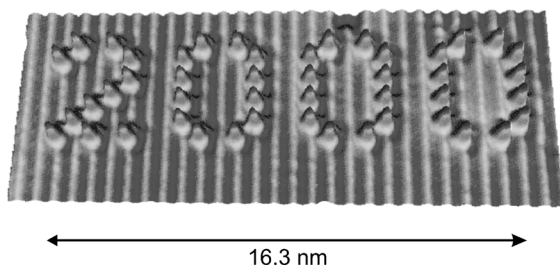


Figure 1.2 The millennium year number 2000 has been written by using 47 CO single molecules. Each protrusion represents an individual CO molecule and the background vertical lines denote the intrinsic Cu surface step edges [24].

This field of nanoscience and nanotechnology is of the greatest interest to physicists and engineers and has already originated many innovative applications, particularly in materials science (nanoparticles, nanostructured materials, nanoporous materials, nanopigments, nanotubes, nanoimprinting, quantum dots, etc.) [25–28]. Manipulation or imaging nanoscale techniques play an important role in basic investigations [29,30].

Case 2

The nanoscale “objects” have complex chemical composition (supramolecular [31] or multicomponent [32] systems), exhibit characteristic structures, show peculiar properties, and perform specific functions. All the artificial molecular devices and machines dealt with in this book belong to this category. Typical examples of such nanoscale “objects,” which will be discussed in detail in the following chapters, are a light-harvesting dendrimer [33], a light-driven rotary motor [34], a prototype of a molecular muscle [35], a unidirectionally rotating four station catenane [36], an artificial molecular elevator [37], molecular [38] and supramolecular [39] logic gates, a light-driven hybrid systems for producing ATP and pumping calcium ions [40], and a DNA biped walking device [41]. All the natural or hybrid molecular devices and machines [14,42–44], from the light-harvesting antennae of the natural photosynthetic systems to the linear and rotary motors present in our bodies or operating in engineered environments, also belong to this category.

Nanoscience and nanotechnology are still in their infancy. At present, new exciting results and, sometimes, disappointing checks alternate on the scene, as it always happens in fields that have not yet reached maturity. Surely, as Feynman said [45], “when we have some control of the arrangement of things on a molecular scale, we will get an enormously greater range of possible properties that substances can have,” and these new properties will lead to a wide variety of applications that we cannot even envisage today.

Hopefully, nanoscience and nanotechnology will contribute in finding solutions for the four big problems that face a large part of the earth’s population: food, health,

energy, and environment. We should not forget, however, that the development of nanoscience and nanotechnology, as it always happens with scientific progress, is also accompanied by risks and fears (Chapter 17).

1.3 Supramolecular (Multicomponent) Chemistry

Supramolecular chemistry [31] is a highly interdisciplinary field, consecrated by the award of the Nobel Prize in Chemistry in 1987 to C.J. Pedersen [46], D.J. Cram [47], and J.-M. Lehn [48]. In a historical perspective [49], 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 some fundamental concepts such as molecular recognition, preorganization, self-assembly, and so on were introduced and since 1990 supramolecular chemistry began to grow up exponentially [50].

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" [31]. As it is often the case, however, problems arise as soon as a definition is established; for example, 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 [50m].

The 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 $[\text{Ru}(\text{bpy})_3]^{2+}$ ($\text{bpy} = 2,2'$ -bipyridine) [51], which are usually considered molecules, should be defined as supramolecular species; if not, systems like the $[\text{Eu}\subset\text{bpy}\cdot\text{bpy}\cdot\text{bpy}]^{3+}$ cryptate [52], which are usually considered supramolecular antenna devices, should, in fact, be defined as molecules (Figure 1.3).

There is, however, a more general problem [53]. Broadly speaking, 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

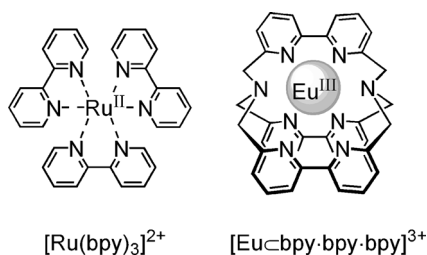


Figure 1.3 $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Eu}\subset\text{bpy}\cdot\text{bpy}\cdot\text{bpy}]^{3+}$: molecular or supramolecular species?

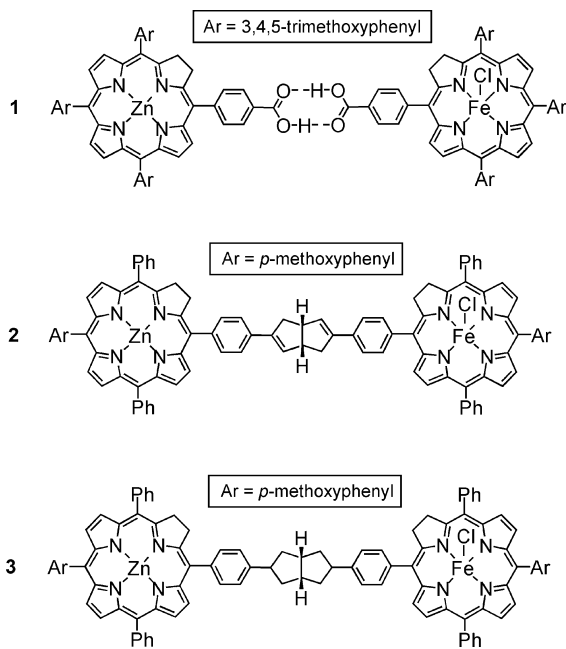


Figure 1.4 Three dyads possessing Zn(II) porphyrin and Fe(III) porphyrin units linked by H-bonded bridge (**1**), a partially unsaturated bridge (**2**), and a saturated bridge (**3**) [54]: molecular or supramolecular species?

particularly important while 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 [54] shown in Figure 1.4, which play the role of molecular-level charge-separation devices (Section 4.4). 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 classical definition of supramolecular chemistry reported above, **1** is a supramolecular species, whereas **2** and **3** are molecules. In each of the three systems, the two components substantially maintain their intrinsic properties and, upon 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 ($k_{\text{el}} = 8.1 \times 10^9$, 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 (Chapter 14).

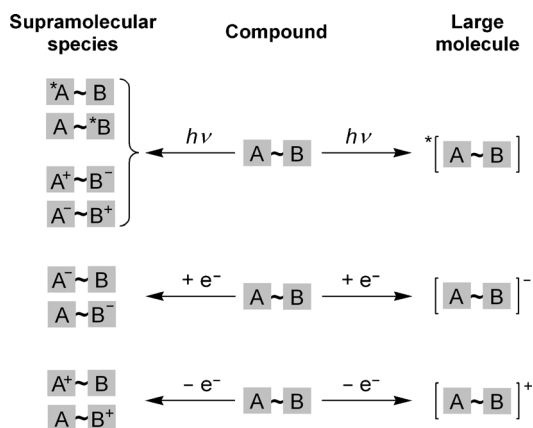


Figure 1.5 Schematic representation of the difference between a supramolecular system and a large molecule based on the effects caused by a photon or an electron input [57].

A pseudorotaxane, as any other type of adduct, can be clearly defined as supramolecular species, whereas a rotaxane and even a catenane, in spite of the fact that they are more complex species than pseudorotaxanes, should be called molecules according to the classical definition.

We conclude that although the classical definition of supramolecular chemistry as “the chemistry beyond the molecule” [31] is quite useful in general, functionally the distinction between what is molecular and what is supramolecular should be better based on the degree of intercomponent electronic interactions [50,53,55–60]. This concept is illustrated, for example, in Figure 1.5 [57]. In the case of a photochemical stimulation, a system $A \sim B$, consisting of two units (\sim indicates any type of “bond” that keeps the units together), can be defined as 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). In contrast, when the excited states are substantially delocalized on the entire system, the species can be better considered as a large molecule. Similarly (Figure 1.5), 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 where the hole or the electrons 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. Species made of covalently linked (but weakly interacting) components, for example, **2** and **3** shown in Figure 1.4, can therefore be regarded as belonging to the supramolecular domain when they are stimulated by photons or electrons. It should 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.

1.4

Top-Down (Large-Downward) Approach

The miniaturization of components for the construction of useful devices and machines at the micrometer level is currently pursued by the top-down (large-downward) approach [61]. 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 until now. It is becoming increasingly apparent, however, that today's computer technology, which relies on silicon-based chips, is rapidly approaching the upper limits of its capabilities [4,62]. In particular, photolithography is subjected to drastic technical and economical limitations for dimensions smaller than 100 nm. 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 [45] stated in his 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 toward further miniaturization, science and technology will have to find new ways.

1.5

Bottom-Up (Small-Upward) Approach

An alternative and promising strategy toward technology at the nanometer scale is afforded 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, 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 [63].

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 [64]. The dominant idea derived from quantum theory [65] was that atoms are fuzzy entities that "must no longer be regarded as identifiable individuals" [66] and "form a world of potentialities or possibilities rather than one of things or facts" [67]. From the point of view of quantum theory, molecular structure is not an intrinsic property [68], but a metaphor [69]. Such ideas, of course, were never shared by chemists who had long before established [70] that atoms are material and reliable building blocks for constructing molecules and that molecules have well-defined sizes and shapes [71]. This concept has been beautifully presented by a great chemist and writer, Primo Levi, in his book "La Chiave a Stella" [72]: "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.”

It was, in fact, Feynman who in his 1959 address to the American Physical Society first mooted the idea that atoms could be used to construct nanoscale machines, “There is plenty of room at the bottom” [45]. The key sentence of Feynman’s talk was the following: “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.

1.6 Bottom-Up Molecule-by-Molecule Approach

The idea of constructing nanoscale devices “atom by atom” was propounded by K.E. Drexler in an exciting and visionary way in the mid-1980s [73] which he expanded in a more scientific, essentially theoretical, way later on [74–77]. The idea, however, which seems so much appealing to physicists, does not convince chemists [77–81]. By knowing the high reactivity of most atomic species, the subtle aspects of chemical bond and the properties of molecules, they strongly believe that molecules are much more convenient building blocks than atoms to construct nanoscale devices and machines [53]. The main foundations of this idea are as follows: (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 (see below); (iii) most laboratory chemical processes are dealing with molecules, not with atoms; (iv) 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 (v) molecules can self-assemble or can be connected to make larger structures.

Point (v) recalls the fundamental principle of *supramolecular chemistry* (Section 1.3) whose rapid growth during the past two decades has shown that the “bottom-up” approach opens virtually infinite possibilities concerning design and construction of artificial molecular-level devices and machines. It has become more and more evident that such an approach can make invaluable contributions to the better understanding of molecular-level aspects of the extremely complicated devices and machines that are responsible for the biological processes [14,42,43,82].

It should not be forgotten, however, that the development of the supramolecular bottom-up approach toward 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 made by organic synthesis which supplied a variety of building blocks, and photochemistry [55,83],