Molecular Devices and Machines: A Journey Into the Nanoworld

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Molecular Devices and Machines - A Journey into the Nano World V. Blzni, A. Crdi, M. Vnturi Molecular Devices and Machines -AJourne into the Nano World. V. Balzani, A. Credi, M. Venmri Copyright � 2003 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim ISBN: 3-527-30506-8

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To Carla, Daniela and Ser�io

I vii Preface Discoveries consist in seeing what evewbody 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 compo- nents employed for the construction of devices and machines has resulted in outstanding technological achievements, particularly in the field of information pro- cessing. 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 Feynmaffs 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: "... pi ragionevole arrivarci a poco per volta, montando prima due pezzi soli, poi il terzo e cos 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 g gid montato. Se quelle pinzette le avessimo (e non g detto che un giorno non le avremo) saremmo gia riusciti a fare delle cose graziose che fin adesso le ha solo fatte il Padreterno, per esempio a wontare non dico un ranocchio o una libellula, ma almeno un microbo oil semino di una muffa." (P. Levi, La Chiave a Stella, Einaudi, Torino, 1978, p. 1S1) [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 func- tions and reactivity, have led to the design and construction of many very interest- ing molecular-level devices and machines. Most of these artificial systems have been investigated in solution, where in- coherence 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 inter- est. As we move further into the new century the bottom-up approach to nano- technology 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 empir- ical and not yet fully mature scientifically, although it seems so dose 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 dearly 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 exdusively 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.

preface 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 mem- bers of our research group for their scientific support and, even more, for their friendship. We particularly are grateful to Roberto Ballardini, Maria Teresa Gan- dolfi, 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, prof- itable, and friendly collaboration in the field of molecular machines. Special thanks go to Paola Ceroni of our research group, and to Nicola Armatoll (ISOF-CNR, Bologna), Sebastiano Campagna (Universitfi di Messina), Fernando Pina (Universidade Nova de Lisboa), and Franco Scandola (Universitfi 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 scien- tific 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, Jul), 2002 Reference English version: "... it is reasonable to proceed a bit at a time, first attaching two pieces, then adding a third, and so on. Ve 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. CEw, The Monkey's Wrench, Penguin Books, New York, 1995, p. 144).

1 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 func- tion. Each component of the assembly performs a simple act, while the entire assembly performs a more complex, useful function, characteristic of that particu- lar device or machine. For example, the function performed by a hairdryer (pro- duction 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 func- tion. 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 com- municate 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 Molecular Devices and Machines -A Journey into the Nano World. V. Balzani, A. Credi, M. Venturi Copyright � 2003 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim ISBN: 3-527-30506-8

General Concepts Macroscopic components Macroscopic device Molecular components Simple acts Molecular-level device I Complex function 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

1.3 Top-down (Large-downward) Approach 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 pm long and 7 pm 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 Phys- ical 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.

41 General Concepts 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 disci- pline, are already at the bottom, because they can manipulate atoms and mole- cules. 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]: "I1 mio mestiere vero, quello che ho studiato a scuola e che mi ha dato da vivere fino ad oggi, 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, perch appunto, le cose che noi manipoliamo SOhO troppo piccole per essere viste, anche col microscopi pig potenti; e allora abbiamo

inventato diversi trucchi intelligenti per riconoscerle senza vederle. Quelli che smontano, cio i chimici analisti, deroho essere capaci di smontare una struttufa 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 Feynmaffs talk was: "The principles of phi,sics 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].

Supramolecular chemistry is a highly interdisciplinary field that has developed astonishingly rapidly in the last two decades [41-4S, 55]. From a historical per- spective, as pointed out by J.-M. Lehn [S6], 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 funda- mental concepts such as molecular recognition, preorganizatiom self-assembly, etc., were introduced and supramolecular chemistry began to emerge as a disci- pline. The most authoritative and widely accepted definition of supramolecular chem- istry is that given by J.-M. Lehm 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 establishe& for example [SSj], the definition of organometallic chemistry as "the chemistry of compounds with metal-to-carbon bonds" rules out Wilkinsors compound, RhCl(PPh3)3, which is perhaps the most important catalyst for organometallic reactions. A first problem presented by the above mentioned dassical 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 [S7], should be defined as supramolecular species if not, systems like the [Eucbpy. bpy. bpy] + cryptate, usually considered to be supramolecular antenna devices [S8], 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 deft- [Ru(bpy)3] 2+ [Eucbpy.bpy. bpy] 3+ Fig. 1.3. [Ru(bpy)3] 2+ and [Eu c bpy. bpy. bpy]3+: molecular or supramolecular species. ;)

'l General Concepts Ar Ar A r ' N"/Z NAr Ph Ph Ph [Ar: p-methoxyphenyl] Ph 3 Ar r Ph Ph Fig. 1.4. Three dyads with Zn(11) porphyrin and Fe(111) 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 mole- cule. This point is particularly important in dealing with molecular-level devices and machines, which are usually multicomponent systems in which the compo- nents 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-

44+ O OH +N N + H O_/O/O_/O -- 1.5 Supramolecular (Multicomponent) Chemistry I 9 +N N + 54+ J � "+ +N N + 64+ ICI +'"-0-1 o,_,o,_,o,_,o,_,o Fig. 1.$. Pseudorotaxane (44+), rotaxane (54+), and catenane (64+) [60]: molecular or supramolecular species? induced electron-transfer (kel = 8.1 x 10 9, 8.8 X 10 9, and 4.3 x 10 9 s -1 for 1, 2, and 3, respectively) show that the electronic interaction between the two compo- nents in 1 is comparable with that in 2, and even stronger than that in 3. With regard to photoinduced electron transfer it would dearly 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 supra- molecular chemistry is encountered with pseudorotaxanes and rotaxanes (Fig. 1.5) [60]. A pseudorotaxane, e.g. 44+, can, in the same way as any other type of adduct, be dearly defined as a supramolecular species, whereas rotaxanes, e.g. 54+ (and even catenanes, e.g. 64+), despite being more complex than pseudorotaxanes, should be called molecules, in accordance with the classical definition.

l01 I General Concepts Supramolecular species Compound Large molecule hv hv m-m ; l~l +e- +e- m-m ; -- m-m ; + 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 dassical 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 AB 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 na- ture of the bonds that link the units. Species made of covalently-linked (but weakly

1.5 Supramolecular (Multicomponent) Chemistry interacting) components, e.g. 2 and 3 shown in Fig. 1.4, and 54+ and 64+ in Fig. 1.5, 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, i.e. of an assembly of weakly interacting molecular components, can be known by study of the isolated components or of suitable model molecules. 1.5.2 Self-organization and Covalent Synthetic Design Self-assembly and self-organization [41, 66] are dominant processes in the chem- istry of living biological systems [46, 67]. For example, light-harvesting antemae of bacterial photosynthesis (Section 5.2) are formed by self-assembly and self- organization of many molecular components. It is indeed amazing how Nature is capable of mastering weak intermolecular forces to construct supramolecular devices and machines [46, 67-69]. Construction of artificial supramolecular struc- tures via self-organization needs suitably programmed [41, 44, 45, 55m] 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 [70], grids [71], capsules [72], molecular polyhedra [73]) have indeed been obtained by self-association and self-organization of artificial molecular com- ponents. The construction of artificial supramolecular devices and machines by self-assembly and self-organization is, however, a much more difficult task, be- cause the various molecular components must be programmed not only to ensure their self-assembly into a structurally organized system but also to ensure their functional integration, as required by the operation the device or machine is ex- pected to perform. Supramolecular systems based on weak interaction are, fur- thermore, fragile because they can be easily disassembled by external perturbations (e.g. change of solvent, change ofpH); although this property can be exploited for particular tasks (see, e.g., Chapters 12 and 14) [74], the device or machine should not usually undergo disassembling. Artificial devices and machines are, therefore, often constructed by following a design based on covalent interconnecting bonds, by using the powerful strategies and techniques of modern synthetic chemistry [75]. 1.5.3 Supramolecular Chemistry, Art, and Nanotechnology As mentioned above (Section 1.4.2), the chemical, molecule-by-molecule "bottom- up" approach enables virtually unlimited possibilities of design and construction of supramolecular species of nanoscale dimensions. Leonardo da Vinci did not know chemistry; nevertheless, his sentence "... dove la Natura finisce di produrre le sue spezie, ?uomo quivi comincia con le cose naturali, con ?aiutorio di essa Natura, a create

12 I I General Concepts Fig. 1.7. Molecular architecture: two fascinating nanometer-scale supramolecular species and the corresponding macroscopic counterparts. (a) A resorcarene-calixarene carcerand [7ga] and the Battistero of Pisa (Italy); (b) a norbornylogous-type compound [7gb] and the Olina medieval bridge, Modena (Italy). The geometries of the molecules are constructed by molecular mechanics calculations. infinite spezie ..." [76] is quite an appropriate comment on the outstanding devel- opment of artificial supramolecular chemistry [41]. Several supramolecular species have fascinating shapes [77] that recall those of macroscopic objects and structures encountered in everyday life. Some examples of aesthetically appealing supramolecular species are shown in Figs. 1.7 and 1.8 [78]. As Primo Levi

noticed, "Infatti, accade anche in chimica, come in architettura, che gli edifici bellb>, e cio simmetrici e semplici, siano anche i piti saldi: avviene insomma per le molecole come per le cupole delle cartedrail o per le arcate dei ponti" [79]. Interest- ingly, while chemists build supramolecular systems that mimic macroscopic works of art (Fig. 1.9) [80], artists begin to take supramolecular compounds as models for creating beautiful sculptures (Fig. 1.10, s. page 15) [81]. As shown in the following chapters, the concepts of supramolecular (multi- component) chemistry can be profitably used to design and construct a great vari- ety of artificial compounds capable of performing potentially useful functions. In the three parts of this book we have tried to describe the most recent advances in the fields of.'

1.5 Supramolecular (Multicomponent) Chemistry I 13 b OcoO Fig. 1.8. (a) A trefoil knot, represented by the artist M.C. Escher, and a molecular trefoil knot [78c]; (b) the Olympic Committee symbol and its molecular version, a catenane comprising five interlocked macrocycles [78d]. Crystal structures courtesy of (a) Professor lean-Pierre Sauvage, University of Strasbourg, France, and (b) Professor David]. Williams, Imperial College, London, UK. Fig. 1.9. A supramolecular system consisting of a fullerene covalently linked to a calixarene [80]: (a) classical chemical representation, (b) PM3-calculated space filling model, showing the relationship between the shape of this supramolecular structure and the football World Cup (c). Reproduced by permission of The Royal Society of Chemistry (RSC) and the Centre National de la Recherche Scientifique (CNRS).

,41 General Concepts � compounds for transfer, transport, and collection of electrons or electronic energy, � multistate/multifunctional systems, � compounds capable of performing mechanical movements (machines). Looking at supramolecular chemistry from the viewpoint of functions with refer- ence to devices and machines of the macroscopic world is a very interesting exer- cise that introduces novel concepts, injects daring ideas, and stimulates creativity. The marriage of chemical synthetic talent with engineering mentality, as suggested in Fig. 1.1, is indeed one of the major avenues towards the development of nano- technology. References Funk Waghalls Standard Dictionary of the English Language, International Edition, 1963. (a) V. BALZANI, A. CREDI, M. VENTURI, in Supramolecular Science: Where It is and Where It is Going (Eds.: R. UNGARO, E. DALCANALE), Kluwer,

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19 Part I Devices for Processln� Elerons an(] Electronic Ener�f Molecular Devices and Machines - A Journe into the Nano World. V. Balzani, A. Credi, M. Venmri Copyright � 2003 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim ISBN: 3-527-30506-8

21 2 Fundamental Principles of' Electron and Ener87 Transfer 2.1 Introduction As mentioned in Section 1.4, one of the most important challenges in science and technology is pursuing further miniaturization, which means using chemistry to build devices and machines from the bottom-up instead of carving matter into smaller and smaller pieces. The first steps in the bottom-up strategy consist in the synthesis and character- ization of molecular-level structures capable of responding to external stimuli. Current macroscopic devices make use of electrical and light signals to transfer, store, and retrieve information. Although it is not necessary that the components of the chemical computer [1] operate in ways analogous with those of conventional silicon-based computers, it seems likely that information processing at the molec- ular level will be essentially based on electrical and light stimuli. Molecules can, in fact, process electrons or photons (in 1:1 and other defined stoichiometries), and generate electrons on photoexcitation, and photons on electrical stimulation. It might, therefore, be expected that electronics and photonics will merge increas- ingly as miniaturization proceeds. In the last few years many compounds have been investigated that could prove useful for information processing at the molecular level. It should be pointed out, however, that most such compounds have only been studied in solution, i.e. work- ing on a huge number of molecules which behave incoherently. For most practical applications, problems like the interconnection of molecular components in series or parallel and the interfacing of individual molecules with the external (inevitably macroscopic) world must be solved. Although research on molecular electronics is developing rapidly [2], it seems likely that construction of a really working chemi- cal computer is still far in the future. Apart from futuristic applications, however, the design and realization of a molecular-level electronic set (e.g. wires, switches, plugs, sockets, extensions, rectifiers, antennae, and batteries) is a topic of great scientific interest because it introduces new concepts to the field of chemistry and stimulates the ingenuity of research workers [3]. Most investigations of molecular-level systems

capable of playing functions that mimic those performed by the components of macroscopic electronic devices involve photoinduced electron- and/or energy-transfer processes in supramolecular Molecular Devices and Machines - A Journey into the Nano World. V. Balzani, A. Credi, M. Venturi Copyright � 2003 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim ISBN: 3-527-30506-8

22 I 2 Fundamental Principles of Electron and Energ Transfer species. Photoinduced electron- and/or energy-transfer processes play also a fundamental role in operating biological devices and machines. It is, therefore, appropriate to summarize some basic principles of electron- and energy-transfer processes. Detailed illustrations and discussion of the various aspects of this topic can be found in recent books [4-6]. 2.2 Photoinduced Electron- and Energy-transfer Processes It is well known that an electronically excited state obtained when a molecule absorbs light of suitable energy is a species with properties quite different from those of the ground-state molecule [7, 8]. In particular, an excited state can easily be involved in electron-transfer processes and it can also transfer energy to another molecule. For simplicity, we consider an A-L-B supramolecular system, where A is the light-absorbing molecular unit (Eq. 1), B is the other molecular unit involved with A in the light-induced processes, and L is a connecting unit (often called a bridge). In such a system the photoinduced electron- and energy-transfer processes can be indicated as in Eqs. (2-4): A-L-B -t- hv - *A-L-B photoexcitation *A-L-B - A+-L-B - oxidative electron transfer *A-L-B - A--L-B + reductive electron transfer *A-L-B - A-L-*B electronic energy transfer (2) (3) (4) In the absence of chemical complications (e.g. fast decomposition of the oxidized and/or reduced species), photoinduced electron-transfer processes are followed by spontaneous back-electron-transfer reactions that regenerate the starting ground state system (Eqs. 2' and 3'), and photoinduced energy transfer is followed by radiative and/or non-radiative deactivation of the excited acceptor (Eq. 4'): A+-L-B - - A-L-B back electron transfer (2') A--L-B + - A-L-B back electron transfer (3') A-L-*B - A-L-B excited state decay (4') 2.2.'1 Electron Transfer For photoinduced electron-transfer processes [9] the relevant excited-state thermo- dynamic properties are the reduction potentials for the couples A+/*A (Eq. 2) and *A/A- (Eq. 3). It should be recalled that, because of its higher energy content, an excited state is both a stronger reductant and a stronger oxidant than the corre- sponding ground state [7, 8]. To a first approximation

the redox potentials of the

2.2 Photoinduced Electron- and Energy-transfer Processes I 23 excited state couples can be calculated from the potentials of the ground state couples and the one-electron potential corresponding to the zero-zero excitation energy, as shown by Eqs. (5) and (6) [10]: E (A+/*A) E (A+/A) - E 0-0 (5) E(*A/A-) E(A/A-) + E �-� (6) Kinetically, electron-transfer processes involving excited states, and those involv- ing ground state molecules can be dealt with in the framework of the Marcus theory [11, 12] and of successive, more sophisticated theoretical modds [13-17]. Quantum mechanically both the photoinduced and back-electron-transfer pro- cesses can be viewed as radiationless transitions between different, weakly inter- acting electronic states of the A-L-B supermolecule. The rate constant of such processes is given by an appropriate Fermi "golden rule" expression: k d = (4r/h)(Hd)2FC d (7) where H d and FC d are, respectively, the electronic coupling and the Franck- Condon density of states. 2.2.1.1 The Electronic Factor In the absence of any intervening medium (through-space mechanism), the elec- tronic factor decreases exponentially with increasing distance: f fid H el= Hel(0)exp [--(rAB- r0)] (8) where tAB is the donor-acceptor distance, Hd(0) is the interaction at the "contact" distance r0, and fid is an appropriate attenuation term. The 1/2 factor arises because originally fid was defined as the exponential attenuation parameter for rate constant rather than for dectronic coupling (Eq. 9): kel oc exp(--?elrAB) (9) For donor-acceptor components separated by vacuum, fid is estimated to be in the range 2-5 A -. When donor and acceptor are separated by "matter" (in our example, the bridge L), the electronic coupling can be mediated by mixing of the initial and final states of the system with virtual, high energy electron-transfer states involving the intervening medium, as illustrated in Fig. 2.1a (superexchange mechanism) [13-18]. The second-order perturbation expression describing the superexchange cou- pling is: He 1 HiHf Hil, Hf (10) -

24 I 2 Fundamental Principles of Electron and Energ Transfer Hi/ H12 lllll lllll Fig. 2.1. State diagram illustrating the superexchange interaction between an excited state electron donor (*A) and an electron acceptor (B) through simple (a) and modular (b) bridges. In the second example only the electron-transfer virtual states of the bridge are shown. H3f lllll lllll where Hi, Hf, Hih, and Hfl, are the appropriate donor-bridge and bridge-acceptor coupling

elements (Fig. 2.1a), and AE and AEh are the energy differences between the virtual states and the initial or final state (these energy differences are taken at the transition state nuclear geometry, where the initial and final state have the same energy). From Eq. (10) it follows that readily reducible bridges are good electron-transfer mediators, and readily oxidizable bridges are good hole-transfer mediators. For modular bridges the superexchange model can be extended to involve virtual electron-transfer states localized on each modular unit, as shown schematically in Fig. 2.lb. For a system involving n identical modular units, Eq. (8) can be replaced by Eq. (11): Hel_ HiHnf (H2 n- (11) In such a case, an exponential dependence on number of modular units contained in the bridge is obtained, which translates into an exponential dependence

on donor-acceptor distance (measured along the bridge). Equations (8) and (11) can be related considering that r0 is the length increment associated with a single module, Ha(O) is the donor-acceptor coupling for a one-module bridge (HiiH,/AE), and the attenuation factor fia is a bridge-specific parameter which depends on the magnitude of the coupling between adjacent modules and on the energy of the electron- (or hole-) transfer states localized on each module.

2.2.1.2 The Nuclear Factor

The FC ei term of Eq. (7) is a thermally averaged Franck-Condon factor connecting the initial and final states. It contains a sum of overlap integrals between the nuclear wavefunctions of initial and final states of the same energy. Both inner and outer (solvent) vibrational modes are included. The general expression of FC el is quite complicated [13, 14]. It can be shown [12] that in the high temperature limit (by < kBT) an approximation sufficiently accurate for many room temperature processes, the nuclear factor takes the simple form: FCel=k,4j exp[-k -] (12) where ,t is the sum of the inner (,ti) and outer (,to) reorganizational energies. The exponential term of Eq. (12) is the same as that predicted by the classical Marcus model [12] based on parabolic energy curves for initial and final states. Both classical and quantum mechanical models contain an important prediction, namely that three distinct kinetic regimes exist, depending on the driving force of the electron-transfer process: � a normal regime for small driving forces (-,t < AG � < 0) in which the process is thermally activated and its rate increases with increasing driving force; � an activationless regime (-,t AG �) in which a change in the driving force does not cause large changes in the reaction rate; � an "inverted" regime for strongly exergonic processes (-,t > AG �) in which the rate of the process decreases with increasing driving force. The three kinetic regimes are shown schematically in terms of the classical Marcus parabolae in Fig. 2.2, where the difference between the predictions of the dassical and quantum mechanical models in the inverted region (parabolic or linear decrease ofln ke with increasing driving force) is also sketched [19]. 2.2.2 Energy Transfer The thermodynamic ability of an excited state to intervene in energy-transfer pro- cesses is related to its zero-zero spectroscopic energy, E �-�. The energy-transfer process must obey energy conservation and requires some kind of electronic inter- action between donor and acceptor.

26 I 2 Fundamental Principles of Electron and Energy Transfer AGo<-. AGo=-. -.<AGO<0 i f i f i J f iIl1 - 0 AG o -I- Fig. 2.2. Free energy dependence of electron-transfer rate (i, initial state;f, final state) according to classical (a) and quantum mechanical (b) treatments. The three kinetic regimes (normal, activationless, and "inverted") are shown schematically in terms of Marcus parabolae. Energy transfer in a supramolecular system can be viewed as a radiationless transition between two "localized" electronically excites states (Eq. 4). The rate constant can, therefore, be again obtained by use of an appropriate "golden rule" expression: = (4/h)(4e)2Fc 03) where H en is the electronic coupling between the two excited states interconverted by the energy-transfer process and FC en is an appropriate Franck-Condon factor. 2.2.2.1 Coulombic Mechanism The electronic factor H en is a two-electron matrix element involving the HOMO and LUMO of the energy-donor and energy-acceptor components. By following standard arguments [7, 8, 15, 16, 20], this factor can be split into two additive terms, a Coulombic term and an exchange term. The two terms depend differently on the parameters of the system (spin of ground and excited states, donor-acceptor distance, etc.) and each can become predominant depending on the specific system and experimental conditions. The orbital aspects of the two mechanisms are rep- resented schematically in Fig. 2.3. The Coulombic (also called resonance, F6rster-type [21], or through-space) mechanism is a long-range mechanism that does not require physical contact

2.2 Photoinduced Electron- and Energy-transfer Processes I 27 o LUMO � oo HOMO Fig. 2.3. o LUMO �+ oo HOMO Coulombic mechanism Energy transfer LUMO LUMO HOMO 0 --00 HOMO Exchange mechanism Pictorial representation of the Coulombic and exchan�e ener��-transfer mechanisms, � � � between donor and acceptor. It can be shown that the most important term within the Coulombic interaction is the dipole-dipole term [21], which obeys the same selection rules as the corresponding electric dipole transitions of the two partners (*A - A and B - *B, Fig. 2.3). Coulombic energy transfer is therefore expected to be efficient in systems in which the radiative transitions connecting the ground and the excited states of each partner have high oscillator strength. The rate constant for the dipole-dipole Coulombic energy transfer can be expressed as a function of the spectroscopic and photophysical properties of the two molecular components: keFn = $.$ X 10 -2s n4rrA6- JF (14) where 4 d JF = (15) where K is an orientation factor which takes into account the directional nature of the dipole-dipole interaction (K2= 2/3 for random orientation), (I) and r are, respectively, the luminescence quantum yield and lifetime of the donor, n is the solvent refractive index, rAB is the distance (in A) between donor and acceptor, and JF is the F6rster overlap integral between the luminescence spectrum of the donor, F(V), and the absorption spectrum of the acceptor, (V), on an energy scale (cm-).

28 I 2 Fundamental Principles of Electron and Energy Transfer With a good spectral overlap integral and appropriate photophysical properties, the 1/r^B 6 distance dependence enables energy transfer to occur efficiently over distances substantially exceeding the molecular diameters. A typical example of an efficient Coulombic mechanism is that of singlet-singlet energy transfer between large aromatic molecules, a process used by Nature in the antenna systems of the photosynthetic apparatus [22]. 2.2.2.2 Exchange Mechanism The exchange (also called Dexter-type [23]) mechanism requires orbital overlap between donor and acceptor, either directly or mediated by the bridge (through- bond) and decay is, therefore, exponentially dependent on distance. The exchange interaction can be regarded (Fig. 2.3) as a double electron-transfer process, one electron moving from the LUMO of the excited donor to the LUMO of the acceptor, and the other from the acceptor HOMO to the donor HOMO. This important insight is illustrated in Fig. 2.4, from which it is clear that the attenuation factor flex for exchange energy transfer should be approximately equal to the sum of the attenuation factors for two separated electron-transfer processes, i.e. fie for elec- tron transfer between the LUMO of the donor and acceptor, and fiht for the elec- tron transfer between the HOMO (superscript ht denotes hole transfer from the donor to the acceptor).

This prediction has been confirmed by experiments [24]. The spin selection rules for this type of mechanism arise from the need to obey spin conservation in the reacting pair as a whole. This enables the exchange mechanism to be operative in many instances in which the excited states involved are spin-forbidden in the usual spectroscopic sense. Thus, the typical example of an efficient exchange mechanism is that of triplet-triplet energy transfer. Although the exchange mechanism was originally formulated in terms of direct overlap between donor and acceptor orbitals, it is clear that it can be extended to coupling mediated by the intervening medium (i.e. the connecting bridge), as discussed above for electron-transfer processes (superexchange mechanism) [20, 25]. 2.2.3 Role of the Bridge The discussion above underlines the important role played by the connecting units (bridges) in the mediation of electron- and energy-transfer processes between donor and acceptor components in supramolecular structures [26, 27]. As a colloquial way of emphasizing this role, it has become customary to consider bridges as "molecular wires" and to talk of their "conducting" properties. It should be remarked, however, that in the superexchange mechanism the bridge levels are always much higher in energy than those of donor and acceptor, so the electron tunnels in a single step from donor to acceptor and the rate of the process varies according to Eq. (9). Electron transfer through such bridges is, therefore, not comparable with electron transfer in macroscopic systems where the electron really moves along the wire. It might happen, however, that the energy level of the bridge is so low that it becomes intermediate between the initial and final states. In such

E hv E h� b Fig. 2.5. Representation of sequential donor-to-bridge-to-acceptor electron transfer (a) and energy transfer (b) hopping mechanisms. cases, electron hopping occurs (Fig. 2.5a) and the bridge is directly involved in the process. A similar situation can also be encountered for energy-transfer processes (Fig. 2.5b). When such a hopping-type mechanism is operative, very small distance dependence of the rate constants is expected [28-32]. If each single hopping step occurs over the same distance the rate constant is inversely proportional to a small power of the number of hopping steps, N: 1-2 (16) Finally, when there is complete mixing among the donor/bridge/acceptor orbitals (large coupling limit [28, 32, 33]) the bridge essentially acts as an incoherent molecular wire, as happens for conjugated conducting polymers [34], and the sys-

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3 Wires and Related Systems 3.1 Introduction The simplest component of an electrical circuit is a wire, and the design of elec- tronic wires at the molecular level has received great attention since the principle of a single molecule acting as an electrical conductor was first put forward in 1974 [1]. A variety of wire- or rod-type supramolecular compounds has been synthesized in the last few years [2, 3]. Although the term "molecular wire" is generally taken to mean a long, highly conjugated molecule (Fig. 3.1), most of the studies have been performed on relatively short, nonconjugated structures which have proven useful for connection of electrodes or photo- and/or redox-active molecular com- ponents. Suitable wire-type compounds have also been used to transfer electronic energy (molecular photonic wires) instead of electrons. In a few instances, electron conductivity has been determined directly by current-voltage measurements on molecular wires connected with two electrodes. Otherwise, rate constants have been measured for electron-transfer reactions across bridging groups connecting: � dectroactive units to metal electrodes, � photoactive units to semiconductors, and, most often � photoactive units to electron acceptors/donors. In agreement with the scope and limitations of this book, we will treat the first two topics only briefly, whereas the third will be discussed in more detail. 3.2 Conductivity Measurements In the past few years extensive efforts have been devoted to measurement of the electronic conductivity of molecular thin films, small ensembles of molecules, down to the limit of a single molecule. The key point of such experiments, which is also a fundamental requirement of molecular electronics [4], is wiring molecules into an electrical circuit. In single-molecule measurements this implies bonding Molecular Devices and Machines - A Journey into the Nano World. V. Balzani, A. Credi, M. Venturi Copyright � 2003 WILEY-VCH Verlag GmbH

& Co. KGaA, Weinheim ISBN: 3-527-30506-8

3.2 Conductivity Measurements I 35 each end of the molecule to a metal conductor. This conceptually straightforward goal is, in practice, difficult to achieve because there can be problems obtaining good and unambiguous contacts [5]. A variety of methods has been used to link molecules to electrodes with the purpose of investigating their conductivity, these include: � probing conjugated molecules inserted into a self-assembled monolayer (SAM) by scanning tunneling microscopy (STM) and related methods [6], � bonding dithiolate molecules on to the two facing gold tips of a break junction [7], � inserting an SAM between two metal electrodes of nanoscale area [8], � dipping nanotubes into a mercury pool with the tip of a scanning probe micro- scope [9], � touching molecules with a conducting atomic force microscope (AFM) [10], � contacting two monolayers together with a mercury-drop electrode [11], � combining a monolayer on a gold surface with gold nanoparticles and AFM [12]. The last technique is, apparently, very reliable. In a recent example, a self- assembled monalayer of octanethiol molecules on a gold electrode was first ob- tained. Some molecules were then replaced by 1,8-octanedithiol molecules, which are capable of chemical bonding to gold at both ends (Fig. 3.2a). The thiol groups at the top of the film of the 1,8-octanedithiol molecules were derivatized by incu- bating the monalayer with a suspension of gold nanopartides (diameter < 2 nm), and a gold-coated conducting AFM probe was then used to locate and contact individual particles bonded to the monalayer. Current-voltage measurements on SSSSSSSS Fig. 3.2. (a) Schematic representation of an experimental arrangement for measurement of the conductivity of a single molecule [12]. (b) A SAM system for investigation of electron transfer between ferrocene units and a gold electrode separated by an aliphatic chain [19].

36 I 3 Wires and Related Systems more than 4000 nanoparticles produced only five distinct families of curves, which correspond to integer multiples of one fundamental curve, assigned to single- molecule contacts. The resistance of a single octanedithiol molecule was found to be 900 Mf, with good reproducibility, whereas the resistance of octanethiol mole- cules (which are chemical bonded at one end only) was at least four orders of magnitude higher

and less reproducible [12]. A series of systematic studies has been conducted on the design [13] and synthesis [3b,o, 41] of oligophenylene- and oligo(phenylene ethynylene)-type mole- cules that could be mounted within addressable scaffolds [14]. In collaboration with physicists and electrical engineers, it has been possible to demonstrate that such molecular wires indeed conduct electrical currents [30, 41, 6-8]. With appro- priate modifications of the molecular structure, more complex current-potential responses were obtained, showing that these devices can also be used to switch electrical signals (Chapters 4 and 9). 3.3 Electron-transfer Processes at Electrodes Electrochemical techniques are particularly well suited to the study of long-range electronic coupling and electron transfer between metal electrodes and attached redox molecules. The organization of monolayers on electrodes, which can be achieved in a spontaneous manner (SAM) with suitable electrode surfaces and compounds, provides a general route to the creation of surface structures in which redox-active molecules can be linked to electrodes via well-defined molecular bridges [15, 16]. These monolayer-based structures can serve as excellent model systems for studying bridge-mediated electron transfer [17] and can also be useful for analytical purposes (e.g. metal-ion sensors [18]). The most extensively studied redox unit in SAM is ferrocene, owing to its reversible redox behavior and the synthetic accessibility of its derivatives. Pioneer- ing work in this field [19] was performed more than 10 years ago on SAM formed on a gold electrode by ferrocene-terminated hexadecylthiolate chains diluted with excess hexadecylthiol (Fig. 3.2b). The kinetics of electron transfer, measured by monitoring the chronoamperometric responses of the SAM system to a range of potential step perturbations, could be quantitatively explained by use of Marcus theory. Many studies have focussed on the distance dependence of heterogeneous electron-transfer rates; this is expected to change as exp(-fir) (Section 2.2.3), where fi is the attenuation factor and r is the donor-acceptor separation. For bridges containing between three and six phenylethynyl units, corresponding to estimated electron-transfer distances between 2.2 and 4.3 nm, a good linear corre- lation was obtained with a fi value of 0.36A - [20], much lower than that found (1 A -1) for aliphatic bridges [15, 21, 22]. The extrapolated rate constants at short distance were almost the same for the conjugated and aliphatic bridges and agreed with a calculated rate constant for the limiting case of adiabatic electron transfer at an electrode [20].

Similar results have recently been obtained for electron transfer through oligo- phenylenevinylene bridges between a gold electrode and a tethered ferrocene unit [23]. Analysis of the distance dependence indicates that the electron-transfer rate constants are not limited by electronic coupling for bridges up to 28 A long. Interestingly, it has been found that a Pt(II)-acetylene complex anchored to two gold electrodes through two sulfur bridges behaves as a single-molecule insulator [24]. 3.4 Photoinduced Electron Transfer Photoinduced electron transfer in wire-type supramolecular species has been extensively investigated in the last fifteen years. This field is very broad and is tra- ditionally subdivided into subfields for both scientific and traditional reasons. Work performed before 1991 has been reviewed elsewhere [25]. Many papers have since appeared and several more recent reviews dealing with specific subfields have been published (see later). For the sake of space, we will illustrate only a few examples of well characterized, rigid modular systems where photoinduced electron transfer can occur over long distances. 3.4.1 Covalently Linked Systems Containing Metal Complexes Many bi- and polymetallic systems capable of performing photoinduced electron transfer have been designed and investigated [26]. A systematic study has been performed on compounds 15+-55+ (Fig. 3.3). Although the photochemical behav- ior of such compounds is complex [26h,i], when excitation is selectively performed in the Ru(II) chromophoric unit prompt intersystem crossing from the originally populated singlet metal-to-ligand charge-transfer (4 MLCT) excited state leads to the long-lived 3MLCT excited state which transfers an electron to the Rh(III) unit, a process that is then followed by a back electron-transfer reaction. Comparison of compounds 15+ and 25+ shows that, despite the longer metal-metal distance, forward electron-transfer is faster across the phenylene spacer (k = 3.0 x 109 s -) than across the methylene spacer (k = 1.7 x 108 s-). This result can be related to the lower energy of the LUMO of the phenylene group, which facilitates superexchange interaction (Eq. 2 in Chapter 2). In the homogeneous family of compounds 25+-45+ the rate constant decreases exponentially with increasing metal- metal distance (Fig. 3.4), yielding a fi value of 0.5A -, which is much lower than that found for rigid saturated bridges (0.8-1.2A -) [27], and similar to that obtained for electron transfer between porphyrins across oligophenylene spacers [28]. For compound 55+, which is identical with 45+ except for the presence of two solubilizing hexyl groups on the central phenylene ring, the photoinduced elec- tron-transfer process is 50 times slower

(Fig. 3.4), presumably because the sub- stituents increase the twist angle between the phenylene units, thereby reducing

38 I 3 Wires and Related Systems N--RuU"N x)--x ', : - 15+ :/ / ,, :/ __</ N__Rhm..N ' x) 25* k= 1.7 x 10 8 S -1 k= 3.0 x 10 9 s '1 35+ k= 4.3 x 10 s S -1 45+ 5 5+ Fi�. 3.3. Binuclear metal complexes ls+-5 s+, used for photoinduced electron-transfer experiments [26i]. k= 3 x 10 7 S -1 k= 1.1 x 10 8 S '1

3.4 Photoinduced Electron Transfer I 39 10 8 4 3 + e 4 + 5 5+ � 2 I I I I I 15 20 25 30 35 r(A) Fig. 3.4. Distance-dependence of the electron-transfer rate constant for the compounds shown in Fig. 3.3. 40 electronic coupling. The electronic connectivity of oligophenylene bridges has also been investigated by intramolecular electron-transfer studies on mixed-valence organic systems [29]. Interestingly, poly-p-phenylene oligomers can be threaded through macrocycles which could play the role of "insulating sheaths" [31]. Hybrid organic/inorganic donor-acceptor species are also very popular com- pounds for electron-transfer studies. For instance, transition metal complexes of the polypyridine family covalently linked to 4,4'-bipyridinium-type electron accept- ors have been widely used to investigate fundamental aspects of electron-transfer processes [30]. Compounds 66+ and 76+ (Fig. 3.5) have recently been synthesized and studied [31], primarily to function as wires for light-driven rotaxane-type molecular machines (Chapter 15). In both compounds a photoinduced electron- transfer process occurs from the 3MLCT excited state of the [Ru(bpy)3] 2+-type unit to the A electron-acceptor. The relatively small difference between the rate con- stants (2.4 x 105 and 5 x 105 s -1, respectively, for 66+ and 76+ in acetonitrile at room temperature), despite the large difference between the distances from the Ru(II) donor to the A acceptor in the two compounds, suggests that a stepwise mechanism involving the A2 unit operates for electron transfer in 66+ (Fig. 3.5). For compound 66+ the back electron transfer is remarkably slow (time constant 1.2 ts), because it lies in the Marcus inverted region, and because the donor and acceptor are separated by a long and rigid spacer. 3.4.2 �ovalently Linked Systems Based on Organic Compounds Most investigations on photoinduced electron transfer have been performed on covalently linked systems based on organic compounds. Several recent reviews [27, 32], including one which is outstanding [27], can be consulted for a detailed

40 I 3 Wires and Related Systems e- --+- Me 6 ' N+ „ ' T' - Nv+. Me -T / e- f ' Fig. 3.. Photoinduced electron-transCer processes in compounds 6 + and 7 + made oCa Ru(11) complex linked to bipridinium-pe electron acceptors [3]]: 7, photoinduced eleron transCer to the prima acceptor; 2, thermal electron transCer to the seconda acceptor; 3, back electron transCer. discussion of the different aspects of this topic (through-bond compared with through-space transfer, interference effects in through-bond coupling, orientation effects, modulation of electron-transfer dynamics by electric fields, etc.). Particularly interesting is the behavior of the recently investigated family of compounds 8-12 (Fig. 3.6a) in which the photoinduced electron-transfer process switches from tunneling (superexchange) to molecular-wire behavior [33]. These systems comprise a tetracene (TET) donor and a pyromellitimide (PT) acceptor, both covalently linked to p-phenylenevinylene oligomers of increasing length, ranging from one aromatic ring (8) to five (12). Rates of photoinduced electron transfer from the locally excited state of TET to PT were measured in methylte- trahydrofuran. Two distinct types of electron-transfer behavior were observed (Fig. 3.6b). For the two shortest bridges the electron-transfer rate falls quite strongly with a fi value of approximately 0.4A -, behavior consistent with the operation of the superexchange mechanism through aromatic bridges. There is, however, an abrupt change in mechanism beginning with 10, for which the electron-transfer rate is greater than that of 8, even if the bridge in the former system is 13 A longer than that in the latter. The extremely weak distance dependence of the electron-

3.4 Photoinduced Electron Transfer I 41 = --N N'CsH17 b 12- 10 �8 switchover of electron transfer from superexchan�e to molecular-wire behavior [33]. (b) Distance dependence of the electron-transfer rate constant. �9 10 10 20 30 40 r(A) Fi�. 3.6. (a) Compounds 8-12 used to investi�ate the

42 I 3 Wires and Related Systems transfer rates observed for the longer members of the series 10-12 can, moreover, be interpreted in terms of molecular wire behavior (Section 2.2.3), because the LUMO of the bridge approaches that for the locally excited TET chromophore and injection of a TET electron into the bridge becomes energetically possible. 3.4.3 Covalently Linked Systems Containing Porphyrins Because of their widespread occurrence in photosynthetic reaction centers and other biological electron-

transfer systems, porphyrin-type chromophores have played a leading role in the study of photoinduced electron-transfer processes. The work in this field has recently been reviewed [27, 34]. Most of the systems containing porphyrin units have been designed not so much for obtaining a fast rate of photoinduced electron transfer, but for generating a long-lived charge-separated state useful for solar energy conversion purposes (Sec- tion 6.3). A variety of multicomponent systems (dyads, triads, tetrads, pentads, hexads) has been studied and for complex compounds, e.g. the pentad shown in Fig. 3.7, it has been shown that charge separation occurs by sequential and parallel electron-transfer processes [35]. An interesting series of compounds is that con- stituted by the three dyads shown in Fig. 3.8. The porphyrin-quinone diad 13 [36] is a model compound for some aspects of electron transfer in the photosynthetic bacterial reaction center (Section 6.2). In 13, photoinduced electron transfer from the excited Zn porphyrin to the quinone unit occurs on a nanosecond time scale, showing that rigid hydrocarbon bridges are good mediators in long-range electron- transfer processes. The charge-recombination rate is approximately one order of magnitude smaller. In the Coo-based dyad 14 [37], the analogous photoinduced charge-separation process is very rapid in polar solvents (subnanosecond time scale), whereas the charge-recombination rate is exceedingly slow. In compound 15 [38], in which the chromophores present in 14 are linked by a single-strand flexible tether, the charge-separation process occurs at a comparable rate, but charge recombination is three orders of magnitude faster (Fig. 3.8). The faster rate for the forward reaction in compounds 14 and 15 compared with 13 is because of the nature of Coo which, owing to its curved surface, can couple with the bridge by means of many more atoms than a planar component, so that the Coo HOMO un- dergoes extensive delocalization into the bridge [39]. The huge difference in the rate for the back electron transfer for compounds 14 and 15 is attributed to orbital symmetry effects. Compound 14 is rigid and belongs to the Cs point group. Because the singlet charge-separated state has A" symmetry and the ground state has A' symmetry, the charge-recombination process is forbidden. In compound 15, however, the flexible nature of the tether removes the symmetry restriction and the process is more rapid. It has been pointed out [40] that the rates of electron-trans- fer processes involving fullerenes can be strongly influenced by the very small re- organization energies of these kinds of molecule. Recently the photoinduced electron-transfer process in a series of free-base porphyrin-oligothiophene-C00 compounds has been examined [41]. The distance

,(0=0 Z'T' ,(3,4 Photoinduced Electron Transfer I 43 (^) B

441 3 Wires and Related Systems 13 r,._. [Ar = phenyl J 0 kcs (s '1) kcr (s '1) 2.7xl 0 9 2.0xl 0 8 14 JAr = 3,5-di-t-butylphenyl I 1.0xl 010 2.4x10 6 Ar Fig. 3.8. Rates of photoinduced charge-separation (kcs) and subsequent charge-recombination (kcr) processes in dyads 13-15 [36-35]. 9.0x10 9 2.0x10 9 dependence of this process has been found to be weak, with an attenuation factor of approximately 0.11 A -. 3.4.4 DNA and Related Systems Although the principal biological function of DNA is not the transfer of electrons or holes, it is very important to know how fast such processes can occur in DNA for several reasons: � both oxidative damage and repair of DNA can involve processes in which an electron or hole migrates over extremely long distances (50 to 300A) [42-44]; � the unique features of recognition, assembly, and specific binding properties of the nucleobases are expected to be useful for the development of DNA-based molecular-level devices [45-47]; � elucidation of the mechanisms and dynamics of charge transfer in a well known structure such as DNA is of basic importance theoretically [48-50]; � the use of DNA as a data carrier provides the conceptual basis for DNA-based computing [51, 52].

3.4 Photoinduced Electron Transfer I 45 During the past decade, a wealth of investigations on photoinduced charge injec- tion, hopping, trapping, and recombination processes in intercalated, substituted, or capped DNA have revealed several important features of electron-transfer processes in DNA [53-55]. It should also be noted that the results obtained from studies of charge transport in DNA have often generated considerable controversy, not yet completely settled. According to the discussion presented in Section 2.2.3, the mechanism of elec- tron or hole transfer in DNA will depend largely on the relative energy levels of the bridge states (i.e. the DNA bases) and the initial state (donor state). If the bridge states are energetically higher than the initial state the electron or hole cannot reside in the bridge, and the charge transfer must occur by a superexchange mechanism, i.e. by a single coherent jump from donor to acceptor. In such cir- cumstances the charge-transfer dynamics will follow an exponential decay with distance according to Eq. (1) (Section 2.2.3): k oc exp(-fir) (1) When, on the other hand, the bridge and donor levels are similar, thermal injection of an electron or hole into the bridge might occur, and the transport will occur by a hopping mechanism for which, as discussed in Section 2.2.3, distance dependence is weak, varying inversely with a small power of the distance: k oc N-'; r/ 1-2 (2) where N is the number of hopping steps. Because of its exponential distance dependence, superexchange-mediated electron and hole transfer in DNA should not be significant for donor-acceptor separation distances exceeding 15 A, whereas a hopping-transfer mechanism can enable much longer range processes, extending beyond 50A. From this discussion it follows that the composition and sequence of the base pairs in DNA should have an important effect. In this regard it is important to notice that guanine (G) is much more readily oxidized than adenine (A), thymine (T) or cytosine (C), and that T and C are more easily reduced than G and A [55]. Consequently, hole injection into the DNA helix will generate a G + cation, and electron injection should involve T or C. Electron injection is, however, much more difficult than hole injection, so investigations have largely focussed on hole injection. Very interesting results have been obtained by using synthetic duplex DNA molecules [43, 56, 57]. When the G + cation has been generated three or four AT base pairs separating G + from a GGG trap site (GGG has a lower oxidation poten- tial than G) are sufficient to totally inhibit oxidative cleavage at the trap site. For the sequences schematized in Fig. 3.9, a plot of In ke against In N yields a /value of 1.7, and fitting the data by a straight line according to Eq. (1) (superexchange mechanism) leads to an unrealistic fi value of 0.07A -. Oxidative cleavage could, furthermore, be observed over much longer distances when a combination of AT and GC base pairs separated the G + and GGG sites. For example, more efficient

51 3 I c G C G C G 51 3 I c G C G C G 51 3 I c G C G C G C C G C G r (A) = kre I = C G + C G + C G + a b c 1 2 4 10 20 40 8.9 2.8 0.88 3 a r/= 1.7 o c 10 20 30 40 "',= r (A) c 0.0 0.5 1.0 1.5 InN Fig. 3.9. Charge transfer (indicated by the arrows) from G + to GGG in DNA involving one (a), two (b), and four (c) hopping steps [56c]; krel is the relative rate constant of charge transfer, evaluated from the oxidative damage at the GGG unit.

cleavage at GGG was observed for a four-base-pair sequence containing a single GC pair than for a three-base-pair sequence containing only AT base pairs. These and other results [43] suggest that the hole can hop incoherently among G bases in a random walk which gives rise to a weak algebraic decay of the rate with distance. Moving the electron from one G unit to the next, however, requires operation of the superexchange mechanism. The higher the density of G bases along the hole- transfer pathway, the faster will be the rate of the process and the further the hole will be able to travel. Very long-distance charge transport is possible because the total distance is split and the largest step becomes rate-determining. With a judi- cious placement of G units, charge transfer has indeed been observed to occur rapidly over distances exceeding 54A. Recent molecular dynamics simulations [58] of DNA embedded in water have provided evidence that the effective electronic coupling between donor and acceptor undergoes large fluctuations, with the qua- dratic average one order of magnitude larger than its mean value. Thus fluctua- tions seem to be the main source of coupling between donor and acceptor. Partic- ularly important is transverse motion of the DNA strands, whereas longitudinal motions are surprisingly ineffective [58]. Investigation of the effect of different ion distributions on long-range DNA charge transport has suggested that the longitu- dinal polarizability of DNA can be an important factor in the transport mechanism [59]. As far as electron transfer is concerned, because T and C should be involved, and one of these is present in each base pair, it has been argued that the process should occur over very large distances and should not be sequence-dependent [56c, 60]. Indeed, it has recently been shown [61] that a single electron can move through a DNA duplex over a distance of 24 A with rather weak distance depen- dence (fi 0.1 A-l), indicating that a hopping mechanism is involved. 3.5 Heterogeneous Photoinduced Electron Transfer In the field of materials science, increasing attention is being devoted to systems of smaller and smaller dimensions. For a variety of metals and metal oxides, particles of controlled nanometer size can be prepared, functionalized, and assembled [62]. Coupling molecular or supramolecular compounds with nanoparticles leads to the so-called heterosupramolecular systems [63]. In such systems, individual nano- particles play the role of additional components of supramolecular assemblies; for example, they can be photoexcited or they can donate or accept electrons. Most investigations in this field have been concerned with spectral sensitization of wide band-gap semiconductors for solar energy conversion [64, 65] (Section 6.5.) Although most of the heterosupramolecular systems investigated so far from the viewpoint of photoinduced electron transfer are dyads, heterotriads based on nanocrystalline TiO2 have also been studied [66]. Fig. 3.10 shows schematically one of the systems investigated [66e]. Photocurrent action spectra showed that light absorption by the Ru complex leads to electron injection into the semiconductor.

4 Fig. 3.10. Schematic representation of photoinduced electron transfer in a heterotriad [66e]: 7 and 2 are the two sequential processes leading to charge injection; 3 is primary recombination; 4 is back electron transfen One third of the photoexcited Ru units undergo direct electron injection into TiO2, presumably because of different orientation at the surface or accidental contacts in small cavities, whereas for the other species the stepwise charge-injection pro- cesses indicated in Fig. 3.10 are observed. Step I has a lifetime of 30 ns and Step 2 of 0.3 ns. Step 2 is 40 % efficient because of competing primary recombination (Step 3). The back electron-transfer reaction from reduced TiO2 to oxidized Ru complex (Step 4) is remarkably slow (ls to ms time scale). 3.6 Energy Transfer Many investigations of electronic energy transfer in supramolecular species have been performed in the past few years. Work performed before 1991 has been reviewed elsewhere [25]. Several more recent reviews have also appeared [26, 27, 34d,e]. The most interesting compounds are those with a rod-like structure. For brevity we will illustrate only a few examples of rigid, modular, well characterized systems for which energy transfer can occur over long distances. 3.6.1 Covalently Linked Systems Containing Metal Complexes Most of the systems in which energy transfer has been investigated contain poly-pyridine metal complexes as donor and acceptor units [26]. Usually, the photo-excited chromophoric group is [Ru(bpy)3] 2+ (bpy = 2,2'-bipyridine) and the energy acceptor is an [Os(bpy)3] 2+ unit. The excited state of [Ru(bpy)] 2+ playing the role of

energy donor is the lowest, formally triplet, meta]-to-]igand charge-transfer excited state, 3MLCT, which can be obtained by visible light excitation (tmax 450 lies 2.1 eV above the ground state, and has a lifetime of 1 Is in aleaerated solutions [67]. This relatively long lifetime is very useful because it enables study of energy transfer over long distances. The occurrence of the energy-transfer pro- cess promotes the ground state [Os(bpy)3] 2+ acceptor unit to its lowest energy ex- cited state 3MLCT, which lies approximately 0.35 eV below the donor excited state. Both the donor and the acceptor excited states are luminescent, so that the occur- rence of energy transfer can be monitored by quenching and/or sensitization experiments with both continuous and pulsed excitation. Ru(II) and Os(II) polypyridine units have been connected by a variety of bridging ligands and spacers. When the metal-to-metal distance is very short, fast energy transfer occurs by a Fbrster-tye resonance mechanism (Section 2.2.2). In other systems the two photoactive units are separated by a more or less long spacer. When the spacer is flexible (e.g. -(CH2),- chains), the geometry of the system is not well defined and it is difficult to rationalize the results obtained. The most interesting systems are those in which the two chromophoric units are connected by rigid, modular spacers, e.g. the [Ru(bpy)3]2+-(ph),-[Os(bpy)3] 2+ (ph = 1,4- phenylene; n = 3, 5, 7) compounds 164+-184+ shown in Fig. 3.11a [68]. In such compounds excitation of the [Ru(bpy)3] 2+ moiety is followed by energy transfer to the [Os(bpy)3] 2+ unit, as shown by the sensitized emission of the latter (CH3CN , 293 and 77 K). The energy-level diagram is shown in Fig. 3.1lb. The rate of the energy-transfer process is almost temperature-independent and decreases with increasing length of the oligophenylene spacer (at 293 K, k = 6.7 x 108, 1.0 x 10 7, 1.3 x 10 6 s -1 for n = 3, 5, and 7, respectively). It can be shown that such rate con- stants are much higher than those expected for a F6rster-type mechanism, whereas they can be accounted for by a superexchange Dexter mechanism, as suggested by the linear plot obtained for the dependence ofln k on metal-to-metal distance. The attenuation coefficient per interposed phenylene unit is 1.5, and the fl value is 0.32 A -. In compounds 164---184-- , the lowest excited state of the spacer decreases slightly in energy as the number of phenylene units is increased, but always lies above the donor and acceptor levels involved in energy-transfer (Fig. 3.1lb). A fur- ther decrease in the energy of the triplet excited state of the spacer would be expected to switch the energy-transfer mechanism from superexchange-mediated to wire-like, similar to what happens for photoinduced electron transfer (Section 2.2.3). When the polyphenylene bridge is replaced by an anthracene-based bridge (compound 194-- in Fig. 3.12), the lowest excited state of which lies in between the 3 M LCT excited states of the Ru(I I) and Os(I I) chromophoric units, energy transfer occurs by a cascade hopping mechanism in acetonitrile at room temperature [69]. Similar systems with ethynylated aromatic spacers have also been described [26g, 70]. When the anthracene unit of compound 19 4+ is oxidized to its endoperoxide derivative, the aromatic character of the bridge is strongly reduced and its lowest triplet excited state moves to much higher energy. As a consequence the rate

50 I 3 Wires and Related Systems a I hox, I '[6 4+ CN- -,II - - Ix'- / rRu_Os: 24 A _ _- ' ,, /-N rRu_O$ = 32.5 A MLCT 20- T1 E (103 cm-1) 3 L 15- hv 10- O- [Ru(bpY)3] 2+ (Ph)n Fi�. 3.11. (a) Formulae o� rod-like, modular binuclear complexes]64+-]84+, and (b) ener�y-level dia�ram �or photoinduced ener�y transCer [68]. The ener�y oCthe lowest triplet state T oCthe oli�ophenylene linker is that estimated �or pentaphenylene. MLCT 3MLCT [Os(bpy)3] 2+ hV 1

19 4+ 20- (10 3 cm -) 15 10 MLCT 3M LCT hV h vT1 0 [Ru(bpy)3]2+ Anthracene Ener�y-level dia�ram for ener�y transfer in compound 194+ [69]. Fig. 3.12. 1MLCT '"1 3MLCT [Os(bpy)3]2+ of energy transfer from the Ru(II) to the Os(II) moiety decreases by a factor of 80 [69]. As discussed in Section 4.3, manipulation of the central unit of a three- component energy-transfer system such as 194+ lays the bases for on/off energy- transfer switching. The effect of the nature of the bridge on the rate of energy transfer is clearly demonstrated by the behavior of compounds 204+ [71] and 214+ [72] (Fig. 3.13) which have almost the same metal-to-metal distance. In compound 204+, in which the two metal-based units are linked by an aromatic bridge, energy transfer occurs with k > 5 x 1040 s - (butyronitrile, room temperature), whereas in compound 214+, in which the bridge is aliphatic, the rate constant is at least three orders of magnitude lower.

52 I 3 Wires and Related Systems 204+ 214+ ..N..R- .N...7 rRu- = 21 Fig. 3.13. Binuclear Ru(11)-Os(11) complexes 204+ and 214+ used to investigate the role of the bridge in energy-transfer processes [7], 72]. For compounds 224+ and 234+ (Fig. 3.14), in which the two chromophoric groups are separated by aliphatic spacers, the observed energy-transfer rate constants (2.0 x 107 and 8.8 x 106 s -1, respectively, in CH3CN at 293 K) can be accounted for by the F6rster mechanism [73]. Energy-transfer studies have also been performed on dinuclear and trinudear Ru(II)-Os(II) terpyridine complexes connected by a 2,5-bis(2,2':6',2"-terpyridin-4-yl)thiophene bridge [74]. 224+ R R R , :Rb. I' II)=o1 I I OI } 1o:(II -I :O.. N* i"N N' ! "N I R = CO2Me I � R R R R]R,',' I' II)=oll '}n--tl .Ol)Uo II -I N' i"N N' i "N Fig. 3.14. Binuclear Ru{1l)-Os{1l) complexes 224+ and 234+ used for energy-transfer studies [73].

3.6 Energy Transfer I $3 24 25 26 r~7 r11 r~16 Fig. 3.15. Excitation of the naphth�1 unit of compounds 24, 25, and 26 is followed by ener�� transfer to the benzo�1 �roup [75]. 3,6.2 Covalently Linked Systems Based on Organic Compounds In organic chromophoric units, energy transfer can occur from short-lived singlet or long-lived triplet excited states. For compounds 24-26 (Fig. 3.15), excitation of the naphthyl unit causes sen- sitized fluorescence of the acceptor benzoyl group [75]. As expected, the rate constant for energy transfer decreases with increasing distance (k = 4.0 x 10 9, 1.0 X 10 9, and 7.4 x 108 s - for 24, 25, and 26, respectively, in cydohexane at room temperature). Computational analysis has shown that both through-bond (Dexter) and through-space (F6rster) mechanisms are involved, with through-bond being dominant at short distances and through-space at long distances. On first inspection compound 27 (Fig. 3.16) could be considered to be made of naphthyl and anthracenyl units separated by a polyphenylene spacer [76]. On this basis one would expect the occurrence of an energy-transfer process, with the naphthyl unit playing the role of a donor and the anthracenyl unit playing the role of an acceptor, mediated by a superexchange mechanism, as occurs for the some- what similar compound 17 4+ (Fig. 3.11a). Comparison of the fluorescence proper- ties of 27 with those of model compounds of donor, acceptor, and spacer showed, however, that for compound 27 the energy level of the pentaphenylene spacer is, in fact, lower than that of the energy donor (Fig. 3.16). On should, therefore, think of comparing 27 with 19 4+, in which energy transfer from the donor to the acceptor occurs by hopping on the anthracene bridge (Fig. 3.12). In fact, the situation for compound 27 is also different from that of compound 19 4+, because the energy levels of the naphthyl donor and of the pentaphenylene spacer are very dose and state mixing occurs, as indicated by the photophysical properties of a dyad made of naphthyl and pentaphenylene units. More correct interpretation of the energy-transfer process responsible for the complete quenching of the fluorescence of the naphthyl and pentaphenylene units and of the corresponding sensitization of the anthracenyl fluorescence is as follows: the excitation energy is delocalized in the naphthyl-pentaphenylene moiety, as in a giant chromophore (molecular wire behavior, Section 2.2.3), and is then trapped (hopping step) by the anthracenyl unit [76]. In other words, the situation is comparable with that observed for electron transfer in compounds 10-12 (Fig. 3.6), discussed in Section 3.4.2. There is ample documentary evidence that both singlet-singlet and triplet- triplet energy transfer can occur over substantial distances by an exchange

54 3 Wires and Related Systems 3O E (103 cm -'1) 25 2O 15 Fig. 3.16. Sl S1' Sl i T 1 hv" Naphthalene (Ph)5 Anthracene Ener�y-level dia�ram �or ener�y transCer in compound :27 [76]. through-bond mechanism in rigid systems containing a donor and an acceptor linked by rigid aliphatic bridges [25, 77-79]. As expected for a through-bond mechanism (Section 2.2), the rate constant is highly exponentially distance depen- dent, with an experimentally determined attenuation coefficient fi in the range 2-2.5 per bond. For example, a value offi 2 per bond was obtained for singlet- singlet energy transfer in the dimethoxynaphthalene-bridge-ketone compounds 28 and 29, in which (Fig. 3.17) the donor and acceptor units are separated by 4 and 6 bonds, respectively [80]. Such a fi value is about twice that found for electron transfer in structurally related compounds, as expected from the postulate that an exchange energy transfer can be viewed as the occurrence of two separated electron-transfer processes (Section 2.2.2.2). Extrapolation of these results would lead to an expected rate of 10 s s - for energy transfer in a compound in which the donor and acceptor units are sepa- rated by ten bonds (12.5A). Quite surprisingly, it has been reported that the

3.6 Energ Transfer I $$ E hv ' OCH3 OCH3 ',hv ' k= 1.2x101� S '1 k= 1.9x10 s S '1 E OCH3 ' ' hv' k = 2.5x10 TM s '1 Fi�. 3.17. Excitation of the dimethoxynaphthalene unit of compounds 28, 29, and 30 is followed by ener�� transfer to the ketone unit [SO, $1]. singlet-singlet energy transfer in compound 30, in which the donor and acceptor units are separated by ten bonds, occurs with the rate constant 2.5 x 1040 s - [81]. The presence of (constructive) interference effects has been invoked as a possible explanation of such an extremely high rate [82]. 3.6.3 Covalently Linked Systems Containing Porphyrins Porphyrin-type chromophores are excellent units not only for electron-transfer, but also for energy-transfer processes. In this regard, the compounds most used are Zn porphyrin and free base porphyrin [34, 83]. The lowest singlet excited state of the former lies approximately 1600 cm - above the lowest excited state of the latter. An excellent example of molecular photonic wire is given by compound 31 shown in Fig. 3.18 [84]. A boron-dipyrromethene dye is excited by 485 nm light and the excited state so obtained transfers energy to the nearby Zn porphyrin. Energy then migrates along the linear array and is transmitted to the free base porphyrin placed at the end of the wire, which emits red light fluorescence. The array is 9 nm long and the quantum yield of energy migration from input to output is estimated to be 76 %.

It has been shown that stepwise energy transfer by the F6rster mechanism could account for less than 6 % efficiency from input to output, suggesting that the diarylethyne linkers play an important role in mediating the energy-transfer process. Several related systems have also been investigated. By using simpler model compounds it has been shown that the

References [51 rate constant for energy transfer from Zn porphyrin to free base porphyrin is 4.2 x 1040 s - [85]. Compound 32 (Fig. 3.18) [86] contains a perylene input unit, a bis(free base porphyrin) transmission unit, and a free base phthalocyanine output unit. Excita- tion at 490 nm, where the perylene absorbs preferentially, results in fluorescence almost exclusively from the phthalocyanine (with a quantum yield of 0.78). Energy transfer is very rapid, because the excited phthalocyanine is formed with time constants of 2 ps (90 %) and 13 ps (10 %). 3.6.4 DNA and Related Systems As discussed in Section 3.4.4, photoinduced electron transfer along DNA wires has been extensively investigated. Most investigations of energy transfer in DNA and related structures have focused on the use of this technique as a spectroscopic ruler [87] and in DNA sequencing and analysis [88]. Long range triplet energy transfer between metallointercalators tethered to opposite ends of DNA duplexes has been investigated [89]. The intercalated species were Ru(II) and Os(II) polypyridine-type complexes containing a 7,8-dimethyl-(dipyridophenazine) ligand. Quenching of the luminescence of the Ru complex was accompanied by sensitization of the luminescence of the Os complex, although the occurrence of electron-transfer quenching could not be excluded. A plot of a logarithmic function of the yield of quenching of the Ru emission as a function of distance had a slope of -O.1A -, suggesting that DNA is a good mediator for energy transfer. Energy transfer between Ru(II) and Os(II) polypyridine complexes covalently bound to synthetic DNA duplexes has also been investigated [90]. In another investigation, three different fluorophores (a fluorescein, F, a rhodamine, R, and a cyanine, C, derivatives) have been covalently linked to a single stranded DNA molecule [91]. Excitation of the F unit at 488 nm is followed by emission from F (525 rim), R (585 rim), and C (670 nm), with 99 % of quenching of the original emission of F and predominant emission from C. Systems of this type can be used for biological labeling and imaging. References A. AVIRAM, M.A. RATNER, Chem. Lett.,

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641 4 Switching Electron- and Energy-transFer Processes 4.1 Introduction The

expression "molecular-level switch" usually has two distinct meanings [1-3]. The first definition is a molecular-level device, incorporated in a molecular-level wire, that can reversibly interrupt the movement of electrons or electronic energy across it, in response to some external stimulus. The second definition, which covers a much larger field and can also be thought to include the first definition, relates to the binary logic of computing, and describes any molecular-level system that can be reversibly interconverted between two (or more) different states by some external stimulus [4-7]. Both kinds of device can be expected to play a fun- damental role in the construction of chemical computers [8]. In this chapter we will illustrate switches of the first type. Switches related to memory or logic func- tions will be discussed in Part II. Switching requires an external stimulus which, at the molecular level, causes both electronic and nuclear rearrangements. Usually one of the two types of rearrangement prevails or is more relevant to the performed function. When switching involves large nuclear movements, particularly in supramolecular sys- tems, the mechanical aspect can become more interesting than the switching function itself. Systems of this type will be discussed in Part III. The three most important types of stimulus that can be used to switch a chemi- cal compound are light energy (photons), electrical energy (electrons or holes), and chemical energy (in the form of protons, metal ions, specific molecules, etc.). In photochemical stimulation the most common switching processes are related to photoisomerization or photoinduced redox reactions. If input is electrochemical the induced processes are, of course, redox reactions. Compared with chemical stimulation, photochemical and electrochemical stimulation have the advantage that they can be switched on and off easily and rapidly. More generally, a distinction can be made between two types of switching pro- cess, depending on whether they operate under thermodynamic or kinetic control [9]. In the former the molecule responding to the stimulus is in thermodynamic equilibrium with its surroundings, so that when the stimulus is removed the mol- ecule reverts to its initial state. A simple example of this behavior is provided by pH indicators, the spectral changes of which cannot be "locked iff' when the pH Molecular Devices and Machines -A Journey into the Nano World. V. Balzani, A. Credi, M. Venuri Copyright � 2003 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim ISBN: 3-527-30506-8

4.2 Switching Electron-transfer Processes change is reversed. Switching related to temperature changes, solvent effects, and, usually, changes in electrochemical potential, are also under thermodynamic con- trol. Kinetic control, which means that the two states are separated by some kinetic barrier, is usually found in systems responding to photonic stimulation. Kinetic control can operate for extremely different time periods, from picoseconds (for some electronic excited states) to years (for some photochromic systems). In kinetically controlled systems exit from the trapping state is usually achieved by means of a second, different photonic stimulus. It should be noted that in a sys- tem under thermodynamic control it is not possible to address a single molecule because of rapid equilibration between them. In contrast, for a system under kinetic control a single molecule of the assembly can be addressed, maintained in the switched state, and interrogated (e.g. by scanning tunneling microscopy or single-molecule spectroscopy). 4.2 Switching Electron-transfer Processes As we have seen in Section 2.2.1, the occurrence of electron transfer from one end of a long molecule to the other requires some kind of electronic interaction between the molecular subunits. Suitable reversible modification of such inter- actions can switch the electron-transfer process on/off. Electronic interaction can also govern the magnetic interaction between unpaired electrons [10], and other properties, such as fluorescence [11] and intervalence transfer bands [12, 13]. Sev- eral types of input can be used to switch electronic interactions on/off. 4.2.'1 Photon Inputs The idea of using single molecules for switching and rectification purposes [14] constitutes one of the basic concepts of molecular electronic devices. Figure 4.1 shows schematically the hypothetical application of photoinduced electron transfer to the switching of electric signals [15]. The relay components are connected to electrodes and separated by a photosensitizer P. Application of a potential differ- ence to the electrodes does not enable electronic migration when P is kept in the dark, because of the positions of the energy of the lowest unoccupied and highest occupied orbitals of P relative to the Fermi levels of the electrodes. On excitation with light, however, an electron is transferred from the highest occupied to the lowest unoccupied orbital of the photosensitizer, making possible the transfer of an electron between the two relays and, therefore, between the two electrodes. Because of the possibility of modifying its electrical resistance with light, this hypothetical photochemical device can be regarded as a phototransistor. The device shown in Fig. 4.1, which works on the well known principle of a triad for photo- induced charge separation, is the basis of the idea of a molecular shift register [16] (Section 8.3.4).

66 I 4 Switching Electron- and Energy-transfer Processes e- e- Electrode Relay 1 P Relay 2 Fi�, 4,1, Schematic representation of a hypothetical molecular device for switchin� electrical si�nals by photoinduced electron transfer, Electrode In the last ten years much work has been performed, mostly in solution, to investigate basic principles of photocontrolled switching of electron-transfer pro- cesses and to test the performance of a variety of molecular components. 4.2.1.1 Long-lived Switching A dassical example of the switching of electronic interactions by photonic stimu- lation is that based on the reversible photoisomerization of 1,2-bis-(3-thienyl)- ethene derivatives (Fig. 4.2) [17]. This well characterized, fully reversible, fatigue- resistant photochromic system has been used as a basis to control a variety of molecular level functions, including electron flow in molecular wires, electro- chemical properties, absorption and emission spectra, magnetic interactions, host- guest interactions, optical waveguide switches, and liquid crystalline phases [18]. When the thiophene rings are attached to the ethylene moiety through the 3-position, as in 1, z-electrons are localized in the thiophene ring in the open-ring isomer la, whereas they are delocalized throughout the molecule in the dosed-ring isomer lb. As a consequence, not only do the absorption bands occur at much longer wavelengths (up to 600-700 nm) for the dosed-ring isomers than for the open-ring isomers (no absorption in the visible region), but also the electronic interaction between the X and Y substituents in I can increase dramatically in

a 4.2 Switching Electron-transfer Processes I $7 OFF ON b F2 F2 X' 'S' 'S -Y Vis X' 'S' ,"" 'S'Y la lb F2 3., za ,n 3 F2 Vis + n3 ZD n 3 F2 (CH3)3Si \sY/'S' /Si(CH3)3 3a UV F2 Vis (CH3)3Si \S '"Y--S 'Si (C H 3) 3 3b F2 16 33 4a + -- C16H33 F2 uv , / Vis + O16 33 -v 4bZ+ v- 016H33 F2 O- F2"F2 O- UV ' " Vis 5a Fi�.4.2. (a) Schematic representation of a switch; (b)li�ht-switchable 1,2-bis-(3-thien�1)ethene derivatives [17-24]. F2 O- F2 ""F2 O-

68 I 4 Switching Electron- and Energy-transfer Processes going from the open- to the dosed-ring form. The open form is therefore indicated as the off state, and the closed form as the on state (Fig. 4.2a). In compound 22+ (Fig. 4.2b), the two pyridinium groups are electronically iso- lated from each other (off state) in the open-ring isomer 2a 2+ (;max = 352 nm). Upon UV irradiation in acetonitrile solution the closed-ring isomer 2b 2+ is formed (;max = 662 nm) which shows a reversible, monoelectronic reduction wave at -230 mV relative

to the SCE; this does not occur with the open-ring isomer [19]. For compound 3 (Fig. 4.2b) oxidation processes occur at +1.57 V and at +0.63 V for the dosed- and open-ring forms, respectively, in acetonitrile solution [20]. When 3 is dispersed in polystyrene film and sandwiched between a Pt and an Au electrodes, hole injection is achieved only with the dosed-ring isomer and photo- switching of the injection current can be observed [18, 21]. Substantially different electrochemical behavior has also been observed for sexithiophenes derivatives [22]. When such photoswitchable chromophores are immobilized on an electrode, vectorial electron flow from the electrode to electroactive species in solution can be controlled by photoexcitation. This result was obtained by using compound 4 2+ (Fig. 4.2b) incorporated in a n-octadecanethiol-modified gold electrode and a solu- tion containing hexacyanoferrate(III) [18]. Almost complete photochemical interconversion is observed for compound 5 (Fig. 4.2b), which carries two nitronyl nitroxide radicals. Magnetic measurements have shown that the antiferromagnetic interaction for the two isomers is quite dif- ferent (2J/kB = -2.2 K for 5a and -11.6 K for 5b). The intramolecular magnetic interaction can be photocontrolled both in fluid solution and in a rigid matrix [23]. Incorporation of p-phenylene spacers reduces the exchange interaction between the two nitronyl nitroxide radicals and the change in the interaction between the open and dosed isomers increases more than 30-fold [24]. When the X and Y substituents in 1 are two Ru(II) cyclometallated bipyridine complexes, photoinduced switching from the open- to the dosed-ring form can again be achieved and the intervalence-transfer bands in the corresponding Ru(II)-Ru(III) complexes show that electronic coupling is noticeable (0.025 eV) for the dosed-ring isomer only [25]. The photoisomerizable dithienylethene unit has also been used as a bridge to achieve optical on/off switching of photoinduced electron transfer in the donor- bridge-acceptor system 6 + (Fig. 4.3) [26]. With this compound, however, the "off' state is that with the bridge in the open-ring form. The reason for this result, at first sight surprising, is that in the dosed-ring isomer energy transfer from excited anthracene to the bridge successfully competes with electron transfer from excited anthracene to the electron acceptor. Furthermore, once energy has been transferred to the bridge, electron transfer to the excited bridge from the electron donor or from the excited bridge to the electron acceptor is thermodynamically forbidden. Electron-transfer processes can also be affected by exploiting the trans-els pho- toisomerization of azobenzene derivatives [27]. In compound 7 (Fig.

4.4a), which consists of a Zn porphyrin separated by an azobenzene unit from a fluorinated, electron deficient, Zn porphyrin, photoinduced electron transfer from the un-

6a + Fa ' N+ H I R = C6H13] UV 4.2 Switching Electron-transfer Processes I 69 6b* F2 L I E -" - II.+..CH 3 /h; e ' Fi�. 4.3. Optical on/offswitchin� of photoinduced electron transfer in the donor-brid�e-acceptor system 6 + [26]. substituted to the fiuorinated porphyrin is not very effective in the trans isomer but becomes more efficient upon photoisomerization to the d,s isomer [28]. The same effect is observed for a system consisting of two analogous free-base porphyrins. Photoisomerization of azobenzene has also been used to modulate electron transfer in a two-component SAM [29]. The photoactive two-component system is made of 99:1 cis-8 and trans-9 (Fig. 4.4b), self-assembled on a gold electrode. With this electrode, electron transfer between solution ferrocyanide and the Au substrate a L Ar = 4-methylphenyl J F -N.. Ar Ar trans-7 kr F Nr(NN' N/Ar r F b cis-8 trans-8 HS-(HaC)11- xO---N trans-9 Fi�. 4.4. Li�ht-switchable systems based on the trons-cis photoisomerization of an azobenzene unit [25,

70 I 4 Switching Electron- and Energy-transfer Processes is forced to occur through mediating ferrocenyl sites in the film, resulting in a diode-like response. When the larger cis-8 is converted photochemically to the smaller trans-8, however, the free volume within the film is increased, thereby enabling direct electron transfer between the solution ferrocyanide and the elec- trode surface, and a normal electrochemical response. This system establishes the concept of photoswitchable diode that is capable of amplifying the signal associated with a photodriven event via an electrochemical response. Potentially very interesting switching units for optical control of photoinduced electron transfer would be molecules in which light causes breaking/restoration of the conjugation of a x-system, e.g. the dimethyldihydropyrene-cydophanediene reversible photoisomerization [30]. Insertion of such switching units in a multi- component system has not yet been reported. 4.2.1.2 Fast and Ultrafast Switching Fast and ultrafast electron-transfer switching processes can be achieved by appli- cation of two successive laser pulses to suitably designed multicomponent systems [f, 3]. The linear triad 10 (Fig. 4.5) consists of a 4-aminonaphthalene monoimide elec- tron-donor (D) and naphthalene-l,8:4,5-diimide (A) and a

pyromellitimide (A2) electron acceptors [32]. Selective excitation of D with a 416-nm laser pulse in tol- uene solution is followed by electron transfer to A with r = 400 ps and (I) = 0.95. Spontaneous charge shift from A- to A2 is thermodynamically uphill and does not occur. However, on excitation with a second laser pulse after 3 ns at 480 nm, which corresponds to an intense absorption band of A-, the D +-'�A--A2 excited state is obtained which can decay to either '�D-A-A2 or D+-A-A2 - (Fig. 4.5). The driving force for the two processes is almost identical, but the electronic cou- pling between A and A2 is stronger than that between A and D, which are sepa- rated by a phenyl bridge. Charge shift to A2 thus occurs with r = 400 fs and quantum yield of 0.88. These results show that it is possible to control the move- ment of electrons within a multisite donor-acceptor array on a femtosecond time scale. Consecutive laser pulses can also be used to control the lifetime of photogenerated ion pairs. The molecular tetrad 11 (Fig. 4.6) consists of a zinc tripentylpor- phyrin electron donor (D), a naphthalene-l,8:4,S-diimide electron acceptor (A), a pyromellitimide electron acceptor (A2), and a phenyl(boron-dipyrromethene) elec- tron donor (D2) [33]. Selective excitation of D2 with 512-nm laser pulses in dioxane results in the formation of the D-A-A2--D2 + charge-separated state with r = 700 ps and unity quantum yield. The lifetime of this charge-separated state is 1.3 ns. If, however, D is excited by a second 416-nm laser pulse with 700 ps delay, the decay of the charge-separated state to the ground state is accelerated by an order of magnitude. This is because of the formation of the D+-A--A2--D2 + state, in which the electric field generated by the D+-A - dipole modifies the electronic environment in the vicinity of A2--D2 +, thereby affecting its decay rate. In the differently designed tetrad 12 (Fig. 4.6), formation of either D+-A - or A2--D2 + in toluene solution is completely inhibited by the presence of an electric

4.2 Switching Electron-transfer Processes I 71 .OO. .O O O -J O--O 0 0 0 D A1 A2 4.0' (eV) 3.0- 2.0-- 1.0-- Fig. 4.5. *D-A-A 2 hv 416 nm D-A1-A 2 / "L0 0 ps D+-*A1--A2 hv' 400 fs 480 nm D +-A1 --A2 Formula and energy-level diagram of the D-A-A2 triad 10 [32]. D+-A1-A2 - fidd produced on a picosecond time scale by photogeneration of the adjacent ion pair [34]. The effect of photogenerated electric fields on optical charge-transfer transitions has also been investigated [35]. In triad 13 (Fig. 4.6), which consists of two free-base tripentylporphyrin electron donors linked to a perylene-(3,4:9,10-tetracarboxylic)diimide electron acceptor, photoinduced electronic switching can be achieved by modulating the intensity of a laser, rather than wavelength and timing. Excitation of the electron donors with 585-nm light in pyridine solution results in single electron transfer with formation of the D+-A--D state. When the intensity of the laser light pulse is increased both D units become excited, resulting in double electron transfer with formation of the D+-A2--D + state [36].

72 I 4 Switching Electron- and Energy-transfer Processes .C5Hn 05Hll D1 A1 A2 D2 11 N 0 O 0 O 0 HllC5 C5Hll D1 A1 A2 D2 12 13 D A D Fi�. 4.6. Formulae oFthe D-A-A2-D2 tetrads 11 and 12 and oFthe D-A-D triad The rate of electron transfer in a D-B-A triad can be optically controlled by changing the electronic state of the bridge. Triad 14 (Fig. 4.7) consists of a zinc porphyrin, D, a perylene-3,4-dicarboximide, B, and a naphthalene-l,8:4,S-diimide A [37]. Selective excitation of D in a tetrahydrofuran solution of D-B-A with 400-nm laser pulses (130 rs) results in photoinduced electron transfer (= 60 ps) to yield the D+-B--A ion pair which undergoes charge shift (= 140 ps) to yield the long lived (700 ns) D+-B-A - state. Subsequent selective photoexcitation of B within D+-B-A - with a 520-nm (150 rs) laser pulse results, after 500 ps, in approximately 20 % of the D+-B-A - population undergoing charge recombination with = 100 ps, i.e. 7000 times faster than the normal recombination rate. Thus, D-B-A can be

4.2 Switching Electron-transfer Processes I 73 I R: p-t-butylphenyl 1 ,C5H11 . OR Q .O o OR C5H D B A 4.0' E (eV) 3.0- 2.0-- Fig. 4.7. 400 nm I D-B-A D+_*B_A - ps 520 nm D_B+_A - D+_B-._A . .^ 100 ps_ (. ,. ff �'[' D+-B-A - ..� ?7o .:,s _,..r-'- Formula (a) and energy-level diagram (b) of the D-B-A triad 14 [37]. viewed as a molecular switch in which the D+-B-A - state can be rapidly turned on and off by use of 400- and 520-nm laser pulses, respectively. A different topological arrangement of the three components of triad 10 enables study of the partitioning of electron transfer in branched arrays [38]. The A-D-A2 system investigated (15, Fig. 4.8) consists of a benzene core on to which are appended the A, D, and A2 components of the previous triad, the energy-level diagram of which is shown schematically Fig. 4.5. Selective excitation of the D component with a 400-nm laser pulse (process 1 in Fig. 4.8) in toluene solution is followed by electron transfer exclusively to A (process 2). Subsequent excitation of A- (process 3) with a 480-nm laser pulse 2 ns after formation of the A--D+-A2

D hv' - 4 6 e- .hv" .,J1,,. ,It/ o A1 e- 5 A2 15 16 Fi�. 4.8. Formulae and schematic representation o� photoinduced electron-transfer processes in compounds 15 [38] and 16 [39]. state results in the formation of the excited doublet state *Ai--D+-A2 which undergoes charge recombination to Ai-*D-A2 (process 4; = 500 rs) and charge shift to A-D+-A2 - (process 5; = 600 rs). The latter state lies 0.3 eV above the A--D+-A2 state and 2.7 eV above the ground state. Charge recombination to the ground state (process 6) is a Marcus-inverted process, so charge shift back to the initial charge-separated state (process 7; = 400 ps) is the exdusive decay path. The lifetime of the electron on the A2 branch can be significantly enhanced by linking a lower-energy acceptor, namely another A unit, to A2.

4.2 Switching Electron-transfer Processes In tetrad 16 (Fig. 4.8), which is related to triad 15, the secondary acceptor A2 is linked to the benzene ring by a bridge containing the poor electron-acceptor naphthalene monoimide A3 unit [39]. Selective excitation of the D component with a 400-nm laser pulse in toluene solution (process 1) is again followed by electron transfer exclusively to A (process 2). Subsequent excitation of A- with a 480-nm laser pulse (process 3) results in the formation of the excited doublet state *A--D+-A3-A2 which, via formation of the intermediate state A-D+-A3--A2 (process 4), in competition with the slower deactivation to the ground state (pro- cess 5), undergoes (r = 5 ps) charge shift to A-D+-A3-A2 - (process 6). In addi- tion to facilitating electron transfer to produce the A1-D+-A3-A2 - state, the A 3 bridge inhibits the return charge-shift reaction to A--D+-A3-A2 by two orders of magnitude compared with triad 15, because mediation by the A-D+-A3--A2 state is thermodynamically unfavorable. These results show that discrete energy levels of bridge units can be used to optimize electron flow within supramolecular architectures designed for potential device applications such as ultrarapid opto- electronic gates. Somewhat related to the above results is the finding that in a Zn porphyrin-Ru(bpy)32+ dyad the rate of photoinduced electron transfer from the porphyrin to the Ru complex occurs with rate constant 6 x 10 s - from the higher S2 excited state of the porphyrin, whereas electron transfer from the lowest excited state S is 102 times slower [40]. Spin properties of charge-separated ion pairs have also been exploited for the purposes of all-optical switching [41] and the effect of magnetic fields on radical- pair reactions has been investigated [42]. We would also like to mention that the results reported above are relevant to the very difficult task of constructing a supramolecular shift register [16] (Section 8.3.4). 4.2.2 Redox Inputs As we have seen in the previous section, a redox input in the form of a dipole cre- ated by photoexcitation can have a switching effect by changing the rate of excited- state-deactivation processes. A few other examples of switching electron-transfer processes by a redox inputs have been reported. Compound 172+ can be reversibly converted into 18 2+ by chemical redox pro- cesses (Fig. 4.9a) [43]. In 172+ the luminescence of the [Ru(bpy)3] 2+ unit is quenched by electron transfer from the appended N,N'-bis(4-aminophenyl)-l,4- phenylenediamine moleties to the excited Ru complex. In the oxidized form 18 2+, luminescence quenching still occurs, but can be assigned to electron transfer in the opposite direction to that in 172+ . The trinudear complex 194+ (Fig. 4.9b) consists of Os(II) and Pd(II) units at the termini, separated by a Ni(0) unit which can be reversibly switched to Ni(II) either by electrolysis at an appropriate potential or by chemical redox reactions, yielding compound 206+ [44]. In the reduced Os(II)-Ni(0)-Pd(II) state 194+, irradiation of the complex with 480-rim light lead to excitation of the Os(II) unit, followed by electron transfer to the Pd(II) unit. In compound 206% however, the excited

76 I 4 Switching Electron- and Energy-transfer Processes 17 2 + 18 2 + b h Ph ?h Ph/Ph Ph ?h --I 4+ . P.....P. _..P..P. .P. „,. (b PY)20s]Z .p.I.. p.. ;Niu .p. .T..p..; Pd.p. . /\ /\ /\ /\ /\ Pl'i PhPIi PhPIi PhPIi PhPIi Ph 19 4+ + 2e- - 2e- e- /v PhhPh/PhPh/PhPhPh 6+ . P........P. ..P._....,P. P PhPH PhPH PhP PhPH Ph e Fi. 4.9. Redox switchable electron-transCer processes in compounds 172+ and 182+ (a) [43], and 194+ and 206+ (b) [44]. 206+

4.2 Switching Electron-transfer Processes I 77 Os(II) unit transfers an electron to the Ni(II) unit to give the transient Os(III)-Ni(I)-Pd(II) state. A rapid back-electron-transfer reaction follows, and restores the Os(II)-Ni(II)-Pd(II) ground state. Thus, in 206+ the photoinduced Os(II) - Pd(II) electron-transfer process is switched off. In a trinickel dipyridylamido complex the three metal ions do not interact, but one-electron oxidation causes metal-metal interaction [45]. This finding has led to the suggestion that such an Ni3 compound, and homologous Nis, Ni7, and Ni9 species, might play the role of diode-like elements in nanoscale circuitry. In [Ru(bpy)3]2+-MV 2+ dyads (MV 2+= 4,4-bipyridinium ion) the luminescent excited state of the Ru(II) complex is quenched by electron transfer from the excited Ru(II) complex to the viologen unit. When the viologen unit is reduced to the MV + or MV forms the luminescence of the excited Ru(II) complex is again quenched but electron transfer occurs in the reverse direction, i.e. with reduction of the excited complex [46]. Figure 4.10 shows schematically the heterosupramolecular system 214+ consisting of a covalent assembly of a TiO2 nanocrystal, a Ru complex, and a viologen unit [47]. At positive applied potentials, light excitation of the Ru complex causes electron transfer almost exclusively to the nanoparticle. At negative applied potentials, however, a substantial fraction of the light-induced electron-transfer processes switches in the opposite direction. The possibility of switching electron- and energy-transfer processes by means of the redox-controlled assembly/disassembly of the donor and acceptor components has been discussed [2b, 48] (see also Chapters 12 and 14). Redox triggering of the electrical conductivity in rotaxane- and catenane-based circuits has also been reported [49] (Chapters 15 and 16). 4.2.3 Acid-Base Inputs Electronic communication between metal centers across a bridging molecular wire can be controlled by protonation/deprotonation of an acidic or basic site on the bridge. The effect occurs because of a change in the energy of the delocalized molecular orbitals of the bridge that mediate electron transfer. An example is given by the binuclear complexes 225+ and 235+ (Fig. 4.11a). In 225+ the Ru 2+ - Ru 3+ intervalence-transfer band is switched off by deprotonation of one of the NH sites of the bridging ligand [50]. In contrast, in 235+ deprotonation of one of the NH sites results in a substantial increase in the Ru2+-Ru 3+ electronic interaction [51]. For other Ru complexes switching occurs via a pH-induced redox reaction [52]. The boronate ester bridge is a Lewis acid site and can be used to regulate electron-transfer reactions. In dyads 24 and 25 (Fig. 4.11b), the fluorescence of Zn porphyrin is quenched by the diimide unit, by electron transfer, in solvents such as benzene and dichloromethane; no fluorescence quenching is, however, observed in highly electron-pair-donating solvents such as dimethylformamide and pyridine or upon addition of fluoride anions [53]. Starting from these results triad 26 (Fig. 4.11b) has been synthesized; in this compound PI and NI acceptors are placed at

78 I 4 Switching Electron- and Energy-transfer Processes Working Electrode -./ O X,,v COOH , ,N-' / Counter 95% � Electrode Reference Electrode At positive applied potentials Working Electrode COOH 4+ II o i -O , ,N_-'

6OOH 214+ Counter 48% � Electrode Reference Elerode At negative applied potentials FiB. 4.10. Redox-switchable electron-transCer processes in heterosupramolecular system 214+ [47]. similar distances from the Zn porphyrin through acetal and boronate-ester bridges, respectively. Photoexcitation of the Zn porphyrin leads preferentially to electron transfer to NI, but in the presence of fluoride ions the photoinduced electron transfer path is completely switched toward PI (Fig. 4.1lb) [53]. In dendrimers containing ferrocene groups in the periphery and amine groups in the interior the voltammetric pattern for ferrocene oxidation can be reversibly

(bpY)21u'zI'N'" H' - [5+ -1H q.N..luni(bpy)2 225+ 4.2 Switching Electron-transfer Processes I 79 b-" Ru n _ .H, 5+ V('--'N I-l I 'hun(bpy)2 H 235+ b C6H13 .C6H13 24 R = PI 25 R= NI O O =--N N-C6H13 NI = -- -C6H13 In the absence of F - e- I hv e- � -Z o '" .o " '7, ', '- ,o o .o '-.i o-' o e e In the presence of F - Fig. 4.11. (a) Electronic communication beeen metal centers of compounds 225+ and 235+ can be switched by protonation [50, 51a]; (b) the formulae of compounds 24 and 25, and switching of electron transfer in compound 26 [53]. switched among several states depending on the number of protonated centers in the interior of the dendrimer [54]. Supramolecular species comprising donor and acceptor units connected by means of noncovalent forces [55] can be disassembled and re-assembled by modulating the interactions that keep the two components together, thereby enabling switching of electron- or energy-transfer processes. Systems of this type are remi-

80 I 4 Switching Electron- and Energy-transfer Processes Input E ore- b 27 "plug inf + + n-Bu3N ,Cc. ou, 282+ ' '+ N', Fi�. 4.12. (a) Schematic representation of a molecular-scale plu� and socket system; (b) switchin� of photoinduced electron transfer related to the acid-base-controlled plu� in-plu� out of the cation [28H] 3+, obtained by protonation of the correspondin� amine, 282+, with (d-)-binaphthocrown ether 27 [56]. niscent of plug and socket electrical devices [2b] and, like their macroscopic counterparts, must be characterized by the possibility of connecting/disconnecting the two components in a reversible way, and the occurrence of an electron or electronic energy flow from the socket to the plug when the two components are connected (Fig. 4.12a). Hydrogen-bonding interactions between ammonium ions and crown ethers are particularly convenient for constructing molecular-

level plug and socket devices because they can be switched on and off quickly and reversibly by means of acid- base inputs. In the system illustrated in Fig. 4.12b, the plug-in function is related to the threading, driven by formation of strong [N+-H ... O] hydrogen bonds in nonpolar solvents, of (+)- binaphthocrown ether 27 by the dialkylammonium moi- ety of the wire-like compound [28H] 3+, obtained by protonation of amine 282+ [56]. In the plugged-in pseudorotaxane structure electron transfer to the bipyr- idinium unit of [28H] 3+ occurs on light excitation of the binaphthyl unit of the macrocyde, causing quenching of the typical binaphthyl fluorescence. Addition of a stoichiometric amount of base, which deprotonates the ammonium ion, causes recovery of the binaphthyl fluorescence, demonstrating that plug out of the pseudorotaxane structure has occurred. The plug and socket concept can be used to design molecular systems which mimic the function of a macroscopic electrical extension cable. An extension cable is more complex than a plug and socket device, because three components are held together by two connections that have to be controllable reversibly and

Input 1 Input 2 E ore- E ore- Input 2 Input 1 b -- -- O- 1 3* /O O O - - O"' + + O O N, :N O O N N _ I o 29 z* . . . [28H] 3' 30 Hydrogen eonding I inmctlons Elecn donor-acceptor I Acid-base ""- o +'-* o Fi 8. 4.13. (a) Schematic representation o a molecular-scale extension cable; (b) a supramolecular system which mimics the unction of a macroscopic extension [57]. independently; in the fully connected system an electron or energy flow must occur between the remote donor and acceptor units (Fig. 4.13a). In an attempt to construct a molecular-level extension cable the [3]pseudorotaxane shown in Fig. 4.13b, made from the three components 292+, [28H] 3+, and 30, has recently been

synthesized and studied [57]. Component 292+ consists of two moleties - an [Ru(bpy)3] 2+ unit, which plays the role of electron donor under light excitation, and a dibenzo[24]crown-8 (DB24C8), which plays the role of a socket. The ammo- nium center of [28H] 3+, driven by hydrogen-bonding interactions, threads as a plug into the DB24C8 socket whereas the bipyridinium unit, owing to electron donor-acceptor interaction, threads as a plug into the third component, 30, a 1,5- dinaphtho[38]crown-10 (1/5DN38C10) socket. In 98:2 (v/v) dichloromethane- acetonitrile solution reversible connection and disconnection of the two plug and socket functions can be controlled independently by acid/base and red/ox stimula- tion, respectively. In the fully connected triad light excitation of the [Ru(bpy)3] 2+ unit of component 292+ is followed by electron transfer to the bipyridinium unit of component [28H] 3+, which is plugged into component 30. Although the trans- ferred electron does not reach the final component of the assembly, the inter- component connections employed fulfil an important requirement - they can be controlled reversibly and independently. Possible schemes whereby the system might be improved have also been discussed [57]. It should be noted that switching of electron-transfer processes in the plug and socket and extension cable devices described above is based on threading and dethreading motions that have been widely exploited for the construction of molecular machines (Chapter 14). 4.2.4 Other Factors Switching of electron-transfer processes can be also achieved by use of other kinds of stimuli. The simplest case is that of switching in going from room temperature fluid solutions to a rigid matrix at 77 K [58]. A [2]rotaxane has been synthesized in which a phenanthroline-containing rod bearing two Zn porphyrin (ZnP) electron donors is threaded through a phenanthroline-containing macrocyde linked to a gold(III) porphyrin (AuP) elec- tron acceptor [59]. Excitation of either AuP or ZnP units leads to a very efficient electron transfer to AuP. On coordination of the phenanthroline units by Ag + or Cu + the rate of electron transfer is considerably enhanced if photoexcitation is performed on AuP whereas it is unaffected or even slowed down on excitation of the ZnP unit. This behavior is interpreted in terms of an enhanced superexchange mechanism for Ag + and a change to a hopping mechanism, involving the oxidized [Cu(phen)2] 2+ unit as an intermediate, for Cu + [59b]. These results show that electron-transfer processes between noncovalently linked reactants can be tuned by appropriate modification of the link; another possibility of control is, moreover, that offered by selective excitation. The electron-transfer properties of conjugated molecular wires can be modified by changing the amount of conjugation of the z-electron component systems, thereby reducing electronic coupling between the two ends. For instance, in poly- phenylene-type and related unsaturated wires this effect can be accomplished by introducing substituents that increase the twist angle between the phenylene

4.3 Switching Energy-transfer Processes I 83 units (Section 3.4). Some researchers have envisaged the possibility of using con- formationa] changes to switch electronic conductivity in molecular wires [60]. In suitably designed systems such control could be exerted by applying an external electric field capable of modifying the conformation, and hence the -over]ap, of a coniugated molecule [61]. Other switchable molecular components, e.g. resonant tunneling diodes and multiterminal molecular wires, have been designed and, occasionally, synthesized and tested (see also Chapter 9) [61-63]. Although such experiments are still at an early stage, this approach to molecular-scale electronics has the potential advantage of being strictly related to the paradigms of current microelectronics technology [62-64]. 4.3 Switching Energy-transfer Processes As we have seen in Section 2.2.2, electronic energy transfer between components of supramolecular systems can occur directly (through space) or can be mediated by the intervening matter. In the latter, manipulation of the interposed matter (e.g. the bridge in a three-component system) can switch the energy-transfer process on and off. In principle, any kind of input causing a reversible modification in a bridging component can be used. 4.3.1 Photon Inputs The electronic properties of bridging units can be altered by means of a photonic input. Since, by definition, switching must be reversible, reversible photochemical reactions must be used. Photochromic molecules are particularly useful in this regard. An example is given by the D-P-A supramolecular species 31 (Fig. 4.14) in which photoinduced energy-transfer from D to A can be switched by photo- excitation of component P [65]. In such a system the "spacer" P is a photochromic fulgide molecule which can be transformed reversibly by light between a dosed, Pa, and an open, Pb, configuration. The donor D is either an anthryl or anthrylvinyl moiety, which can be excited at 258 nm, and the acceptor A is a coumarin mole- cule. When P is in its dosed form Pa (31a) its lowest energy level is lower than the energy level of A, so energy transfer from D to A cannot occur (Fig. 4.14) and the sensitized luminescence of the coumarin cannot be observed on excitation of the anthracene moiety. When, however, the P species is isomerized with 520-nm light to yield the Pb isomer (31b) the energy levels are in scale and the sensitized luminescence of the coumarin component at 500 nm can be observed on excitation of the anthryl component at 258 nm. Because light of three different wavelengths is needed and four different chromophoric units are involved, such a system is not so easy to handle and its behavior is not really on/off. The behavior of triad 324+ (Fig. 4.15), which consists of [Ru(bpy)]32+ and [Os(bpy)]32+ moieties bridged by an anthracene unit, is very peculiar [66, 67].

:320 nm D Pa A 31b D Pb A h E l hv hv Fig, 4.14. Switchin� oFener�y transfer From an anthryl moiety to a coumarin moiety by photoisomerization oF a Ful�ide brid�e [65]. Because the lowest triplet energy levd of the anthracene bridge lies between the lowest triplet MLCT excited state of the Ru- and Os-based complexes, energy transfer from the [Ru(bpy)]32+ to the [Os(bpy)]32+ moiety is very efficient (Section 3.6.1). Continuous irradiation with visible light in deaerated acetonitrile solution causes only the sensitized emission of the Os-based complex. In aerated solution, however, the relatively long-lived excited state of the [Os(bpy)]32+ moiety sensitizes the formation of singlet oxygen which attacks the anthracene ring to form the endoperoxide derivative 334+ (Fig. 4.15). As a consequence delocalization of the z- system on the bridge is reduced, the lowest energy excited state of the bridge moves to much higher energy, and energy transfer is switched off. In principle, the endoperoxide could be transformed back to anthracene but such a reaction is diffi- cult to perform. Energy transfer in 324+ has been defined a "self-poisoning" pro- cess. The intriguing possibility of designing "self-repairing" processes has been advanced [67]. The compounds shown in Fig. 4.16 contain a photochromic nitrospiropyran moiety (Sp) covalently linked to a zinc (34) or a free-base (35) porphyrin [68]. As happens for free spiropyran, excitation of the spiropyran moiety of either dyad with near-UV light results in ring opening to a merocyanine form which is a resonance hybrid of a zwitterionic and a quinoid structure and absorbs at 600 nm. The open form re-doses thermally (r = 20 s in 2-methyltetrahydrofttran) or upon irradia-

by NO2

UV NO2 Vis /. E Sp open 34 M=Zn 35 M=2H NO2 Fi�. 4.16. Li�ht-activated control of the porphyrin excited states in compounds 34 and 35 [65], tion with 600-nm light. The fluorescent excited state of the porphyrin unit is unperturbed by the appended spiropyran open form, but is strongly quenched via singlet-singlet energy transfer by the merocyanine dosed form. This photo- switchable quenching phenomenon enables light-activated control of the porphyrin excited states and, consequently, control of any subsequent energy- or electron-transfer processes that might be initiated by these excited states in more complex molecular-level devices. Optically controlled energy transfer in trichromophoric linear systems has been investigated with the purpose of modeling a supramolecular shift register based on energy transfer [69] (Section 8.3.4). 4.3.2 Redox Inputs Energy-transfer processes can be switched on and off in the compounds shown in Fig. 4.17a. Both compounds consist of three porphyrins and a light-absorbing dye, in a linear (36) or branched (37) arrangement, and operate in an identical manner [70]. The branched design (37) consists of a trisubstituted zinc porphyrin (ZnP) with a boron-dipyrromethene dye (BDPY) and magnesium and free-base porphy- rins (MgP and P) on its periphery. The free-base porphyrin in para position to BDPY has the lowest-energy excited state and fluoresces strongly. The energy-level diagram for compound 37 is shown in Fig. 4.17b. Excitation of BDPY with 485-nm

4.3 Switching Energy-transfer Processes I 87 BDPY , ZnP P F2 MgP BDPY F2B'.;NN/ ZnP ,, 37 p BDPY ZnP MgP Neutral 485 nm Cation 650 nm Fi�. 4.17. (a) Porphyrin arrays 36 and 37 for ener�y-transfer switchin� [70]. (b) Ener�y-level dia�ram for 37.

88 I 4 Switching Electron- and Energy-transfer Processes Fig. 4.18. , hV ,,l! +2e- '7'/.]] --J4+ H ,.N.-O, s (bpY)2 + 2H + . -NN - 2 (bpy) -="+ / hy 394+ Redox-controlled energy transfer occurs in compounds 384+ and 394+ light is followed by stepwise energy transfer which leads to fluorescence from P at 650 nm with (I)= 0.8. One-electron electrochemical or chemical (ferric per-chlorate) oxidation (E/2 = +0.34 V relative to the SCE) of 37 leads to formation of the radical cation MgP '+ which has low lying, nonfluorescent excited states. In the oxidized form of 37, therefore, the fluorescent excited state is either not populated or quenched. The fluorescent signal can be restored by returning to the neutral species via electrochemical reduction or addition of triethyleneamine. It should be noted that in such a system the energy-transfer processes are very rapid but the on/off switching is slow because it relies on diffusional redox processes. Redox-controlled energy transfer occurs in compound 384+ (Fig. 4.18) which consists of [Ru(bpy)3] 2+ and [Os(bpy)3] 2+ moieties bridged by an azo group [71]. In this compound excitation of the [Ru(bpy)3] 2+ unit does not lead to emission, because the luminescent excited state of the Ru(II) complex is quenched by energy transfer to lower energy levels present in the bridge. Reduction of the azo group, however, causes disappearance of such low energy levels and as a result

efficient energy transfer (k = 6.3 x 108 s -1) from the Ru-based to the Os-based unit is observed in compound 394+ . Similar behavior is observed for complexes based on terpyridine ligands [72]. 4.33 Acid-Base Inputs In compound 40 (Fig. 4.19) acid-base inputs switch between energy- and electron- transfer pathways [73, 74]. This compound consists of anthracene and chalcone moieties linked by a piperazine unit. The fluorescent excited state of anthracene lies at higher energy than the fluorescent excited state of the chalcone whereas piperazine has no low-energy excited states. Excitation of anthracene with near- ultraviolet light, however, is not followed by energy transfer to the chalcone moiety, because a fast photoinduced electron transfer occurs from piperazine to anthracene. When piperazine is protonated, however, the electron-transfer process cannot occur and the sensitized chalcone emission at approximately 510 nm can be observed. Reversible tuning of the direction of energy transfer is obtained in the oligophenylenevinylene-phenanthroline dyad 41 (Fig. 4.19) [75]. The phen - OPV energy-

40 Anthracene Piperazine Chalcone X'-._ + 2H+ hv/ "-e- O -2H+ 4.3 Switching Energy-transfer Processes I 89 012H250, 41 C12H250 C/ \ _ OC12H25 C12H250 O ' --)Y /-- N,, N--(Fi�. 4.19. In compound 40 add-base inputs switch between electron- and ener�y-transfer pathways [73] whereas in compound 41 protonation of the phen moiety affects the direction of ener�y transfer [75]. transfer process in CH2C12 solution is reversed on addition of acid, as a result of protonation of the phen moiety. This process, signaled by the on/off switching of the intense OPV fluorescence, is possible because the energy of the OPV lowest singlet level is intermediate between those of phen and [phenH] +. Plug-socket systems similar to that illustrated in Section 4.2.3 have also been developed [76] for switching energy-transfer processes (Section 14.2.2). 4.3.4 Other Factors Switching of energy-transfer processes can also occur as a result of other effects. An example is given by compound 424+ (Fig. 4.20a) in which coordination ofa C1- ion by the macrocydic bridge causes a decrease in the rate of energy transfer from the Ru(II) to the Os(II) unit [77]. Temperature control of the direction of energy transfer is observed in the rack- type compound 432+ (Fig. 4.20b). In a rigid matrix at 77 K the phosphorescence of the anthracene moiety is long-lived, whereas in fluid solution at room temperature emission comes from the metal complex [78]. Such switching is caused by the different intrinsic lifetimes of the lowest

excited states of the two units and the low energy gap between these states. The combination of these properties enables thermal activation of an uphill energy transfer from the anthracene to the Ru(II) moiety. Compound 443+ (Fig. 4.21) consists of luminescent Re(I) and Ru(II) complexes linked by a diaza[18]crown-6 macrocycle spacer. Because the luminescent excited

90 4 Switching Electron- and Energy-transfer Processes '11' LU / o= [4 Z'l = TZ

4.3 Switching Energy-transfer Processes I 91 (H20)(CO)3Re, L -,. I/"O""1 13+ ., ' '_[,N O. li '"1 J r'?.', I..O../I '"J'/N'-un(bpy)2 443+ h, e- hv' At room temperature At room temperature E C At77 K E d At77 K Fig. 4.21. Effect oFtemperature and Ba 2+ ions on the photophysical processes of compound 443+ [79]. (a) Room temperature, no Ba2+; (b) room temperature, with Ba2+; (c) 77 K, no Ba2+; (d) 77 K, with Ba 2+. state of the Re(I) complex is higher in energy than that of the Ru(II) complex, Re(I) - Ru(II) energy transfer can, in principle, be expected. The behavior of this compound depends, in fact, on the experimental conditions [79]. In fluid solution at room temperature, energy transfer does not occur, because the excited state of the Re(I) complex is quenched by electron transfer from an amine group of the aza-crown ether bridging unit (Fig. 4.21a). On addition of Ba 2+, which is hosted by the aza-crown ether, the electron-transfer process does not occur, but energy transfer cannot be seen either (Fig. 4.21b). In a rigid matrix at 77 K electron transfer is again prevented and energy transfer occurs very efficiently (k = 2 x 108 s-l), as shown by the sensitized emission of the Ru(II) complex (Fig. 4.21c). When the aza-crown ether contains the barium ion, the energy-transfer process at 77 K is much slower (k = 7 x 106 s-l), SO the luminescence of the Re(I) unit is only partly quenched (Fig. 4.21d). A likely explanation of this result is that binding of Ba 2+ in

92 I 4 Switching Electron- and Energy-transfer Processes the aza-crown bridge causes a conformational rearrangement that increases the distance between the Re(I) and Ru(II) centers. Finally, in some heterodinudear catenanes with coordination centers involving 1,10-phenanthroline and/or 2,2':6',2"-terpyridine ligands the direction of photo- induced processes is controlled by suitable choice of the phenanthroline-bound metal ion [80]. This is a consequence of the dramatic effect on the energy content and redox

character of phenanthroline-type coordination sites of varying the com- plexing cation [81].

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961 5 Light-harvesting Antennae 5.1 Introduction An antenna for light harvesting (Fig. 5.1) is an organized multicomponent system in which several chromophoric molecular species absorb the incident light and channel the excitation energy to a common acceptor component [1]. For artificial systems the term "antenna effect" was first used [2] in discussion of strongly emitting but weakly absorbing lanthanide ions surrounded by strongly absorbing ligands, in which the luminescence of the lanthanide ion was sensitized by exci- tation in the ligand-centered excited states. Research in this area is still very active [3]. Antenna systems are widely used by Nature to solve the problem of light- harvesting efficiency in the photosynthetic process in which

light is converted into chemical energy [4]. Collecting light by means of an antenna system might, how- ever, also be useful for other purposes, e.g. signal amplification in luminescence sensors [5], sensitization of photovoltaics [6], and exciton sources in near field and scanning exciton microscopy [7]. A large dendrimer, in which an array of chromo- phoric units absorbs light and transfers energy to a luminescent core, can be con- sidered a spatial and spectral energy concentrator ("molecular lens") [8]. The antenna effect can be obtained only in supramolecular arrays suitably organized in the dimensions of time, energy, and space. Each molecular compo- nent must absorb the incident light, and the excited state so obtained must transfer electronic energy to a nearby component before undergoing radiative or non- radiative deactivation (organization in the time dimension). For energy transfer to occur the energy of the acceptor excited state must be lower or, at most, equal to the energy of the excited state of the donor (organization in the energy dimension). Finally, the successive donor-to-acceptor energy-transfer steps must result in an overall energy-transfer process leading the excitation energy towards a selected component of the array (organization in the space dimension). In the course of evolution, Nature has succeeded in building antenna systems that fully satisfy these requirements. In green plants such natural antennae collect an enormous amount of solar energy and redirect it as electronic excitation energy to reaction centers where subsequent conversion into redox chemical energy occurs [4]. In recent years, the development of supramolecular chemistry (in par- ticular, dendrimer chemistry) and the high level of experimental and theoretical Molecular Devices and Machines -A Journey into the Nano World. V. Balzani, A. Credi, M. Venturi Copyright � 2003 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim ISBN: 3-527-30506-8

5.2 Natural Antenna Systems I 97 Light absorption Fig. 5.1. Schematic representation of a light-harvesting antenna system. Squares stand for light-absorbing molecules. P is the molecule to which excitation energ 7 is channeled. Excited state energy decreases with increasing shade. efficacy achieved by photochemistry have enabled scientists to design and construct several interesting artificial antenna systems [9]. 5.2 Natural Antenna Systems The best known natural antennae are the light-harvesting complexes of photo-synthetic purple bacteria [10]. A major breakthrough in the field was the high res- olution X-ray determination of the crystal structure of the light-harvesting antenna complex LH2 of the photosynthetic unit of Rhodopseudomonas acidophila (Fig. 5.2) [11]. The complex is composed of two rings of bacteriochlorophyll (BChl) molecules - a set of 18 molecules close to the membrane surface in an almost face-to-face arrangement like a turbine wheel, and another set of nine molecules all lying in a plane perpendicular to the rings of the BChl of the first type, in the middle of the bilayer. These structures are contained within the walls of two protein cylinders with radii of 1.8 and 3.4 nm. Because of the different chemical environments, the two sets of BChl have different absorption and photophysical properties. The 18 BChl belonging to the larger wheel have the lowest energy absorption maximum at 850 nm (and are therefore named B850) and the nine BChl in the middle of the bilayer have the lowest energy absorption maximum at 800 nm (B800). There are other significant differences between the two sets of pigments [12] - the B800 species are largely monomeric whereas the B850 species are strongly exciton-coupled with the exciton state delocalized over several (presumably four) BChl molecules. All the BChl are maintained in a fixed spatial relationship by the surrounding polypeptides. Carotenoids are also associated within the LH2 structure with the dual function of contributing to light harvesting and protecting the system against photoxidation, by quenching the singlet oxygen molecules produced by photosensitization [4a]. The light absorbed by the B800 array is transferred to the B850 wheel within i ps. Energy migration among the different exciton states of B850 then occurs on the 300 fs timescale [12]. The energy collected by the LH2 antennae is then transferred to another antenna complex, LH1, which surrounds the reaction center (RC). The RC is the final destination of the collected energy and is the site where charge separation occurs. A schematic view of the overall light-harvesting process is shown in Fig. 5.3. The structure of LH1 is not known at the same level of definition as that of LH2, but an analysis by electron crystallography of two-dimensional crystals of the LH1 complex of Rhodospl, ri, llum rubrum [13] has provided evidence of clear similarity of LH1 and LH2 - LH1 is formed from 32 BChl molecules arranged as the B850 molecules of LH2, so that the LH1 wheel is much larger. LH1 absorbs at 880 nm (B880). LH1 and LH2 are in close contact (estimated to be closer than 30A)

Fig. 5.2. Structure of the LH2 light-harvesting antenna system of Rhodopseudomonas acidophila which contains rings and 9 (b) bacteriochlorophy11 molecules. For more details, see text. Reprinted by permission from Ref. [11].

so LH2 - LH1 energy transfer is quite fast (3 ps). The rate of the successive energy- transfer step from LH1 to the embedded RC is more than ten times slower (35 ps). Because the molecules of the LH1 wheel are exciton-coupled like those of B850, such an energy-transfer process should occur from approximately eight sites of LH1, each comprising four delocalized BChl subunits, to RC (assuming i RC per 32 BChl LH1 molecules) [12]. In conclusion, in natural light-harvesting antennae ultrarapid energy migration within almost isoenergetic subunits of a single complex is followed by fast energy transfer to a complex of lower energy with minimal losses. All processes are believed to occur by a F6rster mechanism (Section 2.2.2). The light-harvesting complexes of green plants are not well known and are probably more complex than those of bacterial photosynthesis [14, 15]. There

LH1 LH2 5.3 Porphyrin-based Arrays I 99 h� LH2 Fig. 5.3. Schematic representation o�the overall light- harvesting process by LH2 and LH1 antenna complexes in bacterial photosynthesis. RC is the reaction center. are good reasons to believe, however, that the governing principles of operation are similar to those discussed above. 5.3 Porphyrin-based Arrays Porphyrins, the main chromophores of natural photosynthesis, are obvious candi- dates for the design of artificial antenna systems. Arrays containing porphyrin molecules are certainly the largest dass of artificial antennae. We will discuss only a few representative examples. More extensive discussions can be found in recent reviews [16-21]. The synthesis and properties of multiporphyrin arrays have been investigated systematically [22-29]. By means of a modular approach [23], a variety of di-, tri-, tetra-, and pentameric porphyrin arrays have been obtained (see also Sections 3.6.3 and 6.3.5.1). The arrays have been constructed by using an ethyne linkage between aryl groups on adjacent tetraarylporphyrin macrocycles; this provides a semirigid architecture that limits direct chromophore interactions. The center-to-center and edge-to-edge distances for the porphyrins in these systems are approximately 20 and 13.5 A, respectively. Among other species, the star-like pentameric array 1 (Fig. 5.4) has been constructed [22]; in this compound efficient energy transfer from the peripheral Zn-containing units to the free-base core was observed. Thorough photophysical investigation of 1 and related systems [24] has shown that:

100 I 5 Light-harvesting Antennae Fig. 5.4. A star-like pentameric array of porphyrins for light harvesting [22]. � singlet excited-state energy transfer

from the Zn porphyrin to the free-base por- phyrin is extremely efficient (95-99 %); � competitive electron-transfer reactions are not observed; � the mechanism of energy transfer predominantly involves through-bond communication via the ethyne linker; � energy transfer between two isoenergetic Zn porphyrins is very rapid. Structural control of energy transfer between adjacent and distant sites has also been investigated [25]. These studies demonstrate that extended multiporphyrin arrays can be designed rationally with predictable photophysical features and effi- cient light-harvesting properties.

p 'pX 2- P Fi�. 5.5. A nine-component antenna comprisin� ei�ht peripheral boron-dipyrrole pi�ments and a porphyrin core [30], 5.3 Porphyrin-bosed Arrays I 101 CBF2 z yN. In the light-harvesting compound 2 containing only one porphyrin (Fig. 5.5) [30], excitation of the eight peripheral boron-dipyrrole pigments is followed by energy transfer to the central porphyrin with a quantum yield higher than 85 % and rate constant of the order of 5 x 10 TM s -. An array made of eight porphyrins and one phthalocyanine playing the role of energy trap has been studied [31] and even larger arrays have been constructed [32, 33]. An analytical method for simu- lating energy-transfer dynamics in weakly coupled multipigment systems has been developed with the aim of arriving at a rational design of large light-harvesting antennae [34]. Attempts to build artificial antennae by self-assembly of porphyrin components have been reported. Compound 3 in Fig. 5.6 is a perpendicular side-to-face pen- tameric porphyrin array made of two types of molecular component - a porphyrin unit with 4'-pyridyl substituents, and four ruthenium carbonyl tetraphenylpor- phyrins [35]. The two types of unit are assembled by axial coordination of the 4'-pyridyl groups of the former on to the metal center of the latter. To check pos- sible effects of the mutual orientation of the porphyrin rings, the analogous canted side-to-face array was synthesized by using 3'-pyridyl substituents as connecting groups. The photophysical behavior of the arrays is practically inde- pendent of their perpendicular or canted geometry and shows that, in the free-base arrays, irreversible quenching of the ruthenium porphyrin triplet and sensiti- zation of the free-base triplet occur [35]. Investigations have since been extended to more complex systems, e.g. the hexameric porphyrin array 4 shown in Fig. 5.6 [35d]. An alternative way of self-assembling porphyrins is based on hydrogen bonding and [z-z] interactions [36]. The crystal structure of bis[4-(hydroxymethyl)phenyl]-

porphyrin shows the presence of strong hydrogen bonds between the hydroxy group and pyrrole nitrogen atoms in neighboring molecules, resulting in a two-dimensional network. Laddered stacks are present, because of [z-z] interactions. An interesting self-assembly system based on porphyrins bearing pyrazine arms to hook zinc porphyrins has led to the formation of heptadecameric species [37]. The energy-transfer results obtained are, however, difficult to understand.

5.5 Dendfimers I 103 5 Fi�. 5.7. A light-harvesting c�clodextrin derivative [38, 39], 5.4 Multichromophoric Cyclodextrins Cyclodextrins (CD) are cydic oligosaccharides shaped like truncated cones. Com- monly available CD are those with six, seven, and eight glucose units, which are called y-, fi-, and ?-CD, respectively. The photophysical properties of fi-CD func- tionalized with seven (compound 5 in Fig. 5.7) or fourteen 2-naphthoyloxy chro- mophores have been investigated [38, 39]. Hopping of excitation energy between the chromophores occurs with essentially randomly oriented transition moments and is much faster than the intrinsic decay of the chromophores. In rigid glass a decrease of energy transfer was observed upon red-edge excitation as a result of inhomogeneous broadening, because of solvation heterogeneity. Energy hopping was therefore shown to be not chaotic, but directed toward lower-energy chromo- phores. This effect is somehow reminiscent of the environmental effects used by Nature to fine-tune the energies of the antenna chromophores (Section 5.2). An investigation on the dynamics of energy hopping in compound 5 (Fig. 5.7) indicated there was no preferred mutual orientation between the chromophores and that energy transfer occurs with a dipole-dipole (F6rster) mechanism [40]. Theoretical aspects of energy hopping taking care of the orientation of the chro- mophoric groups have also been investigated [41]. CD are capable of accommodating guest molecules in their internal hydrophobic cavity (diameter approximately 5 (-), 7 (fi-), and 8.5 (7-) A, respectively). Fluores- cence measurements have shown that when a merocyanine dye is enclosed in the cavity of a fi-CD containing seven naphthoyl chromophores as substituents, light excitation of the appended chromophores is followed by 100 % efficient energy transfer to the enclosed dye [42]. When the guest is a nitrone, the antenna effect causes its photoisomerization [43]. 5.5 Dendrimers Dendrimers are well-defined macromolecules with a tree-like structure. Dendrimer chemistry is a rapidly expanding field for both basic and applicative reasons [44].

104 I 5 Light-harvesting Antennae dendron or wedge finrations Fig. .8. Schematic representation ofa dendrimer. In this section we will discuss dendrimers used for light harvesting. The interest- ing redox properties of suitably designed dendrimers [45] will be examined in Section 8.4. The schematic representation of dendrimers shown in Fig. 5.8 is reminiscent of the architecture of natural light-harvesting complexes (Section 5.2), where antenna molecules surround the reaction center. Dendrimer structures are, therefore, very attractive for the construction of artificial antennae [46-48], also because their convergent and/or divergent synthesis enables the assembly, in a few synthetic steps, of many chromophores in a restricted space and with high topological con- trol. Topologically dendrimers contain three different regions - core, branches, and surface (Fig. 5.8). Photoactive units can be directly incorporated or appended with covalent or coordination bonds in different regions of a dendritic structure and can also be noncovalently hosted in the cavities of a dendrimer or associated with the dendrimer surface, as shown schematically in Fig. 5.9 [49]. Because of their prox- imity, the various functional groups of a dendrimer can easily interact with one another. 5.5.1 Dendrimers Containing Metal Complexes 5.5.1.1 Metal Complexes as Cores In the dendritic complex 62+ shown in Fig. 5.10a, the 2,2'-bipyridine ligands of the [Ru(bpy)3]2+-type core carry branches containing 1,3-dimethoxybenzene- and 2- naphthyl-type chromophoric units [50]. Because such units (and the core) are sep-

5.5 Dendfimers I 105 a b c d e f g h Fig. 5.9. Schematic illustration of the possible location of photoactive units, represented by circles, in a dendrimer [49]. arated by aliphatic connections, the interchromophoric interactions are weak and the absorption spectrum of the dendrimer is substantially equal to the sum of the spectra of the chromophoric groups present in its structure. The three types of chromophoric group - [Ru(bpy)3] 2+, dimethoxybenzene, and naphthalene - are potentially luminescent species. In the dendrimer, however, the fluorescence of the dimethoxybenzene- and naphthyl-type units is almost completely quenched in acetonitrile solution, with concomitant sensitization of the luminescence of the [Ru(bpy)3] 2+ core (;max = 610 nm). These results show that a very efficient energy-

106 transfer process occurs, converting the very short-lived UV fluorescence of the aromatic units of the wedges to the long-lived orange emission of the metal-based dendritic core. It should also be noted that in aerated solution the lttminescence intensity of the dendrimer core is more than twice as intense as that of the [Ru(bpy)3] 2+ parent compound, because the dendrimer branches protect the Ru- bpy-based core from dioxygen quenching [51]. In conclusion, because of the very high absorbance of the naphthyl groups in the UV spectral region, the high energy- transfer efficiency, and the strong emission of the [Ru(bpy)3]2+-type core, UV excitation of dendrimer 62+ (Fig. 5.10a) resttits in strong visible emission, even in very dilute (10 -7 mol L -1) solutions [50]. The [Ru(bpy)3] 2+ core has also been used to construct first-generation dendrimers containing coumarin-450 chromophoric groups. In acetonitrile solution energy transfer from the excited cottmarin units to the [Ru(bpy)3] 2+ core - the excited state of which is again protected from dioxygen quenching - occurs with almost 100 % efficiency, and absorbance of near UV light leads to the characteristic orange emission of the core [52]. When two first- or second-generation 1,3,5-

5.5 Dendfimers I 107 ig. 5.10. (continued) phenylene-based dendrons are appended to the 3 and 8 positions of the phenan- throline ligand of the [Ru(bpy)2(phen)] 2+ complex (phen = 1,10-phenanthroline), excitation in the phenylene dendrons is followed by very efficient (>98 %) energy transfer to the Ru(II)-based moiety [53]. A series of dendrimers with a [Cu(phen)2]+-type core and 4, 8, or 16 peripheral C60 units has been prepared. With these energy transfer occurs from the core to the periphery, as part of an intriguing "black-box" effect exerted by the fullerene units toward the central chromophore [54]. Self-assembly of functionalized carboxylate-core dendrons around Er 3+, Tb 3+, or Eu 3+ ions leads to the formation of dendrimers (Fig. 5.10b) [55]. Experiments per- formed in toluene solution showed that UV excitation of the chromophoric groups

108 I 5 Light-harvesting Antennae contained in the branches caused the sensitized emission of the lanthanide ion, presumably by an energy-transfer Fbrster mechanism. The much lower sensitiza- tion effect found for Eu 3+ compared with Tb 3+ was ascribed to weaker spectral overlap, but it is also possible that Eu 3+ can quench the donor excited state by electron transfer [56]. Addition of water to a THF-mesitylene solution of these dendrimers

showed that access of water molecules to the lanthanide core is easier for larger dendrimers, presumably because steric crowding weakens the coordination of the carboxylate ligands to the metal ion [55]. 5.5.1.2 Metal Complexes in Each Branching Center Polypyridine ligands have been extensively used to build polynuclear complexes with dendritic structures [46, 48, 49, 57]. In such dendrimers the metal units are linked by bridging ligands. The choice of suitable bridging ligands is crucial in determining the properties of dendrimers, because: � their coordinating sites (and those of the "terminal" ligands) influence the spec- troscopic and redox properties of the active metal-based units; � their structure and the orientation of their coordinating sites determine the architecture of the dendrimer; � their chemical nature controls electronic communication between the metal- based units. Although a variety of dendrimers containing Ru(II) and, less frequently, Os(II) polypyridine complexes has been reported, only those based on 2,3- and 2,5-bis(2-pyridyl)pyrazine (2,3- and 2,5-dpp) as bridging ligands and 2,2'-bipyridine (bpy) and 2,2'-biquinoline (biq) as terminal ligands (Fig. 5.11) have been carefully investigated photophysically [46, 48, 49]. The typical strategy used to prepare den- drimers containing the 2,3- and 2,5-dpp bridging ligands is the so-called "com- plexes as metals and complexes as ligands" approach [58-60]; this has enabled the construction of species containing 4, 6, 10, 13, and 22 metal-based units. A docosa- nuclear dendrimer of that family, such as that shown schematically in Fig. 5.11, is a 44+ cationic species made of 1090 atoms, with an estimated size of 5 nm. Besides the 22 metal atoms, it contains 24 terminal ligands and 21 bridging ligands. Such dendrimers can be viewed as ordered ensembles of [M(L),BL)3_, 2+ complexes [M = Ru(II) or Os(II); L = bpy or biq; BL = 2,3- or 2,5-dpp] which are known to have: � intense ligand-centered (LC) absorption bands in the UV region and moderately intense metal-to-ligand charge-transfer (MLCT) bands in the visible region, � relatively long-lived luminescence in the red spectral region, originating from the lowest 3MLCT level. In the dendrimers, there is only a small electronic interaction between nearby mononuclear units and the absorption spectrum is, therefore, practically the sum of the spectra of the constituent units. In the dendrimers of higher nucle-

'J 44+ Fig. 5.11. Schematic representation of a dendrimer containing Ru and/or Os complexes in each branching site [58-60]. The formulae of the 2,3- and 2,5-bis(2-pyridyl)pyrazine (2,3- and 2,5-dpp) bridging ligands and of the

2,2Cbipyridine and 2,2 - biquinoline (bpy and biq) terminal ligands are also shown. 5.5 Dendfimers I 109 Metals -. Ru]z, Os]z Bridging ligands 2,3-dpp 2,5-dpp Terminal ligands C bpy arity, therefore, the molar absorption coefficient is huge throughout the entire UV- visible spectral region (e = 202,000 L mol - cm - at 542 nm for a docosanudear dendrimer in which all the metal ions are Ru(II) [58]), so that most of the photo- chemically active part of sunlight can be absorbed. In these dendrimers the small, but not negligible, electronic interaction between nearby units is sufficient to cause very fast energy transfer that leads to the quenching of potentially luminescent units with higher-energy 3MLCT levels and sensitization of the luminescence of traits with lower-energy 3MLCT levels. Recent studies have suggested that energy transfer between nearby units occurs within 200 fs, probably from non thermalized excited states [61]. The energy of the 3MLCT excited state of each trait depends on metal and ligands in a predictable way and the modular strategy used [58, 59] enables high synthetic control of the nature and position of metal centers, bridging ligands, and terminal ligands. Such a synthetic control translates into a high degree of control on the direction of energy flow within the dendritic array, as shown by the deca- nuclear compounds represented in Fig. 5.12. On increasing the nudearity, how- ever, a unidirectional gradient (center-to-periphery or vice versa) for energy transfer cannot be obtained with two types of metal [Ru(II) and Os(II)] and ligand (bpy and 2,3-dpp) only [46, 59]. An extension of this kind of antenna is a first-generation heterometallic dendrimer with appended organic chromophores like pyrenyl units [62].

Light-harvesting Antennae Fig. 5.12. Schematic representation of the different energy-transfer patterns that can be obtained in decanuclear dendrimer-type compounds by choice of different metals and ligands [46, 48, 49]. The arrows indicate the energy transfer steps; gray and black circles indicate Ru(11) and Os(1l), respectively; in the peripheral positions, circles and squares indicate M(bpy)2 and M(biq)2 components, respectively. The compounds have 20+ electric charge. As we will see in Section 8.4, these metal-based dendrimers also have quite interesting electrochemical properties [45e, 46, 63]. 5.5.2 Dendrimers Based on Organic Chromophores Energy-transfer studies have been performed on perylene-terminated phenyl- acetylene dendrons [64]. In compounds of type 7 (Fig. 5.13a), all the units of the dendron are equivalent so there is no energy gradient from the periphery to the focal perylene unit. In such compounds the light-harvesting capacity increases with increasing generation, because of the increase in the molar absorption coefficient, but the efficiency of energy transfer from the dendron to the perylene unit decreases with increasing generation (from 95 % for the first generation dendron to 50 % for the sixth generation dendron). In compound 8 (Fig. 5.13b), however, there is a variable monomer type in each generation, so an energy gradient is present. In such compound energy transfer to the perylene core is very fast (1.9 x 10 s -1) and very efficient (98 %) [65]. These results show that, as expected theoretically [66], "random walk" energy transfer from periphery to core is less productive than a directional multistep process.

5.5 Dendfimers I 111 Dendrimers with a polyphenyl core around a central biphenyl unit decorated at the rim with peryleneimide chromophores have been investigated both in bulk and at the single-molecule level to enable understanding of their time- and space- resolved behavior [67]. The results obtained have shown that the conformational distribution plays an important role in the dynamics of the photophysical processes. Energy transfer in a series of shape-persistent polyphenylene dendrimers substituted with peryleneimide and terryleneimide chromophoric units has been investigated in toluene solution [68]. Energy hopping among the peryleneimide chromophores, revealed by anisotropy decay times [69], occurs with a rate constant of 4.6 x 109 s -1. When three peryleneimide and one terryleneimide chromophores are attached to the dendrimer rim, energy transfer from the former to the latter units occurs with >95 % efficiency. All the observed energy-transfer processes can be interpreted on the basis of the F6rster mechanism. Polyphenylene dendrimers with a perylene diimide as a luminescent core have also been investigated [70]. In a dendrimer consisting of a terrylenediimide core and four appended peryleneimide units the antenna effect has been studied at the single-molecule level [71]. Very interesting antenna systems have been constructed by functionalizing the chain ends of a poly(aryl ether) convergent dendritic backbone with coumarin-2 (-em = 435 nm) and its focal point with coumarin-343 (-em = 490 nm) [72]. The fourth generation dendrimer 9, reported as an example of this family, is represented schematically in Fig. 5.14. In these dye-labeled dendrimers light absorbed by the numerous peripheral coumarin-2 units is funneled to the coumarin-343 core with remarkably high efficiency (in toluene solution it is 98 % for the first three generations and 93 % for compound 9 shown in Fig. 5.14). Given the large transition moments and the good overlap between donor emission and acceptor absorption, energy transfer occurs by the Fbrster mechanism [72b]. Oligo(p-phenylenevinylene) (OPV) units are increasingly used to obtain photo- active dendrimers and polymers [73]. In OPV-substituted poly(propylene amine) dendrimers interchromophoric interactions are sufficiently strong in 2-methylte- trahydrofuran to induce delocalization of the excitation over more than one chro- mophoric group [74], which is a phenomenon observed in natural light-harvesting complexes (Section 5.2). In OPV-terminated dendritic wedges functionalized with C60 at the focal point, the excited OPV moieties transfer energy to the fullerene core by Fbrster-type singlet-singlet energy transfer in dichloromethane solution [75]. An ultrarapid fluorescence anisotropy study of the interactions between branch chromophoric units in small model dendritic systems has shown that coherent or incoherent energy migration processes can prevail, depending on the specific structure of the dendrimer [76]. 5.5.3 Dendrimers Containing Porphyrins Besides being used as components of the arrays illustrated in Section 5.3, por- phyrins are also employed as components of light-harvesting dendrimers.

Morphology-dependent antenna properties have been reported [77] for a series of dendrimers of general formula (L).P, where P is a free-base porphyrin core bearing different numbers (rr, from 1 to 4) of poly(benzyl ether) dendrons (L) at the meso position of the central porphyrin (Fig. 5.15a). In dichloromethane solution excita- tion of the chromophoric groups of the dendrons causes singlet-singlet energy- transfer processes that lead to the excitation of the porphyrin core. It was found that the energy-transfer quantum yield is much higher for the (L)4P dendrimer (0.8), which has spherical morphology, than for the partially substituted (L)P, (L)2P, and (L)3P species (quantum yield < 0.32). Fluorescence polarization studies on (L)4P showed that the excitation energy migrates very efficiently over the den- drons within the excited state lifetime, so that the four dendrons can be viewed as a single, large chromophore surrounding the energy trap. Temperature-dependent effects suggested that increased flexibility and conformational freedom were responsible for the decreased energy-transfer efficiency when the number of den- drons was reduced. Only the highly crowded (L)4P dendrimer retained a constant level of energy transfer, even at high temperatures. It was also postulated that cooperativity between dendrons, which decreases with increasing conformational mobility, is necessary for efficient energy transfer [77]. Such behavior would mimic that of natural photosynthetic systems (Section 5.2), in which energy migration within "wheels" of chromophoric groups results in efficient energy transfer to the reaction center. More recently the morphology effect was investigated by using much larger por- phyrin dendrimers consisting of a free-base porphyrin core, P, with up to four dendrons attached, each containing seven zinc porphyrin units (compound 10 in Fig. 5.15b) [78]. The presence of poly(benzyl ether) dendritic wedges at the periphery makes such dendrimers soluble in common organic solvents. Experiments performed in THF showed that in the star-shaped (10)4P dendrimer, energy transfer from the excited singlet states of dendrons 10 to the focal P core occurs with a rate constant of 1.0 x 109 s - and 71% efficiency, whereas in the conically shaped (10)P dendrimer the energy-transfer rate constant was 10 times smaller and the efficiency 19 %. This result shows that morphology indeed has a noticeable effect on the rate of energy transfer. Excitation of (10)4P at 544 nm with polarized light resulted in highly depolarized fluorescence from the Zn-porphyrin units (fluorescence anisotropy factor 0.03, compared with 0.19 for a monomeric refer- ence compound), indicating efficient energy migration among the Zn porphyrin units before energy transfer to the free-base core. For the conically shaped com- pound (10)P the fluorescence anisotropy factor was much higher (0.10). These results suggest cooperation of the four dendrons of (10)4P in facilitating the energy migration among the Zn porphyrin units. Clearly the (10)4P system, which incor- porates 28 light-absorbing Zn porphyrin units into a dendritic scaffold with an energy-accepting core, mimics several aspects of the natural light-harvesting LH1 complex. Rapid energy migration dynamics have also been observed for multi-porphyrin functionalized poly(propylene amine) dendrimers [79]. When a porphyrin core is linked to four 1,3,5-phenylene-based first- and second-generation dendrons, energy transfer from the excited dendrons to the porphyrin core is very efficient in dichloromethane solution (98 % for the largest dendrimer) [80]. This much higher efficiency, compared with the above described ayl ether dendrimers, has been ascribed to energy transfer through the cross conjugation of 1,3,5-phenylene-based dendrons and/or larger spectral overlap. Electrostatic assembly of negatively and positively charged dendritic pophyrins has been investigated by means of energy-transfer measurements [81]. The com- pounds used were made from zinc and free-base porphyrin cores surrounded by second generation Fr6chet-type dendrons functionalized at the periphery with ammonium and carboxylate units, respectively. The energy-transfer rate constant was found to be 3.0 x 109 s -1, in satisfactory agreement (Fbrster mechanism) with the expected core-to-core distance in the assembly of the positively and negatively charged dendrimers. A poly(L-lysine) dendrimer which carries 16 free-base porphyrins in one hemi- sphere and 16 zinc porphyrins in the other has been synthesized and studied in DMF solution [82]. In this dendrimer energy transfer from the Zn porphyrin units to the free-base units has been observed to occur with 43 % efficiency. When the 32 free-base and zinc porphyrins were placed randomly the efficiency of energy transfer was estimated to be 83 % [83]. Very efficient (98 %) energy transfer from Zn to the free-base porphyrins was also observed in a rigid, snow-flake-shaped structure in which three Zn porphyrin units alternated with three free-base por- phyrin units [84].

5.5.4 Host-Guest Systems

An important property of dendrimers is the presence of internal cavities which can accommodate ions or neutral molecules [85, 86]. This property has the potential to be exploited for a variety of purposes, including catalysis and drug-delivery. Energy transfer from the numerous chromophoric units of a suitable dendrimer to an appropriate guest might result in a light-harvesting antenna system. One advan- tage of such host-guest light-harvesting systems is that the wavelength of the resulting sensitized emission can be tuned by use of the same dendrimer and dif- ferent types of guest. Dendrimers of the poly(propylene amine) family functionalized with fluorescent dansyl units at the periphery have been used as hosts for fluorescent dye molecules (dansyl is the commonly used name for the 5-dimethylamino-l-naphthalenesul- fonamido chromophoric group) [87]. Each dendrimer rD, for which the generation number, r, goes from i to 5, comprises 2 + (i.e. 64 for 5D) dansyl functions in the periphery and 2 - 2 (i.e. 62 for 5D) tertiary amine units in the interior. The fourth-generation dendrimer 4D (11) is shown in Fig. 5.16. These dendrimers have intense absorption bands in the near UV spectral region ('truax = 252 and 339 nm; emax 12,000 and 3900 L mol - cm -, respectively, for each dansyl unit) and a strong fluorescence band in the visible region ('truax = 500 nm; (I) = 0.46, = 16 ns). In dichloromethane solution the rD dendrimers extract eosin from aqueous solutions, with the maximum number of eosin molecules hosted in the den-

5.5 Dendfimers I 119 .NMe2 ..,.NMe; -NMe2 NMe2/=' {--\ f.__ 'V'-' '/' ' NMe2 Me2 X n . 02 27 Nae2 ' 02S u. NH Ht NMe2 H " { Nh ' os .) . os.. -/ 2.NH J. ' .... NMe2 Me2 O2SN _ / O2 [NHSNe O- 'N. h F N -- H O2 - - N % /NN .T 'NEe2 O2S,N / / ../] N O2 Me2N H _(N' '--N N NMe2 H ,, sH J N NH - Me2 NH) (H H NMe2 2 O NH NH , 02 [. II Me2N /) Me N .... Ue2N 2 Me2N Me2N gCOO- Br iBr -o- '?' -o- 'T--o Br Br Eosin Fig. 5.16. Structure formulae of eosin and of the fourth generation pol�(prop�1ene amine) dendrimer 11 functionalized with fluorescent dans�1 chromophoric groups [$7].

120 I 5 Light-harvesting Antennae drimers increasing with increasing dendrimer generation, up to a maximum of 12 for the 5D dendrimer. The fluorescence of the peripheral dansyl units of the den- drimers is completely quenched via energy transfer (Fbrster mechanism) by the hosted eosin molecule, the fluorescence of which ('kmax = 555 nm) is, accordingly, sensitized. The behavior of fluorescein and rose bengal is qualitatively similar to that of eosin, whereas naphthofiuorescein is not extracted. Quantitative analysis of the results obtained has shown that a single eosin guest is sufficient to quench completely the fluorescence of any excited dansyl unit of the hosting dendrimer, and fluorescence lifetime measurements indicated that the dye molecules can occupy two different sites (or two families of substantially different sites) in the interior of the dendritic structure. Dendrimer 12 (Fig. 5.17), consists of a hexaamine core surrounded by eight dansyl-, twenty-four dimethoxybenzene-, and thirty-two naphthalene-type units [88]. In dichloromethane solution characteristic absorption bands of the compo- nent units and strong dansyl-type fluorescence are observed for 12. Energy transfer from the peripheral dimethoxybenzene and naphthalene units to the fluorescent dansyl units occurs with >90 % efficiency. When the dendrimer hosts a molecule of the fluorescent eosin dye (12 = eosin), the dansyl fluorescence, in its turn, is quenched and sensitization of the fluorescence of the eosin guest can

be observed. Quantitative measurements showed that the encapsulated eosin molecule collects electronic energy from all 64 chomophoric units of the dendrimer with an effi- ciency >80 % (partial overlapping between dansyl and eosin emission predudes better precision). Both intramolecular (i.e. within dendrimer) and intermolecular (i.e. dendrimer host - eosin guest) energy-transfer processes occur very efficiently by a Fbrster-type mechanism because of the strong overlap between the emission and absorption spectra of the relevant donor and acceptor units. Dye molecules can also be hosted by poly(propylene amine) dendrimers surface- modified with OPV units [89]. In these systems energy transfer from the OPV flu- orescent units ('kmax = 492 nm) to the enclosed dye molecules is not efficient in solution (40 % efficiency at maximum loading), but is very efficient in spin-coated films of dendrimer-dye assemblies. Dendrimer 13, shown in Fig. 5.18, is quite interesting because its interior con- tains 18 amide groups, which are known to coordinate lanthanide ions strongly, and the periphery contains 24 chromophoric dansyl units, which, as mentioned above, have intense absorption bands in the near-UV spectral region and an intense fluorescence band in the visible region [90]. Addition of lanthanide ions to 5:1 (v/v) acetonitrile-dichloromethane solutions of dendrimer 13 causes quench- ing of the fluorescence of the dansyl units. At low metal ion concentrations each dendrimer hosts only one metal ion and, when the encapsulated metal ion is Nd 3+ or Eu 3+, the fluorescence of all the 24 dansyl units is quenched with 100 % effi- ciency. Quenching by Nd 3+ occurs by Fbrster-type energy transfer from the fluo- rescent excited state of the dansyl units to a manifold of Nd 3+ energy levels and is accompanied by the sensitized emission in the near infrared region ('kmax = 1064 nm) of the lanthanide ion. Quenching by Eu 3+ is not accompanied by any sensitized emission, because it occurs by electron transfer owing to the low reduc-

5.5 Dendfimers I 121 Me2N. Me2 hv' O,,, Me2N NMe 2 [12 Eosin] Fi�. 5.17. Schematic representation of the ener�y-transfer processes occurrin� in dendrimer 1:2, which contains three different types of li�ht-harvestin� chromophoric unit [88]. All the excitation ener�y can be channeled in a hosted eosin molecule. tion potential of Eu 3+. In a rigid matrix at 77 K, however, where dectron transfer is disfavored, the quenching of the dansyl unit by Eu 3+ occurs by energy transfer, as demonstrated by the presence of the sensitized Eu 3+ emission [90b]. Lanthanide ions and divalent metal ions have also been incorporated into chiral dendritic polymers [91] and a single-molecule study of a host-guest system con- sisting of a second generation polyphenylene dendrimer and a cyanine dye has also been reported [92].

122 I 5 Light-harvesting Antennae O25 Me2N NH NMe2 Me2-- 2 X H NMe2 Z O2 M,,N"-.. �,l NHHSb HN .. O2 NH O NMe 2 -o ...... � o t 1 N ... ,, Me2N' O2 h .SO hv 3+ NH O m ' 2 [13 Nd] _ HN N H H H �o / H oNy....., Ne Q -"NH H O O2 Me2N NH N. so2 N. SO2 N. .... NMe2 T -02� O2 L H Me2N Me2N ..... ') F I Z w2 x // 02 Me2N NMe2 Fi�. 5.18. Schematic representation of the energy-transCer processes occurrin� in dendrimer 13 hostin� an Nd 3+ ion [90]. 5.5.5 Photoinduced Electron Transfer In all the dendrimers discussed above light harvesting is followed by more or less efficient energy-transfer processes which usually lead to the emission from a focal point of the dendrimer. As mentioned in Section 5.2, to mimic the natural photo- synthetic apparatus an artificial antenna system must be connected to an artificial reaction center to obtain photoinduced charge separation. Despite the extensive growth of dendrimer chemistry, very modest results have been obtained in this direction.

5.6 Other Systems I 123 Photoinduced electron transfer has been reported to occur in a po]yether den- dron end-capped with pyrenyl groups and functionalized at the focal point with a 3-(dimethylamino)phenoxy electron donor unit [93], in a polyether dendrimer with a 4,4'-bipyridinium core [94], and in a trinudear metal complex with an appended tetrathiafulvalene electron donor [95]. A very interesting analysis of paired electron transfer induced by the absorption of two photons in dendrimers with a 4,4'- bipyridinium core and naphthalene peripheral groups has recently been reported [96]. 5.6 Other Systems Light harvesting has also been investigated in a variety of other systems, e.g. membranes, self-assembled monolayers, polymers, and zeolites. Only a few of these systems will be mentioned briefly. The basic principles, of course, are always the same and the active components are usually those employed to construct the supramolecular arrays discussed in the previous sections of this chapter. Examples in which light harvesting has been coupled with photoinduced electron transfer are discussed in Section 6.3.5. 5.6.1 Polyelectrolytes In water-soluble polyelectrolytes the antenna effect has been used to amplify the photoreactivity of an energy trap [97]. In such compounds, referred to as photo- zymes (artificial photochemical enzymes), light is absorbed by an array of chro- mophores that transfer energy to an energy trap (usually an aromatic hydrocarbon) the excited state of which can promote an appropriate photochemical reaction. This effect can be used to destroy hydrophobic substrates (pollutants) [97a], to cause specific reactions [97b], and even to generate hydrogen [97c].

5.6.2 Polymers

Energy transfer in derivatized polymers with attached chromophores has been ex- tensively investigated [98-100]. For example, Ru(II) and Os(II) polypyridine complexes have been attached by amide linkage to a 1:1 styrene-p-aminomethylstyrene copolymer of polydispersity 1.5 and an average of 16 repeating units [99]. A mixed polymer was prepared by sequential coupling, first with a limited amount of the less reactive Os(II) complex and then with the more reactive Ru(II) complex to fill all the remaining free sites. In a mixed polymer containing the lower energy Os(II) complex and the higher energy Ru(II) complex in a 3:13 ratio (subsequently cor- rected to 5:11 [99c]), triplet -triplet energy trans fer from the excited Ru(I I) complex to the Os(II) complex was observed with efficiency higher than 90 % in acetonitrile

solution. Poly(amino acid)s have also been used as backbones in the construction of antenna systems [101]. Copolymerization of a styrene-functionalized $[\mathrm{Ru(bpy)_3}]^{2+}$ monomer with a styrene-functionalized coumarin-2 monomer in a 1:3 ratio in dimethylformamide was found to yield a copolymer in which energy transfer from the coumarin-2 donor to the $[\mathrm{Ru(bpy)_3}]^{2+}$ acceptor unit occurs by a F6rster-type mechanism with high efficiency (up to 98 %) [102]. The occurrence of directional singlet energy migration and directional charge separation has been shown in a series of well-defined block copolymers labeled with aromatic chromophores and quenchers [103].

5.6.3 Rotaxanes

Artificial antenna systems in which several chromophoric units are mechanically linked together in a polyrotaxane structure have recently been reported [104]. Such species comprise many c-cyclodextrin units, each bearing one or more naphthyl chromophoric groups, threaded by a poly(ethylene glycol) chain and stoppered by bulky groups. The polyrotaxane 14, shown schematically in Fig. 5.19 [104a], con- tains approximately 15 c-cydodextrins, each bearing two naphthalenesulfonate units, and an axle comprising an average of 45 $-\mathrm{OCH_2CH_2}-$ units, stoppered by two adamantane groups. When the dansyl-modified fi-cyclodextrin 15 is added to 14 in aqueous solution at 298 K a photoinduced energy-transfer process occurs from the naphthyl chromophoric groups of 14 to the dansyl unit of 15, which binds to the adamantane stoppers by virtue ofhydrophobic interactions (Fig. 5.19). This process, evidenced by the quenching of naphthalene fluorescence and sensitization of dansyl fluorescence, can be switched off by adding 1-adamantanol, which competes with the adamantane extremities of 14 for the cavity of 15. In successive, related, work [104b] anthracene units have been used as stoppers for a series ofpolyrotaxanes - indeed, an efficient energy-transfer process from the naphthalene units of the c-cydodextrin rings to the anthracene stoppers occurs within the polyrotaxanes. Fluorescence anisotropy measurements also indicate excitation-energy migration between naphthalene chromophoric units. The rotax- ane architecture, in conjunction with the threading procedure employed for the synthesis of this series of compounds, gives the interesting opportunity of adjusting the number of chromophores simply by changing the ratio between naphthalene-modified and plain c-CD units during the preparation of the poly- rotaxanes. 5.6.4 Zeolites Light-harvesting antenna systems based on zeolite L have been thoroughly investigated [105]. Zeolite L is a crystalline alumosilicate in which the SiO4 and A104

'=15 5.60her Systems I 125 (H3C)2 SO 2 15 Fi�. 5.19. Association of polyrotaxane 14 and dansyl-modified fi-cyclodextrin 15 in aqueous solution, and schematic representation of the ener�y-trans�er process that occurs in the resultin� complex [104a]. '=15 tetrahedra give rise to one-dimensional channels arranged in a hexagonal struc- ture. The diameter of the channel windows is 0.71 nm and the largest free diame- ter is 1.26 nm. Crystals of defined dimension in the size range from 30 to 3000 nm can be obtained [106]. Zeolite L has been used as a host for organization of dyes to furnish antenna properties. As shown in the schematic view of Fig. 5.20, a zone of the zeolite nanocrystal (e.g. the central zone in each channel, as in the figure), can be filled with molecules of a specific dye (dye1, e.g. 1,2-bis-(S-methylbenzoxazol-2- yl)ethene); then, under appropriate experimental conditions, second (dye2, e.g. pyronine) and third (dye3, e.g. oxonine) dyes are successively inserted into the channels. If the three dyes are suitably chosen, light excitation of dye1 located in

126 I 5 Light-harvesting Antennae h� l hv b l hv' hv' Fi�. 5.20. (a) Principle of an antenna based on zeolite nanocrystals containing organized donor (light gray rectangles) and acceptor (dark gray rectangles) dyes [107]. (b) Schematic

view of the result obtained with a bipolar three-dye antenna. the middle part leads to energy-migration processes on both sides of the channels giving rise to the sensitized emission of dye3 [107]. The energy-transfer scheme can also be reversed [108] and closure (stopcock) molecules can be used both to prevent the dyes from leaving the channels and to interface the dye molecules contained in the channels with the outside world [109].

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6 Photoinduced Charge Separation and Solar Energy Conversion 6.1 Introduction Sunlight is our ultimate energy source, and we need to understand better how stmlight is used by Nature to power life. This fundamental issue of scientific research has been beautifully expressed in poetic sentences by Wilhelm Ostwald [1]: "Die Rolle des fallenden Wasser aber wird bei der Maschine des Lebens yon den Sonnenstralen ibemommen; ohne die Sonnenstralen kann das rad des Lebens nicht im Gang erhalten werden und wir werden noch genauer erforschen missen, auf welchen Verhtiltnissen und Naturgesezen diese merknvirdige Umwandlung der Sonnenstralen in Nahrungsmittel und Wtirme beruht". Sunlight in the geological eras has also

provided us with fossil fuels, a non- renewable energy source that we are so eagerly consuming. In contrast, we are not yet able to take full advantage of the extraordinary amount of energy that the sun is supplying us every day. This paradox was first pointed out by Giacomo Ciamician in a famous lecture entitled "The Photochemistry of the Future" delivered in New York at the VIII International Congress of Pure and Applied Chemistry (1912) [2]: "So far human civilization has made use almost exclusively of fossil solar energy. Would it not be advantageous to make a better use of radiant energy?". Ciamician also real- ized that a civilization based on solar energy could re-equilibrate the economic gap, already existing at that time, between the northern and southern regions of the world: "Solar energy is not evenly distributed over the susface of the earth. There are privileged regions, and others that are less favored by the climate. The former ones would be the prosperous ones if we should become able to utilize the energy of the sun. The tropical countries would be conquered by civilization which would in this manner return to its birth-place". The final sentence of that paper presents a concept quite mean- ingful even today (we should only add off and nuclear energy to coal): "If our black and nervous civilization, based on coal, shall be followed by a quieter civilization based on the utilization of solar energy, that will not be harmful to the progress and to human happiness." Light excitation can induce a variety of chemical reactions. As discussed in other chapters of this book, several types of photochemical reaction are indeed used, in natural and artificial systems, for information processing. For energy-conversion purposes, however, photoinduced electron transfer is by far the preferred reaction in Nature. This process generates a charge-separated state which is then used to Molecular Devices and Machines -AJoume 7 into the Nano VdorId. V. Balzani, A. Credi, M. Venturi Copyright � 2003 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim ISBN: 3-527-30506-8

6.2 Natural Reaction Centers I 133 prepare the various high-energy molecules which fuel the organism. After the energy crisis of the nineteen-seventies several types of endoergonic photochemical reaction (e.g. photodissociation, valence photoisomerization) [3] have been pro- posed for artificial conversion and storage of solar energy, but the results have been disappointing. When the mechanism of natural photosynthesis had been eluci- dated in sufficient detail, mimicry of this natural process for artificial solar energy conversion began to be pursued by several research groups, as forecasted by Cia- mician [2]: "The photochemical processes, that hitherto have been the guarded secret of the plants, will have been mastered by human industr which will know how to make them bear even more abundant fruit than nature, for nature is not in a hurr but man- kind is." It should be pointed out, however, that only hopes, not fruit, are abundant so far. In this chapter we will first illustrate the working principle of the natural reac- tion centers in which electronic energy resulting from light excitation is used to perform charge-separation reactions. We will then examine some attempts to con- struct artificial systems capable of producing photoinduced charge-separation reactions and we will review some recent results in the field of solar energy con- version. 6.2 Natural Reaction Centers 6.2.1 Introduction As discussed in Chapter 5, antenna systems are widely used by Nature to solve the problem of light-harvesting. Such natural antennae collect large amount of solar energy and redirect it as electronic excitation energy to reaction centers (Fig. 5.3) where subsequent conversion into redox chemical energy occurs. The simplest and best understood reaction center is that found in purple bacte- ria, which can be taken as a model of all the photosynthetic reaction centers [4, 5]. The most important solar energy-conversion process, however, is that occurring in green plants [6-8], where the reaction center of Photosystem II has an electron- acceptor side quite similar to that of the bacterial reaction center and a very pecu- liar donor side which can use water as an electron source and produce dioxygen as a "waste" product. Because this peculiar feature is particularly relevant to the design of artificial systems capable of performing photoinduced water splitting, the donor side of the reaction center of Photosystem II will also be illustrated. 6.2.2 Bacterial Photosynthesis The structures of several bacterial reaction centers are known precisely as a result of X-ray crystallographic investigations [9, 10]. The photosynthetic reaction centers of bacteria and other organisms consist mainly of protein, which is embedded in and spans a lipid bilayer membrane. The basic photochemistry is performed by

Cell exterior Cell interior Fig. 6.1. Cy p BC BP QA A simplified view of the structure of the reaction center of Rhodopseudomonas viridis. cofactors buried within it [11]. A simplified view of the structure of the reaction center of Rhodopseudomonas viridis is sketched in Fig. 6.1. Detailed photophysical studies of this reaction center have led to a precise picture of the sequence of events participating in photoinduced charge separation [11, 12]. The key molecular components are a bacteriochlorophyll "special pair" (P), a bacteriochlorophyll monomer (BC), a bacteriopheophytin (BP), a quinone (QA), and a four-heme c-type cytochrome (Cy). These molecules are held in a fixed geometry by surrounding proteins, so that the twofold axis of P [13] is perpendicular to the membrane, the periplasmic face lies approximately between P and Cy, and the cytoplasmic face is at the level of QA. In the reaction center excitation of P by absorption of light or, more commonly, by singlet-singlet energy transfer from different antenna systems is followed by very fast (3 ps) electron transfer to the BP "primary" acceptor (whether the interposed BC plays the role of mediator in a superexchange mecha- nism or directly intervenes as an intermediate electron acceptor has been the object of debate [14]). The next step is a rapid (200 ps) electron transfer from BP to QA followed by a slower (270 ns) reduction of the oxidized P by the nearest heme group of Cy [1S]. At that stage, transmembrane charge separation has been achieved with an efficiency approaching unity and an extremely long lifetime with respect to charge recombination. The rate constants of the different electron-transfer steps involved in the charge- separation process are summarized in the approximate energy-level diagram of

6.2 Natural Reaction Centers I 135 Cy~*P~Bp~Q A 3 x 10 s - 1.0 - CY~P+~BP-~QA " 5 x 10 s - E (eV) c, Cy~P+~BP~QA - h 0.5 - ', c, .; ' 10 2 s - 0- Cy-P-BP-QA Fi�. 6.2. Ener��-Ievel dia�ram and rate constants of the electron-transfer steps involved in the char�e-separation process in the reaction center of Rhodopseudomonas ,iddis. Cy+~P~BP~QA - Fig. 6.2, together with those of the non-occurring BP-- P+ and QA-- P+ charge-recombination steps (as determined from experiments with modified reac- tion centers lacking the possibility of competing forward processes) [16]. Figs. 6.1 and 6.2 point out the importance of the supramolecular structure of the reaction center. The achievement of efficient photoinduced charge separation over a large distance is made possible by optimization of several aspects of this photochemical device: � the organization of the molecular components in space, � the thermodynamic driving force of the various electron-transfer steps, � the kinetic competition between forward (useful) over back (dissipative) electron- transfer processes. How this occurs can be reasonably well understood in terms of electron-transfer theory (Section 2.2.1). In particular, the charge-separation process is highly effi- cient because the charge-recombination steps are slow, since they lie in the Marcus- inverted region. For highly efficient charge separation the photoinduced electron-transfer process must, furthermore, proceed only along one of the two branches of the apparently symmetric reaction center (Fig. 6.1). It is likely that mutations have broken the symmetry, imposing unfavorable Frank-Condon factors on the dis- favored side. It has also been observed [4] that if the distance between BP and Q^ were just a few angstroms longer, or the driving force of this reaction were several tenths of an eV larger or smaller, the quantum efficiency of the reaction center would suffer as charge recombination became more common. If, on the other

QBH2 Cytochrome Reaction center bc 1 complex H 4- Proton channel Fig. 6.3. Schematic representation of the bacterial photosynthetic membrane and of the different protein components. ATP Synthase hand, the driving force for the BP- to P+ ground-state reaction were reduced, this inverted region reaction would accelerate and also reduce the efficiency of the pro- ductive charge separation. Experiments with reaction centers oriented in an exter- nal electric field have provided some evidence that this is true [17]. In the process described above the ultimate electron acceptor is a quinone Q^. The process then continues with many other steps. The electron migrates to a second quinone QB and, after reduction of the oxidized special pair P by a c-type cytochrome (vide infra), the energy of a second photon is used to transfer a second electron to QB. Reduction of QB to its hydroquinone form involves the uptake of two protons from water on the internal cytoplasmic side of the membrane. The hydroquinone then diffuses to the next component of the apparatus, a proton pump, denoted the cytochrome bc complex (Fig. 6.3). This complex oxidizes the hydroquinone back to a quinone, using the energy released to translocate protons across the membrane and establish a proton concentration and charge imbalance (proton-motive force, pmf). The oxidation process is ultimately driven, via a variety of cytochrome redox relays, by the oxidized special pair P+, which becomes reduced to its initial state. Finally, the enzyme ATP synthase, a rotary motor described in Section 13.2, enables protons to flow back across the membrane, down the thermodynamic gradient, driving the release of adenosine triphosphate (ATP) formed from adenosine diphosphate (ADP) and inorganic phosphate (Pi). The ATP satisfies most of the energy needs of the bacterium. 6.2.3 Photosystem II Photosystem II (PSII) performs all the processes needed for photosynthesis - light absorption in antenna components, energy transfer to a reaction center, charge

6.2 Natural Reaction Centers I 137 a evolution ' ' reduction e- b 02 + 4H+ ,.... j2H20 hv hv hv hv X e- e- e- e- Fig. 6.4. (a) Schematic representation of the charge-separation process in PSII. (b) The five redox states (So - S4) of the Mn4 cluster. separation, and charge stabilization. It is, furthermore, capable of using water as the reductant of the quinone which is at the end of the acceptor side. To do that, PSII must: � reach potentials high enough to oxidize water (>+0.9 V relative to the NHE), � handle such a high oxidation potential in fragile biological structures, � couple the one-photon/one-electron charge-separation process to the four- electron water oxidation process. The water oxidation moiety of PSII [6, 18] consists of a triad composed of a multiruer of chlorophylls (denoted P680), a redox-active tyrosine amino acid (Tyrz), and a cluster containing four manganese ions (Mn4) (Fig. 6.4a). PSII spans the thylakoid membrane in the chloroplasts and the water oxidizing triad is located dose to one side of the membrane. The Mn4 cluster also contains a C1- and a Ca 2+ ion which are tightly coupled to the Mn ions. On direct absorption of a photon or energy transfer from the antenna units, P680 is excited and becomes a strong reductant. An electron is then transferred from excited P680 to the acceptor system (pheophytin and two quinones, Q^ and QB) on the other side of the mem- brane (Fig. 6.4a). The oxidized primary donor, P680 +, is one of the most oxidizing species found in Nature and reaches a potential of +1.2 V relative to the NHE. P680 + is rapidly reduced by Tyrz (r = 20-200 ns, depending on the S state of the Mn4 duster, see later) which, in its reduced state, is hydrogen-bonded to a nearby histidine residue [19]. Such a hydrogen bond facilitates oxidation of Tyrz which occurs with concomitant deprotonation. The oxidized Tyrz radical so obtained is reduced by electrons which ultimately are derived from water. How this happens is

138 I 6 Photoinduced Charge Separation and Solar Energy Conversion still largely unknown. When PSII works at full speed approximately 200 water molecules per second can be oxidized. This suggests that the kinetic barriers must be very low. On the other hand, oxidation of water to dioxygen is a four-electron process, so the results of four charge-separation events must be accumulated. This role is played by the Mn4 duster, which is close to Tyrz and is oxidized stepwise by the Tyrz radical to a series of states, as shown in Fig. 6.4b. Dioxygen evolution occurs when the most oxidized duster state, S4,

returns, in a four-electron reduction process, to the most reduced state, So. This process involves oxidation of two water molecules which have probably been coordinatively-bound to the manganese cluster. Although the nature of the interaction of the manganese cluster with the Tyrz radical is not fully understood, recent studies indicate a concerted proton- electron transfer (H-atom abstraction) mechanism of the manganese-bound water molecules by the tyrosine radical [20]. 6.3 Artificial Reaction Centers 6.3.1 Introduction The complexity of natural photosynthetic systems is clearly beyond the reach of the synthetic chemist. This complexity is, however, largely related to their living nature and it is entirely plausible that a single photosynthetic function, e.g. photoinduced charge separation, can be duplicated by relatively simple artificial systems. The lesson from Nature is that the achievement of such a function requires supra- molecular structures with very precise organization in the dimensions of space (relative location of the components), energy (excited states energies and redox potentials), and time (rates of competing processes). Such organization, which in natural systems comes as a result of evolution and is dictated by intricate intermolecular interactions, can be imposed in artificial systems by molecular engineering exploiting covalent bonding [21]. Artificial charge-separation devices can be constructed with synthetic strategies somewhat similar to those used for multicomponent systems to be used as "wires" in optoelectronic molecular-level circuits (Chapter 3), even though the properties desired are, of course, somewhat different - in "wire-type" applications one is looking for fast and efficient (i.e. high quantum yield) electron transfer over long distances whereas for photosynthetic applications rate and distance, as such, are not important requirements, and a high quantum yield must be coupled with a high fraction of the energy of each absorbed photon remaining available after the charge-separation process. More difficult is the design and construction of artificial systems for oxygen evolution. The main problem is coupling photoinduced charge separation, a one- electron process, with oxygen evolution, a four-electron process. Nature's answer is

7 $ 6.3 Art�ial Reaction Centers I 139 b Fig. 6.5. (a) Schematic energy-level diagram for a dyad. (b) Structure formula of the porphyrin-fullerene dyad 1 [37]. the Mn4 cluster, i.e. a catalyst for multielectron transfer, capable of releasing elec- trons in a stepwise manner at constant potential and oxidizing water molecules in a concerted manner, to avoid the formation of high-energy intermediates (Fig. 6.4b). The design of specific multielectron redox catalysts

is a fascinating and chal- lenging problem of modern chemistry [22]. 6.3.2 Dyads The minimum model reaction center must consist of an electron-donor (or acceptor) chromophore that absorbs visible light, an additional electron-acceptor (or donor) moiety, and an organizational principle that controls their distance and electronic interactions (and therefore the rates and yields of electron transfer). Many such dyads have been constructed and investigated [12, 23-36]. The energy-level diagram for a dyad is shown schematically in Fig. 6.5a. All the dyad-type artificial reaction centers suffer to a greater or lesser extent from rapid charge recombination (process 4). In the recently reported dyad I (Fig. 6.5b), exci- tation of the porphyrin chromophoric unit to its singlet excited state (1.97 eV above the ground state) is followed by rapid (3.3 x 10 n s -) electron transfer to full- erene with a quantum yield of unity [37]. The charge-separated state lies 1.39 eV above the ground state and undergoes charge recombination with a rate constant 2.1 x 109 s-L This dyad thus converts a substantial fraction (F = 71%) of the excited state energy into chemical potential, but the converted energy is stored for a time too short to be used in subsequent chemical reactions. As we have seen above, the problem of rapid charge recombination has been overcome by Nature by use of a series of short-range, rapid, and efficient electron-transfer processes that

Fig. 6.6. Schematic representation of the two possible arrangements for charge-separating triads. lead to a charge separation over a long distance (Fig. 6.2). This strategy has there- fore been followed by several laboratories in the past 20 years. 6.3.3 iads Two possible schemes for charge-separating triads are shown in Fig. 6.6 [21]. Although the scheme in Fig. 6.6b is reminiscent of the natural photosynthetic reaction center, that of Fig. 6.6a seems to be more popular in the field of artificial triad systems. The functioning principles are shown in an orbital-type energy dia- gram in the lower part of Fig. 6.6. In both schemes excitation of a chromophoric component P (step 1) is followed by primary photoinduced electron transfer to a primary acceptor (2). This process is followed by a secondary thermal electron- transfer process (3) - electron transfer from a donor component to the oxidized chromophoric component (case a), or electron transfer from the primary acceptor to a secondary acceptor component (case b). The primary process competes with excited-state deactivation (4) whereas the secondary process competes with primary charge recombination (5). Finally, charge recombination between remote molecu- lar

components (6) leads back the triad to its initial state. For case a, the sequence of processes indicated above (-2-3) is not unique. Actually, the alternate sequence 1-3-2, would also lead to the same charge- separated state. In general, these two pathways will have different driving forces for the primary and secondary steps, and thus one might be kinetically favored over the other. Occasionally one of the two pathways is thermodynamically allowed and

by Fig, 6,7, 6.3 Artcial Reaction Centers I '14] hv / � -- ,N'- -N ,N-C. H17 ,3co � 7 TM o 4 Structural formulae of triads 2 [38] and 3 [41-43]. the other is not, although in a simple one-electron energy diagram such as Fig. 6.6a this aspect is not apparent. The performance of a triad is measured by the following properties: � the lifetime of charge separation (depending on the rate of the final charge- recombination process, r = 1/k6); � the quantum yield of charge separation (depending on the competition between forward and back processes, (I) = [k2/(k2 q- k4)][k3/(k3 q- ks)]); � the efficiency of energy conversion (which depends on the quantum yield and on the fraction, F, of the excited-state energy conserved in the final charge-separated state, %.cov. = (I) x F). To put things in a real perspective, it should be recalled that the "triad portioff' of the reaction center of bacterial photosynthesis discussed above (Section 6.2) converts light energy with r 10 ms, (I) = 1, and /e.cov. 0.6. Of many triad systems developed by a variety of laboratories, a few examples will be discussed briefly here. Several reviews are available [12, 23-36]; the report given in Ref. [33] is particularly detailed. Triad 2, shown in Fig. 6.7, works according to the scheme in Fig. 6.6a, with a porphyrin as light-absorbing chromophore, naphthoquinone as acceptor, dimethyl- aniline as donor, and tripticene bridges as connectors [38]. Charge separation is very efficient (O = 0.71) and long-lived (r = 2.5 ps) in room-temperature butyronitrile solution, and the charge-separated state has an energy of 1.39 eV. The charge-separation function is completely suppressed by cooling the system to low-temperature rigid solutions, behavior contrary to what happens for natural photosynthetic systems. The reason is that blocking the reorientation of solvent dipoles strongly destabilizes the charge-separated states relative to the fluid solution [39]. In particular, the forward secondary electron-transfer step 3 (which in fluid solution is exergonic by 0.14 eV) becomes endergonic in a rigid matrix. As proof, in a triad containing a higher-energy chromophore and better electron- acceptor and -donor components (driving force of secondary electron-transfer step in fluid solution, 0.45 eV), photoinduced charge separation proceeds even at 5 K in 2-methyltetrahydrofuran [40]. Interestingly, under these conditions the charge-separated state can be detected as a spin-polarized transient EPR signal, which gives information about donor-acceptor electronic coupling. Interesting triads have also been obtained by using aromatic diimides (see, e.g., triad 3 in Fig. 6.7). In these linear, rod-like compounds all the relevant states, i.e. the excited singlet state of the aromatic diimides and both ion pairs, are spectroscopically distinct from each other and fully resolved by transient absorption spec- troscopy [41-43]. In the MeOAn-ANI-NI triad 3 excitation of the charge-transfer state of ANI results in a subnanosecond formation of the MeOAn'+-ANI-NI '- charge-separated state (92 % yield in toluene), which decays with a lifetime of 310 ns [41] to the MeOAn-ANI-3NI triplet excited state [42]. The charge-separation process causes an increase in the dipole moment from 12 to 87 D, measured by transient dc conductivity [43]. In a recently investigated porphyrin-pyromellitimide- fullerene triad, it has been found that the mechanism of the charge-recombination process switches from sequential to superexchange on changing the linkage moi- eries [44]. Triad 4 (Fig. 6.8) consists of a porphyrin bearing a fullerene as in dyad 1, and a carotenoid (C) secondary electron donor. Excitation of the porphyrin unit of the triad in 2-methyltetrahydrofuran causes the events shown schematically in the energy-level diagram of Fig. 6.8 [45, 46]. The C-1p-c60 excited state decays almost exclusively by electron transfer (step 2) with formation of C-P'+-C60 '- with k2 = 3.3 x l0 ll s -1 and quantum yield unity. A small fraction of C-p-1c60 excited states is also obtained, but these also decay to C-P'+-C60 '- by electron transfer, steps 3 and 4. According to what happens in dyad 1, C-P'+-C60 '- can return to the ground state by charge recombination with k7 = 2.1 x 109 s -1. Electron transfer from the carotenoid to the porphyrin is, however, much faster (k8 = 1.5 x 10 The C'+-P-C60 '- state is therefore produced with an overall quantum yield of 0.88. It decays slowly by charge recombination to yield the carotenoid triplet (k9 = 2.9 x 106 s-l). In conclusion, the two-step electron-transfer sequence in triad 4 has increased the lifetime of charge separation by a factor of nearly 103 relative to dyad 1. Triad 4 has also been found to have other properties that are present in the reaction centers, but not common in artificial biomimetic systems [47, 48]. For example, the formation of C'+-P-C60 '- occurs even in a glass at 8 K. Charge recombination of C'+-P-C60 '-

yields 3C-P-C60 with a unique EPR-detectable spin polarization pattern and occurs by a radical pair mechanism [47], as observed in natural reaction centers. Transfer of triplet excitation energy by a relay mechanism related to that found in some reaction centers is, furthermore, also observed for this triad. In contrast with what happens in 2-methyltetrahydrofuran, in toluene solution the C-P-1C60 excited state of 4 does not undergo electron transfer, decaying instead by intersystem crossing to yield C-p-3c60. This triplet excited state decays with the rate constant 9 x 106 s -1 to give the carotenoid triplet, 3C-P-C60, via the slightly endergonic formation of the C-3p-c60 excited state [49]. In Nature the quenching of the chlorophyll triplets by carotenoids is an important protective mechanism against photodegradation caused by formation of singlet oxygen [50].

6.3 Art�ial Reaction Centers H N-C o c 143 P C6o 2.0' E (eV) 1.0-- C-1p-C6o C-P-C6o Fi�. 6.8. Structural formula and enersy-level dia�ram for triad 4 [45]. 3[C'+-p-c] 3 C - p - C6o iCH3 OCH3 0 ,N+ / /', 52+ Fig. 6.9. Structural formula of triad 5 2+ [51].

144 I 6 Photoinduced Charge Separation and Solar Energy Conversion In triads, complications may arise from the structure. For example, triad 52+ is not linear, as would appear from the simple representation shown in Fig. 6.9, but has a U-shaped conformation [51]. This triad, which, in principle, is of the type shown in Fig. 6.6b, consists of a porphyrin chromophoric unit rigidly linked to two electron acceptors - a quinone and a methylviologen derivative. Because the bridge curves back towards the porphyrin, the viologen unit is rather dose (10A) to the center of the porphyrin. Excitation of the porphyrin yields the porphyrin-viologen charge-separated state with a rate constant 3 x 109 s -4. Whether or not the naphthoquinone plays a role (with or without its intermediate reduction) is un- clear. Charge-recombination is biphasic, with rate constants 2 x 106 s -4 (70 %) and <1 x l0 s s -4 (30 %). Several triads in which at least one of the molecular components (usually that which absorbs light) is a transition-metal coordination compound have also been designed and investigated [34, 52]. Acceptor molecular components are often viologens or quinones, whereas donor units are most often phenothiazine or amine moieties. Some representative examples are shown in Fig. 6.10. Extensive studies have been reported on compounds 63+ [53, 54]. When R = R' = CH3, the system behaves according to the scheme in Fig. 6.6a, with k2 and k3

greater than 2 x 108 s -4 and a charge-recombination rate constant k 6 of the order of i x 107 s M. The yield of formation of the charge-separated state is 0.25. When R = COOH and R' = CH3, small energy changes improve the charge-separation efficiency [53a]. The possibility of spin chemical control of the rates of the electron-transfer pro- cesses occurring in these compounds has also been investigated [55]. Several triads consisting of a bis-terpyridine metal complex linked to a zinc or free-base porphyrin as electron-donor photosensitizer and a gold(III) porphyrin as a final electron acceptor have been investigated [56-64]. In the recently studied family of triads 7 + [60-64] (Fig. 6.10), both the photophysical and electrochemical properties of the central metal complex are crucial in determining the nature and the rates of the photoinduced events. When the complex is bis-terpyridine Ru(II) the singlet excited state of the porphyrin is quenched by energy transfer whereas with bis-terpyridine Ir(III) photoinduced electron transfer to the central metal complex occurs with a rate constant of 3.3 x 10 TM s -4 for the free-base porphyrin followed by slower (1.2 x 10 TM s -4) electron transfer from the Ir complex to the gold porphyrin. The back electron-transfer process occurs with a rate constant of 2.8 x 108 s -4 [62]. Extended investigations have also been performed on porphyrin-stoppered rotaxanes [65-67]. Compound 82+, shown in Fig. 6.10, is an example of a triad of the type shown in Fig. 6.6a. Excitation of the Cu(I) complex directly or via energy transfer from the Zn porphyrin leads to very rapid electron transfer to the gold porphyrin; this is followed by secondary electron transfer from the Zn porphyrin to the oxidized Cu(II) complex, followed by back-electron-transfer to the initial ground state (k = 2 x 108 s -4) [67]. The machine-like behavior of 82+ will be dis- cussed in Section 13.4.1. Other triads based on catenanes, somewhat related to artificial photosynthesis, have been investigated [68, 69]. Compound 96+ (Fig. 6.11) has some similarity with

, R R']3+ z N'"qu]--N, , / ", N -N N 6.3 Artcial Reaction Centers I 145 6a 3+ R=R'=CH3 6b 3+ R = COOH R' = CH 3 M = Zn, 2H x=0,1 I M,=Run, lrm n=3,4 ' n+ Fig. 6.10. Structural �ormulae of triads 63+ [53], 7 " [60-64], and 82+ [67].

146 I 6 Photoinduced Charge Separation and Solar Energy Conversion _' N" Ru,.n--N_ -- ; ', -- . (' N. 0 N 0 9 6+ ooo. N'.r.ia.--N*,. h I N" '" NO -h 0 126+ FiB. 6.. Structural ormulae ocompounds 96+ [6] 06+ [7b], and triads 6+ and

26+ [72]. the photosynthetic reaction center, because its has "redox asymmetry". Electron transfer from the excited Ru(II) complex to the external viologen unit is more exergonic (AG�=-0.32 eV) than that to the viologen unit surrounded by the electron-donor crown ether (AG � = -0.19 eV) [68]. If the other relevant parame- ters (electronic coupling and Franck-Condon factor) are identical for the two reac- tions, such redox asymmetry would suggest that 85 % of the observed quenching of the luminescence of the Ru(II) complex is because of electron transfer to the

6.3 Artificial Reaction Centers [147 external vio]ogen. Unfortunate]y, however, the two reduced vio]ogens cannot be distinguished by spectroscopic means, so this interesting hypothesis could not be verified. A coordinating bipyridyl unit can also be incorporated in an electron-donor macrocycle. An artificial dyad 106+ (Fig. 6.11), consisting of a crown ether con- taining a [Ru(bpy)3]2+-type unit, mechanically linked in a catenane fashion to a cydobis(paraquat-p-phenylene) moiety (CBPQT4+), has been prepared and inves- tigated [70]. The photophysical behavior of this dyad in aqueous solution showed that the excited Ru(II) complex is quenched by electron transfer to the viologen moieties with a rate constant >2 x 108 s-L A semisynthetic approach to artificial photosynthesis was then performed using compound 106+ [71, 72]. The artificial photosynthetic reaction centers 116+ and 126+ (Fig. 6.11) were constructed on a protein surface by cofactor reconstitution. Reconstitution of apo-myoglobin (Mb) with 116+ and 126+ afforded the two Mb-based artificial triads Mb(FenOH2) - [Ru(bpy)3]2+-CBPQT 4+ and Mb(Zn)-[Ru(bpy)3]2+-CBPQT 4+ [72]. Excitation of the [Ru(bpy)3] 2+ moiety of 116+ derivative Mb(FemOH2)-[Ru(bpy)3]2+-CBPQT 4+ in aqueous solution causes photoinduced electron transfer from the Ru complex to the CBPQT 4+ electron-acceptor unit, followed by a proton-coupled electron transfer that leads, with a quantum yield of 0.005, to the final charge-separated state con- taining a porphyrin cation radical and a reduced viologen radical, Mb(Fe4V=o) - [Ru(bpy)3]2+-CBPQT '3+. This species lies 1 eV above the ground state and has a lifetime (>2 ms) comparable with that of the charge-separated state in the natu- ral photosynthetic process. With Mb(Zn)-[Ru(bpy)3]2+-CBPQT 4+ the charge- separated state Mb(Zn)'+-[Ru(bpy)3]2+-CBPQT '3+ is obtained, with the same excess energy, much higher quantum yield (0.08), but much faster (102-103-fold) recombination rate. The longer lifetime of the 116+ derivative is attributed to the involvement of protons in the electron-transfer process. Triad 126+ was also incor- porated into cytochrome b562 (Cy-b562). Comparison of the rates of various pro- cesses, particularly the rate of charge recombination [300 ns for 126+ , 600-900 ns for Cy-b562(126+), and 1.1-1.8 Is for Mb(126+)] showed that the protein matrix plays an important role in biological electron-transfer processes [73]. 6.3.4 Tetrads and Pentads The extension of triads to larger systems - tetrads and pentads - for photoinduced charge separation can be exemplified by the series of compounds 13, 14, and 15 shown in Fig. 6.12 [27, 74]. The key point is the introduction of further molec- ular components (a secondary acceptor as in 14 and 15, a secondary donor/ chromophore as in 15), and thus of further electron-transfer steps which result in charge separation over increasingly larger distances. As the number of molecular components increases, so also does the mechanistic complexity, as shown by Fig. 6.13, in which the possible charge-separation pathways of 15 are indicated in an energy-level diagram [75]. The improvement in performance with increasing complexity can be seen by comparing data for the triad and the pentad: for 13,

O' 0=l _=0 O (o= ___-/o (O= 0 O= z-l- z j z-l- 0 =0 . N ZT

r = 300 ns, (I)= 0.04, and qe.cov. = 0.02 (dichloromethane); for 15, r = 55 (I) = 0.83, and /e.cov. = 0.5 (chloroform). A tetrad comprising a ferrocene group, a Zn porphyrin, a free-base porphyrin, and a C60 unit, Fc-ZnP-P-C60, has recently been reported [76]. In this system excitation of the Zn or the free-base porphyrin causes electron transfer, leading to Fc-ZnP-P'+-C60'-; successive charge-shift processes produce the final charge- separated state, Fc+-ZnP-P-C60 '-, with (I)= 0.24 and /e.cov. = 0.13 (benzo- nitrile solution). Lifetime measurements reveal that in solution charge recom- bination occurs mainly via bimolecular processes, i.e. the intramolecular charge recombination is too slow to compete with diffusion-limited intermolecular elec- tron transfer. The lifetime of charge separation has been measured in a frozen matrix by time-resolved EPR experiments; it was found to be remarkably long (380 ms in benzonitrile at 193 K). In the related tetrad Fc-(ZnP)2-C60 [77] the final charge-separated state, Fc+-(ZnP)2-C60 '- , with (I)= 0.80 (/e.cov. 0.4) is obtained by excitation of the zinc porphyrin dimer in benzonitrile solution at 295 K. In this species charge recombination (r = 19 its) apparently occurs via a reversed stepwise process, that is, a rate-limiting electron transfer from (ZnP)2 to Fc + followed by a fast electron transfer from C60'- to (ZnP)2 '+, which regenerates the ground state. Tetrads based on imide acceptors have been studied for optical switching pur- poses [78] (Section 4.2.1.2). The results obtained with other multicomponent systems have been reported in several reviews [29-35]. In summary, artificial

supramolecular systems for photoinduced charge separation have reached a well- developed stage, occasionally approaching the performance of natural reaction centers. 6.3.5 Antenna-Reaction Center Systems It can be noticed that both energy transfer and photoinduced electron transfer occur in pentad 15. Energy- and electron-transfer processes are observed after photoexcitation for a variety of other systems (e.g. tetrads 16 [79], 17 [80], and 18 [81], shown in Fig. 6.14) [82]. Coupling energy- and electron-transfer processes is indeed an interesting issue. As we have seen in Section 6.2, in natural systems the solar energy collected by the antenna devices at the end of the energy-transfer chain is used to promote a charge-separation reaction, i.e. to obtain redox energy. To mimic the natural photosynthetic apparatus, an artificial reaction center must be connected with an artificial antenna system [83]. 6.3.5.1 Porphyrin-based Arrays An interesting attempt to couple energy- and electron-transfer processes is repre- sented by compound 19 (Fig. 6.15) which consists of four covalently linked zinc tetraarylporphyrins, (ZnPp)3-ZnPc (p stands for peripheral, c stands for central) covalently joined to a free base porphyrin-fullerene dyad, P-C60, to form the (ZnPp)3-ZnPc-P-C6o hexad [84]. Results obtained from careful time-resolved emission and absorption investiga- tions in 2-methyltetrahydrofuran solution, compared with those obtained for some model compounds, have led to the following picture: � excitation of any peripheral zinc porphyrin is followed by singlet-singlet energy transfer to the central zinc porphyrin (Eq. 1) with a rate constant kl = 2.0 x 1010 � singlet-singlet energy transfer from the central zinc porphyrin to the free-base porphyrin (Eq. 2) occurs with a rate constant k2 = 4.1 x 109 � electron transfer from the excited free-base unit to the fullerene unit (Eq. 3) is very rapid, k 3 = 3 x lO ll � the lifetime of the charge-separated state is 1.3 ns (Eq. 4, k4 = 7.5 x 10 8 1 (ZnPp)3_ZnPc_P_C6 � _ (ZnPp)3_lZnPc_P_C60 (ZnPp)3-1ZnPc-P-C60 - (ZnPp)3-ZnPc-lP-C60 (ZnPp)3-ZnPc-lP-C60 - (ZnPp)3-ZnPc-p'+-C60 '- (ZnPp)3-ZnPc-p'+-C60 '- - (ZnPp)3-ZnPc-P-C60 (1) (2) (3) (4) The quantum yield of the charge-separated state is unity on excitation of the free- base porphyrin, because of the very large rate constant for photoinduced electron

6.3 Artificial Reaction Centers [151 O_N/C6H13 o 18 Fig. 6.14. Structural formulae oftetrads 16 [79], 17 [80], and 18 [$1]. transfer (Eq. 3); on excitation of the Zn porphyrin units, however, the quantum yield drops to 0.70, because of the competition between intrinsic decay and energy transfer to the central free-base porphyrin. The non-unit quantum yield of charge separation and the short lifetime of the charge-separated state left room for improvement of the performance of the hexad by dever molecular engineering of

152 I 6 Photoinduced Charge Separation and Solar Energy Conversion ' ZnPp ZnPp E I ZnPp ', Free base porphyrin / 060 P 20 P = - - 19 P= Fig. 6.15. Schematic representation of the energy- and electron-transfer processes that occur in hexads 19 [84] and 20 [85].

6.3 Amfi�ial Reaction Centers [153 the free-base porphyrin unit. Replacement of the free-base diaryloctaalkylporphyrin of 19 with a meso-tetraarylporphyrin gives compound 20 (Fig. 6.15) [85]. In 2-methyltetrahydrouran solution this hexad leads to faster energy transfer from the central Zn porphyrin to the free-base porphyrin compared with 19, thereby increasing the overall yield of charge separation. Because the tetraarylporphyrin employed in 20 has a higher oxidation potential than its octaalkylporphyrin analog in 19, migration of the positive charge from the free-base porphyrin to the Zn porphyrin system (Eq. 5) occurs, moreover, with a rate constant ks = 2.6 x 109 s -1. The lifetime of the final charge-separated state is increased to 240 ns (Eq. 6; k 6: 4.2 x 10 6 s-l). (ZnPp)3-ZnPc-P'+-C60 '- - [(ZnPp)3-ZnPc]'+-P-C60 '- (5) [(ZnPp)3-ZnPc]'+-P-C60 '- - (ZnPp)3-ZnPc-P-C60 (6) Coupled light harvesting and charge separation has also been obtained in modi- fied windmill porphyrin arrays [86]. In the compounds shown in Fig. 6.16, which bear a naphthalenetetracarboxylic diimide or a meso-nitrated free-base porphyrin electron acceptor attached to the two ZnPc units, energy transfer from the periph- eral porphyrins, ZnPp, to the two ZnPc porphyrins is followed by electron transfer to the electron acceptor, A, and then by hole transfer from the oxidized ZnPc units to a peripheral Zn porphyrin, as indicated in the following reactions (for clarity only one ZnPp, ZnPo and A units are indicated): 1ZnPp-ZnPc-A - ZnPp-lZnPc-A ZnPp-ZnPc-A - ZnPp-

ZnPc'+-A '- ZnPp-ZnPc'+-A '- - ZnPp'+-ZnPc-A '- ZnPp'+-ZnPc-A '- - ZnPp-ZnPc-A (7) (8) (9) The charge separation efficiency is, however, low, because the hole-transfer reaction (Eq. 9) is slower than the charge-recombination reaction in the ZnPp-ZnPc '+- A'- species. 6.3.5.2 Bilayer Membranes A bilayer membrane made of two amphiphiles has been constructed [87]. One amphiphile has an N-ethylcarbazolyl light-absorbing group, A, and the other has an energy-acceptor anthryl group, B, appended to an electron-accepting viologen group, C. Light excitation of the A absorbing species is followed by energy migration among the A groups until energy is irreversibly transferred to the B group with 70 % efficiency. The excited B group then transfers an electron to the appended viologen unit with 95 % efficiency. 6.3.5.3 Self-assembled Monolayers Mixed self-assembled siloxane monolayers containing coumarin-2 and coumarin- 343 have been constructed on a silicon wafer [88]. The two dyes are the same as

154 I 6 Photoinduced Charge Separation and Solar Energy Conversion ZnPp R RhZnPP ZnPc e R R ZnPc -Zrt- R ZnPp ZnPp AF R = C6H13 A = -- -C8H17 O '=' O Ar = 3,5-di-octyloxyphenyl or NO2 Fig. 6.16. An antenna-reaction center complex based on windmill porphyrin arrays [86].

6.3 Artfi�ial Reaction Centers [155 those used to functionalize a light-harvesting dendrimer discussed in Section 5.5.2. Single coumarin-2 molecules and dendron-type structures containing two and four coumarin-2 donor units were used. The energy-transfer efficiency from excited coumarin-2 to coumarin-343 was found to depend, as expected, on the composition of the mixture and on the branched nature of the energy donor. Mixed self-assembled monolayers (SAM) have been prepared on gold surfaces to study light harvesting and photocurrrent generation [89]. Pyrene or boron-dipyrrin were used as light-harvesting units and porphyrins as acceptors. Energy-transfer efficiency was 100 % for a donor/acceptor ratio of 7:3. In SAM containing the boron-dipyrrin energy donor and a ferrocene-porphyrin-fullerene (Fc-P-C60) triad, energy transfer from boron-dipyrrin to porphyrin is followed by electron transfer from porphyrin to fullerene and then by electron transfer from ferrocene to the oxidized porphyrin, with formation of the Fc+-P-C60 '- charge-separated state of the triad. In the presence of an electron carrier such as 1,1-dimethyl-4,4 - bipyridinium (methylviologen, MV2+), the reduced fullerene is re-oxidized in a bimolecular process and the ferrocenium ion receives an electron from the gold electrode, resulting in current generation with an incident photon-to-current effi- ciency of 1-2 %. 6.3.5.4 Lameliar Assemblies and Zeolites Layered compounds have unique characteristics in electron-transfer processes owing to their low dimensionality [90]. A light-harvesting and redox-active assembly (Fig. 6.17) has been constructed by deposition of consecutive nanometer-thick thin films to create a five-component layered structure capable of stepwise energy and electron transfer [91]. The light-harvesting part of the system consists of coumarin (C)- and fluorescein (F)-derivatized poly(allylamine hydrochloride), C-PAH and F-PAH, palladium(II)- tetrakis(4-N,N,N-trimethylanilinium)porphyrin, or palladium(II)tetrakis(4-sulfo- natophenyl)porphyrin (P) layers, interleaved with anionic a-zirconium phosphate sheets. Another a-zirconium phosphate or an HTiNbO5 sheet separates P from a polyviologen (V) layer. The three C, F, and P chromophoric units collect a sub- stantial fraction of the visible light spectrum and direct excitation of P, or C - F - P, energy transfer results in the formation of a long-lived triplet excited state of P. Electron transfer from the excited P to the viologen follows, with for- mation of a long-lived charge-separated state with 50 % efficiency. Because of their regular microporous framework, zeolites have also been used as hosts to organize supramolecular assemblies for photoinduced charge-separation [92-95]. 6.3.6 Oxygen-evolving Systems Lack of knowledge of the intimate mechanism of the catalytic process that leads to oxygen production in natural photosynthesis (Section 6.2.3) is slowing down the design of model systems. Despite this difficulty, interesting studies aimed at

156 I 6 Photoinduced Charge Separation and Solar Energy Conversion (CH2CH)0.44- (CH2CH)o. 17 -- (CH2CH)o.39 CH3 Br [N'V ,N Me Electron acceptor Inorganic layer Light-harvesting layer C s F C-PAH R1 = C F-PAH R = F (CH2--CH)-- (CH2--CH) ' I"NHR1 ["NI-I Cl- R2. / _R2 "R [R2= Nae3 + or SO- R 2 -Zirconium phosphate or HTiNb05 Fig. 6.17. Schematic representation of a light-harvesting and redox-active assembly [91]. Absorption of photons by the C (coumarin), F (fluorescein), and P (palladium complex) chromophoric units results in electron transfer to the electron acceptor V (viologen) units. developing strategies to obtain functional models of PSII have been reported [96]. Ru(II) oligopyridine complexes, in particular [Ru(bpy)3] 2+, were chosen to mimic the natural P680 photoactive species [96-102], because of' their well known photochemical, photophysical, and

electrochemical properties [103]. A variety of' mono- and multinuclear Mn(II) complexes was then covalently linked to the Ru complex. Furthermore, inspired by the presence of' tyrosine as a mediator in the photooxidation of' the Mn cluster in the natural process (Section 6.2.3), tyrosine itself' or another type of' phenolate moiety (hereafter denoted ArOH) were intro- duced in the model systems designed. Some of'the investigated systems are shown in Figures 6.18 and 6.19. It should be noted that the oxidizing species is never the excited state of' [Ru(bpy)3] 2+, a rel- atively weak oxidant (" [Ru(bpy)3]2+/[Ru(bpy)3] +) = +0.84 V relative to the NHE)

N" "N 2 e- A = H3C-+N/_--C/N'CH3 (MV 2+) or [com(NH3)5CI] 2+ Fig. 6.18. Model systems �or the PSII center: (a) intermolecular and (b) intramolecular photochemical oxidation o� binuclear Mn(11) complexes [97-99]. but is the [Ru(bpy)3] 3+ unit ([Ru(bpy)3] 3+/[Ru(bpy)3] 2+ = +1.26 V relative to the NHE) generated by bimolecular reaction of the excited [Ru(bpy)3] 2+ moiety with an electron acceptor, methylviologen (MV 2+) or [Co(NH3)5C1] 2+. In the example illustrated in Fig. 6.18a [97, 99], the intermolecular photoinduced electron-transfer process (step 2) is followed by electron transfer from the tyrosine moiety to the [Ru(bpy)3] 3+ unit with generation of a tyrosyl radical (evidenced by EPR experi- ments) which is able to oxidize the dinuclear Mn complex. Actually, competing energy- and electron-transfer processes also occur. In the system shown in Fig. 6.18b [98] a dinudear Mn complex is linked to the Ru(II) complex. In flash pho- tolysis experiments the excited state of the Ru(II) complex was quenched by inter- molecular dectron transfer to MV 2+ or [Co(NH3)sC1] 2+ (step 2) and the Ru(III) complex obtained was reduced by rapid (k > 1 x 10 7 s -1) intramolecular dectron transfer from the Mn complex that was oxidized to the Mn(II)-Mn(III) state. Fig. 6.19a shows a complex consisting of three [Ru(bpy)3] 2+-type units attached to a Mn(IV) complex in which Mn is coordinated to dectron-rich phenols [101]. Light excitation in the presence of MV 2+ or [Co(NH3)sC1] 2+ leads to the formation

HCO O' '0 A= HaC-+Nt_CN-CHa (MV 2+) or [com(NH3)5CI] 2+] b Fig. 6.19. Model systems for the PSI1 center: intramolecular photochemical oxidation of a phenolate ligand (a) and of a trinuclear Mn(11) complex (b) [101].

of a [Ru(bpy)3] 3+-type unit (step 2). Intramolecu]ar electron transfer (k _> 5 x 107 s -1) from the phenolate Jigands to the oxidized Ru complex then occurs, with formation of a (complexed) phenoxy radical. In the system shown in Fig. 6.19b, however, in which [Ru(bpy)s]2+-type units are linked to a trinudear Mn(II) com- plex, the source of the electron that reduces the photochemically generated [Ru(bpy)3] 3+-type species is not a phenolate but a Mn(II) [101]. Other structural models of the oxygen-evolving complex of Photosystem II have been proposed [104] and some theoretical dues to the reaction mechanism have been discussed [105]. Although the results reported above are interesting, and can facilitate under- standing of the working principles of PSII, we are dearly very distant from an artificial system capable of performing photoinduced dioxygen evolution. 6.4 Hybrid Systems 6.4.1 Conversion of Light to a Proton-motive Force Although conversion of light into chemical energy by means of artificial systems seems to be a somewhat distant goal (see also next section), a hybrid natural- artificial system capable of using light to obtain proton-motive force and then ATP synthesis has been constructed [30, 106, 107]. These results have been achieved by coupling the photoinduced electron-transfer capacity of artificial triads with the movement of protons across a membrane. As illustrated in Fig. 6.20 [106], the molecular triad 13 (Fig. 6.12), which com- prises a light-absorbing tetraarylporphyrin (P) covalently linked to a quinone acceptor (Q) and a carotenoid donor (C), was incorporated into the bilayer of a lip- osome. When excited in a variety of solvents this triad undergoes photoinduced electron transfer from the singlet excited state of the porphyrin moiety to yield the intermediate charge-separated state C-P'+-Q '- with a quantum yield of 1 (Section 6.3.3). Subsequent electron transfer from the carotenoid to the porphyrin radical cation competes with charge recombination to give the C'+-P-Q '- charge- separated state with quantum yield of 0.15. Liposomes were prepared from a liquid mixture that contained the lipid-soluble 2,5-diphenylbenzoquinone, Qs, and pyraninetrisulfonate (PS), a water-soluble dye the fluorescence of which indicates the pH of the solution. Vectorial electron and proton transport requires asymmetric insertion of the triad into the liposomal bilayer membrane. This result was achieved because the negatively charged car- boxylate group dose to the quinone resides near the outside of the liposome sur- face, whereas the lipophilic carotenoid extends into the oily portion of the bilayer. Excitation of the porphyrin moiety of 13 in liposomes with S-ns light pulses resulted in the formation of C'+-P-Q '-, as detected by the characteristic transient absorbance of the carotenoid radical cation at 930 nm. The yield of this species is

160 I 6 Photoinduced Charge Separation and Solar Energy Conversion H + Fig. 6.20. Schematic representation of the liposome-based proton pump powered by a photoinduced charge-separation process [106]. 10 %; its lifetime, which is 110 ns in the absence of Qs, is reduced to 60 ns when Qs is present in the liposomes. Under the latter conditions the PS dye indicates that light excitation drives protons into the interior aqueous phase of the liposomes, as expected on the basis of the shuttling mechanism based on Qs shown schematically in Fig. 6.20. Step I includes excitation and two-step charge separation. In step 2, Qs, near the external aqueous phase, accepts an electron from the C'+-P-Q '- species, as expected on thermodynamic grounds. In step 3, Qs'- accepts a proton from the aqueous phase, as required by the pKa of Qs. The semiquinone formed diffuses across the bilayer (step 4) and is oxidized by the car- otenoid radical cation (step 5). The protonated quinone then releases a proton (step 6) with the driving force related to its pKa (approx. -6) and Qs diffuses back to the exterior region of the bilayer (step 7). A pH gradient is thus created between the inside and outside of the liposome. The quantum yield of the proton transport in the first minute of irradiation was found to be 0.004. The efficiency of the system can be increased if an ionophore, e.g. valinomycin, is added to relax the membrane potential. In this system photon energy is transduced into vectorial intramembrane redox potential and then into proton-motive force, i.e. the biological analog of the elec- tromotive force, by a chemically cyclic mechanism. It does not require sacrificial electron acceptors or donors and, as happens in natural systems, the redox poten- tial remains confined to the membrane.

ATP ADP + H + H20 _._----' -120 Fi�. 6.21. Schematic representation oFthe process leadin� to li�ht-driven production o�ATP [107]. 6.4 Hybrid Systems I 161 6.4.2 Light-driven Production of ATP In principle, proton-motive force generated by the light-driven process described above can be used to perform work. This result has been achieved [107] by use of the system illustrated in Fig. 6.21. FoF-ATP Synthase (ATP = adenosine triphos- phate) has been incorporated, with the ATP-synthesizing portion extending out into the external aqueous solution, into liposomes containing the components of the proton-pumping photocycle. As described in Section 13.2, FoF-ATP synthase is a molecular-scale rotary motor moved by a proton gradient and capable of syn- thesizing ATP from adenosine diphosphate ADP and inorganic phosphate (Pi). Irradiation of the membrane shown schematically in Fig. 6.21 with visible light leads to the charge-separation process that causes the above described proton translocation, with generation of a proton-motive force. On accumulation of suffi- cient proton-motive force, protons flow through the FoF-ATP synthase, with the formation of ATP from ADP and Pi. The functioning of the system was monitored by means of the luciferin-luciferase fluorescence assay. The results show that the synthesis of ATP occurs against an ATP chemical potential of 12 kcal mol - and with a quantum yield of more than 7 %. One molecule of ATP is synthesized per 14 absorbed photons of 633 nm light, an observation which means that up to 4 % of the initial energy incident on the sample is stored by the system. The photocyclic system operates efficiently over a timescale of hours with a turnover number of 7 ATP per FoF per second. This number is similar to that observed in bacteriorhodopsin/ATP synthase constructs [108]. This is the first complete biomimetic system which effectively couples electrical potential, derived from photoinduced electron transfer, to the chemical potential associated with ADP-ATP conversion, thereby mimicking the entire process of bacterial photosynthesis. As discussed in Section 13.3, it constitutes a synthetic

biological motor that, in principle, can be used to power anything which requires a proton gradient or ATP to work, e.g. to pump calcium ions across a lipid bilayer membrane [109] or even future nanomachines. 6.5 Artificial Solar Energy Conversion 6.5.1 Conversion of Light into Fuels Solar energy conversion by artificial photosynthetic systems is certainly one of the most challenging goals in chemistry. From many points of view the most attractive fuel-generating reaction is the cleavage of water into hydrogen and oxygen (Eq. 11) [21, 83, 110-116]. 1/2H20 - 1/2H2 -t- 1/402 (11) A possible scheme for an artificial photosynthetic system based on such a reac- tion is shown in Fig. 6.22 [83]. From the standard redox potentials of the two corresponding half-reactions, the free energy demand of Eq. (11) is 1.23 eV. For many of the charge-separated states discussed in Section 6.3 the difference in redox potentials of the oxidized and reduced molecular components is larger than this value. Thus light-energy con- Sun light Absorption catalyst Catalyst (charge pool) (charge pool) for 02 evolution e- for H 2 evolution 2 H20 ll 2H + 02 +

e- e- H2 4-electron 2-electron process process Fig. 6.22. Schematic representation of photo- chemical water splitting (artificial photo- synthesis) [83]. Five fundamental components can be recognized - an antenna for light harvesting, a charge separation triad D P A, a catalyst for hydrogen evolution, a catalyst for oxygen evolution, and a membrane separating the reductive and the oxidative processes.

version by means of photoinduced charge separation, followed by Eqs. (12) and (13), is thermodynamically feasible by use of such systems. D+-P-A - d- H20 --> D+-P-A d- 1/2H2 d- OH- D+-P-A + 1/2H20 - D-P-A + 1/402 + H + (12) (13) None of these systems, however, would evolve hydrogen and oxygen on simple irradiation in aqueous solution. As already pointed out, there is, in fact, a funda- mental kinetic problem. The photoinduced charge separation is a one-electron process (i.e. D + and A- are one-electron oxidants and reductants). On the other hand, the reactions depicted by Eqs. (12) and (13), although written in one-electron terms for stoichiometric purposes, are inherently multi-electron processes (two electrons for Eq. 12, four electrons for Eq. 13). Thus, although relatively long-lived charge separation can be achieved with supramolecular systems, the reactions depicted by Eqs. (12) and (13) are too hopelessly slow to compete with charge recombination. This problem is common to any conceivable fuel-generating pro- cesses. The answer to this general problem lies in the possibility of accelerating multi- electron redox reactions by use of catalysts. A catalyst for multielectron redox pro- cesses is essentially a "charge pool", that is, a species capable of.' � acquiring electrons (or holes) from a one-electron reducing (or oxidizing) species in a stepwise manner at constant potential; � delivering these electrons (or holes) to the substrate in a "concerted" manner, to avoid the formation of high-energy intermediates. From the field of heterogeneous catalysis, metals and metal oxides are known to be good candidates for this type of process. Photochemical "water splitting" cycles based on bimolecular reactions between the molecular species P, A, and D were actively studied some time ago [111, 112, 114]. The main result of such studies (which did not lead to any practical success with regard to water splitting) was the optimization of several heterogeneous catalysts. For example, colloidal platinum was found to be a superior catalyst for photochemical hydrogen evolution and col- loidal RuO2 was identified as an efficient catalyst for photochemical oxygen for- mation. Apart from solid-state materials, discrete supramolecular species can also be conceived as catalysts for multielectron redox reactions. This is what happens, as we have seen above, in green plant photosynthesis, where an enzyme (still not well characterized, but containing four manganese centers) catalyzes oxidation of water by the hole left on PSII. A supramolecular catalyst for multielectron redox processes must contain several equivalent redox centers (at least as many as the electrons to be exchanged) [117], with the appropriate redox properties to mediate between the charge-separated state and the substrate. The electronic coupling between such centers should be not too strong, otherwise the "charging" process (stepwise one-electron transfer to the catalyst) could not occur at a reasonably constant potential. The centers should, on the other hand, be sufficiently close to be able to cooperate in binding and reducing (or oxidizing) the substrate. Although these requirements might not be easy to meet, research in this field is active, as we have seen in Section 6.3.6. The lesson coming from Nature (Section 6.2.3) is that multiple electron-transfer processes can be profitably accomplished when accompanied by proton transfer, but other strategies might, perhaps, also be used. Research related to this area is that on two-electron mixed-valence photocatalysts [118] and on systems in which four electrons can be stored [119]. Any efficient artificial photosynthetic system must satisfy another requirement - the oxidized and reduced products should be produced in physically separated compartments of the system to avoid uncontrolled energy-wasting back reactions and to facilitate collection and storage of the fuel. As occurs in natural systems, therefore, some kind of membrane is needed to separate the oxidative and reductive part of the process (Fig. 6.22). This, in turn, requires that every charge-separating molecular device is specifically organized and oriented with respect to such a membrane. This problem should be addressed by research on self-assembling processes and organized media [120-124]. As we have seen above (Section 6.4), artificial triads have already been successfully inserted into bilipid membranes [106, 107]. In summary, plausible artificial photosynthetic systems should include several basic features (Fig. 6.22):

- an antenna for light harvesting;
- a reaction center for charge separation;
- catalysts as one-to-multielectron interfaces between the charge-separated state and the substrate;
- a membrane to provide physical separation of the products.

Noticeable

progress has been made with regard to the first two of these points, but much remains to be made concerning catalysts and membranes. The overriding principle in the construction of each component and in their assembly is that of organization [125]. 6.5.2 Conversion of Light into Electricity The reaction center mimics illustrated in Section 6.3 are molecular-level photovoltaic devices. An alternative possible means of using sunlight is, in fact, to convert it directly to electricity. Photochemical generation of electricity is perhaps a less ambitious goal than photochemical generation of fuels, and it is certainly much closer to real application since overall power conversion efficiency in excess of 10 % has been achieved [126]. Such a process is based on the use of dyes capable of injecting electrons (or holes) into semiconductors on excitation with visible light [127]. Although the basic principles of dye sensitization of semiconductors have long been established [128], the application of such techniques to light-energy conversion became appealing only when new nanocrystalline semiconductor electrodes of very high surface area had been developed [129]. The basic steps occurring in a sensitized semiconductor cell are shown in Fig. 6.23a. The system comprises a photosensitizer (P) linked in some way to the semiconductor surface, a solution containing a relay electrolyte (R), and a metallic counterelectrode. The sensitizer is first excited by light absorption. The excited sensitizer then injects an electron into the conduction band of the semiconductor (step 1 in Fig. 6.23a) [130]. The oxidized sensitizer is reduced by a relay molecule (step 2), which then diffuses to discharge at the counterelectrode (step 3). As a result a photopotential is generated between the two electrodes under open-circuit conditions, and a corresponding photocurrent can be obtained on closing the external circuit by use of an appropriate load [131]. Such a cell might seem at first sight quite different from the photosynthetic systems discussed in Section 6.3. On closer inspection, however, analogies do appear. The system is clearly based on photoinduced charge separation. From this viewpoint the system can be regarded as a "pseudo-triad" in which the semiconductor surface acts as the primary acceptor and the relay as the secondary donor. As in any triad, the efficiency of charge separation and energy conversion depend critically on the kinetic competition between the various forward processes and charge recombination steps. The main difference from photosynthetic systems is simply that the redox potential energy of the charge-separated state is not stored in products of subsequent reactions, but rather it is directly used to produce a photocurrent. Taking this comparative analysis a step further, one might consider applying some of the strategies of photosynthesis to increase the efficiency of photoelectrochemical cells [132-134]. In this regard, it is appropriate to notice that several possible processes, not shown in Fig. 6.23a, can provide "short-circuit" paths within the photoelectrochemical cell. The most important of such dissipative processes is charge recombination between the hole in the oxidized sensitizer and the injected electron (step 4). This process is always thermodynamically allowed, and can be avoided only if it is disfavored for kinetic reasons compared with the other "useful" processes. Photoinduced charge separation within the sensitizer, before electron injection, can help to prevent the detrimental charge-recombination step. A simple triad system, as shown schematically in Fig. 6.23b could be used to produce the hole in the oxidized sensitizer and the injected electron at spatially remote sites. For this idea to be implemented, of course, several nontrivial problems must be solved [135] (see also Section 3.5 and Figure 3.10). Experiments have been performed on TiO_2 electrodes with dyads consisting of a $[Ru(bpy)_3]^{2+}$-type complex linked to phenothiazine [136], Ru(II) and Os(II) oligopyridine compounds [137], and the Ru(II)-Rh(III) dyad shown in Fig. 6.24a [138, 139]. The antenna effect could also find useful application in these systems. With a conventional semiconductor electrode and a simple molecular sensitizer, light absorption is often quite inefficient at monolayer coverage. Multilayer adsorption, on the other hand, does not help, because the inner layers tend to act as insulators relative to the outer layers [140]. Although this type of limitation is now much less severe, because of the introduction of nanostructured electrodes of exceptionally high surface area [129], the search for sensitizers with high intrinsic light harvesting efficiency is still of considerable interest in the field [133]. One possibility in this direction is to replace the sensitizer molecule at the semiconductor-solution interface with an antenna-sensitizer molecular device (Fig. 6.23c) [141]. A further advantage offered by antenna devices is that appropriate selection of the spectral properties of the various chromophoric groups can lead to better matching between absorption spectrum and solar emission spectrum. The trinuclear complex shown in Fig. 6.24b has been developed in a first attempt to demonstrate the applicability of the antenna effect in semiconductor sensitization [141]. The presence of the carboxylic groups, besides being relevant to the energetics of the system, is essential for grafting the complex, via its central com- ponent, to a TiO2 surface. Experiments performed using TiO2-coated electrodes (aqueous solution, pH 3.5, NaI as electron donor) showed that the photocur- rent spectrum reproduces closely the absorption spectrum of the complex. This indicates that, as a consequence of efficient energy transfer to the central unit bound to the semiconductor, all the light energy absorbed by the trinuclear com- plex, including that absorbed by the peripheral units, is used for electron injection. Remarkably high efficiencies (7 %) of conversion of incident light into electricity have been obtained by use of this trinuclear complex on high surface area nano- crystalline TiO films [142]. Substantial efficiencies have also been achieved with related compounds [143]. One-dimensional systems that could stack perpendicu- larly to the surface (with the different antenna units working in series rather than in parallel) would be an even more interesting means of increasing the ratio of chromophoric components to occupied surface area. Recently, multilayer organic-inorganic thin films analogous to those described in Section 6.3.5.4 have been successfully used to generate photocurrents; the quan- tum yield was 4 % [144]. Great effort is also devoted to the development of organic materials for photovoltaic devices [145]. References W. OSTWALD, Die Muehle des Lebens, Thomas, Leipzig, 1911. This book has not been translated in English. 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177 7 Bistable Systems 7.1 Introduction As already mentioned in Chapter 4, the expression "molecular-level switcl' [1] usually has two distinct meanings [1-6]. The first definition is a molecular-level device, incorporated in a molecular-level wire, that can reversibly interrupt the movement of electrons or electronic energy across it in response to an external stimulus. Switches of this type are described in Chapter 4. The second definition relates to the binary

logic of computing, and describes any molecular-level system that can be reversibly interconverted between two or more different states by use of an external stimulus. These systems will be discussed in this chapter and in the following chapters of Part III. Both kinds of switch can be expected to play a fun- damental role in the construction of chemical computers [7]. Any molecular-level system that can be reversibly switched between two different states by use of an external stimulus can be taken as a basis for storing information, i.e. for memory purposes [1]. An ideal molecular-level memory should be stable and easy to write, and its switched form should be stable, easy to read, and erasable when necessary. Systems that undergo an irreversible change can be used as permanent memories (e.g., photography, dosimetry). In more complex systems, e.g. those dis- cussed in Chapter 8, switching can be performed among more than two states. This possibility can be exploited to obtain memories which are permanent unless they are erased on purpose, or for performing logic operations (Chapter 9). As already remarked in Chapter 4, switching processes can be performed under thermodynamic or kinetic control [4]. Systems under complete thermodynamic control can be stable, easy to write, easy to read, and erasable, but for some appli- cations they are useless, because they need permanent stimulation - as soon as the stimulus is removed the molecule reverts to its initial state. An example is fluo- rescence sensors the emission intensity of which is modulated by the presence of a particular substrate. The most interesting systems for memory purposes are those in which at least one stage is under kinetic control, with the metastable species separated from the thermodynamically stable state by an energy barrier high enough to delay, or, in a limiting case, to prevent the back thermal reaction. Kinetic control can operate for extremely diverse time periods, from picoseconds (for some electronic excited states) to years. In kinetically controlled systems a second stimulus can be used to detrap the metastable state and to reverse the process. It Molecular Devices and Machines -AJourne into the Nano World. V. Balzani, A. Credi, M. Venturi Copyright � 2003 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim ISBN: 3-527-30506-8

178 I 7 Bistable S)stems should be noted that in a system under thermodynamic control it is not possible to address a single molecule because of rapid equilibration between them. In con- trast, for a system under kinetic control a single molecule of the assembly can be addressed, maintained in the switched

state, and interrogated (e.g. by single- molecule spectroscopy [8]). Three important types of stimulus that can be used to switch molecular or supramolecular species are light energy (photons), electrical energy (electrons/holes), and chemical energy (in the form of protons, metal ions, etc.). In photochemical stimulation the most common switching processes are related to photoisomeri- zation or photoinduced redox reactions; for electrochemical inputs, the induced processes are, of course, redox reactions. Compared with chemical stimulation, photochemical and, to some extent, electrochemical stimuli can be switched on and off easily and rapidly. A further advantage of the use of photochemical and electrochemical techniques is that photons and electrons, besides supplying the stimulus to make a switch work (i.e. "to write" the information bit), can also be useful "to read" the state of the system and thus to control and monitor its operation. It should also be noted that photo- chemical and electrochemical inputs and outputs are among the easiest to inter- face to macroscopic systems, making them amenable to the multi-scale engineer- ing required for the eventual creation of real devices. Another important distinction can be made [5, 9]. The external stimulus causes, of course, both electronic and nuclear rearrangements in the molecular-level sys- tem to which it is applied. Usually one of the two types of rearrangement prevails or is more relevant to the performed function. When switching involves large nuclear movements, particularly in supramolecular systems, the mechanical aspect might become more interesting than the switching process itself [10, 11]. Systems of this type will be discussed in Part III. The field of switching is very broad and has been extensively reviewed. This chap- ter is intended to illustrate some basic principles and peculiar aspects of switching processes, making use of examples which have recently appeared in the literature. Readers interested in exhaustive and thorough discussions of switching processes in a variety of materials should refer to several books [1, 12-23] and to the abundant current literature on fluorescent sensors [24], electrochemical sensors [25], optical switches [26], photochromic molecules [27], photoresponsive polymers [28], photo- chromic crystals [29], photorefractive materials [30], electrochromic materials [31], spin-transition materials [32], single molecule magnets [33], nonlinear optics [34], photoswitchable biomaterials [35], chitoptical switches [36], surfaces, monolayers, and LB films [37], liquid crystals [38], hole burning [39], and holographic data stor- age [40]. 7.2 Photochromic Systems The term "photochromic" is applied to molecules that can be reversibly inter- converted, with at least one of the reactions being induced by light excitation,

7.2 Photochromic Molecules between two forms with different absorption spectra. The two forms, of course, differ not only in their absorption spectra, but also in several other properties such as redox potentials, dielectric constant, etc. In contrast with most of the topics discussed in this book, photochromism (once called phototropism) has long been described in the scientific literature - the first example was reported in 1867 [41]. In his famous paper entitled "The Photo- chemistry of the Future" [42] Giacomo Ciamician discussed the importance of photochromic substances and also mentioned the possibility of using such com- pounds for an unexpected purpose: "Phototropic substances, which often assume very intense colors in the light, and afterwards return in the darkness to their primitive color, might be used very ectivel 7. Such substances might well attract the attention of fashion ... The dress of a lady, so prepared, would change its color according to the intensity of light. Passing from darkness to light the colors would brighten up, thus conforming automatically with the environment: the last word of fashion for the future". Photo- chromism is also a natural phenomenon characteristic of most biological photo- receptors such as rhodopsin (vision) and phytochrome (photomorphogenesis) [43]. Until the middle of the last century research on photochromic compounds was performed mainly in academic research centers. Around 1960, however, it was recognized that this phenomenon has considerable commercial interest (e.g. photo- chromic glasses); since then, most of the research has been performed in industrial laboratories. The design and synthesis of photochromic molecules is currently an intense research area because of their potential application for information stor- age, imaging devices, smart windows, ophthalmic lenses, protective lenses, and filters. By reducing the switching elements to molecular size the memory density of com- puters could be increased by several orders of magnitude and the power input re- duced very significantly [27n, 44]. A CD-ROM (compact disk, read only memory) holds approximately 108 bits cm -2. Use ofphotochromic materials could increase this to 2 x 109 bits cm -2 on the basis of diffraction-limited spot-size considerations, and three-dimensional addressing [45], the use of excitonic waveguides [46], and near- field optical techniques [27n, 47] could enable vastly increased resolution. Other advantages of photochromic-based memories are, furthermore, a simple readout mechanism, the occasional possibility of optical replication, and selective erase and rewrite facilities. In photochromic systems the interconverting species are isomers, because the photoreaction simply causes rearrangement of the electronic and nuclear structure of the molecule, with or without reversible bond breaking. Light excitation causes switching from a stable isomer A to a higher-energy isomer B which is expected to reconvert to A on overcoming a more or less high energy barrier (Fig. 7.1). Photochromic systems, therefore, are under kinetic control. After photochemical conversion (a process that, by use of lasers, can be performed in a few femtoseconds [48]), a spontaneous back reaction is expected to occur. This reaction, however, can be fast or slow depending on the system. Sometimes the photoproduct might be kinetically inert and the process can be reversed only by use of a second light stimulus. Depending on the thermal stability of the photogenerated isomers photochromic systems can thus be classified in two categories: � T-type (thermally reversible type) - the photogenerated isomers revert thermally to their initial forms, � P-type (photochemically reversible type) - the photogenerated isomers do not revert to the original isomers even at elevated temperatures. For the latter compounds it is particularly important that the absorption bands of the two forms do not overlap if selective excitations are to lead to pure species. It should be noted that, with a few exceptions [49, 50], the photogenerated isomer B cannot be converted, by excitation with light of the same or different wavelength, into a third isomer C [51]. In Section 7.7 it will be shown that electrochromic and photochromic systems behave quite differently. The most extensively used families of photochromic compounds are (Fig. 7.2): diarylethenes [27h], fulgides [27j], spiropyrans [27e], azobenzenes [27k], dihydroazulenes [27i], and flavylium compounds [271]. Only two families, furylfulgide derivatives and diarylethene derivatives are P-type compounds. Great attention is also devoted to the use of native and modified biological photochromic molecules as elements for optical memory [52]. Photochromic reactions are always accompanied by undesirable side reactions; this might compromise the use of these compounds for practical applications. If a photochromic reaction occurring with almost unitary quantum yield is accompanied by a side reaction with quantum yield 0.001, 63 % of the initial concentration will be

a b Excited states h� , hv ' State 0 State I E h� A h� I __ B Activation barrier

Fig. 7.1. Schematic representation of a photochromic system (a) and of its energy profile (b).

decomposed after 1000 cycles. Most photochromic compounds have low fatigue resistance. With diarylethenes, however, satisfactory photochromic performance can be maintained even after more than 104 cycles [27h]. The response time of the photochromic reactions is usually very short. For diarylethenes, for example, the photochemical electrocyclic ring-opening and ring-closure reactions, which occur in the conrotatory mode, take place in a few picoseconds both in solution and in the solid state [27h, 53].

a F2 Z3 Modulation of Host-Guest Interactions] 181 Fe b c NO2 v ', /f 02 I d hv N:N e NO2 " CN NO2 '/v ', z N f i['L-.r-OH im"OCH3 hv. OH r'"w "Ocli3 � I o Fi�. 7.2. Some important families of photochromic compounds: (a) diarylethenes; (b) ful�ides; (c) spiropyrans; (d) azobenzenes; (e) dihydroazulenes; (f) flav�1ium compounds. 7.3 Modulation of Host-Guest Interactions Switching host-guest interactions by means ofphotochromic reactions might lead to a variety of sensors and to transport of guest molecules across a membrane, as shown by the following examples.

182 I 7 Bistable Systems F2 Vis I UV F2 Ho, B'oH Ho'B,oH Fig. 7.3. Saccharides F2 Photoswitchable recognition of saccharides by diarylethene derivative 1 [54]. Boronic acids are widely used for recognition of saccharides. Compound 1 (Fig. 7.3), which consists of a diarylethene moiety with two boronic acid groups attached, can reversibly host glucose because it forms a 1:1 complex by ester for- mation between the two facing boronic acids and four hydroxyl groups [54]. After photoisomerization to the dosed-ring form, however, the two boronic acid groups are much more distant from each other and complexation is much weaker. The switching of the complexation can be measured by circular dichroism spectro- scopy. From a "machine" viewpoint, this system can be viewed as a pair of tweezers, a function that will be discussed in more detail in Section 12.3.1. The effect on lectin binding of photoisomerization of azobenzene compounds derivatized with glycopyranoside moieties has been investigated [55]. Irradiation in acetonitrile solution of compound 2 at 369 nm results in the formation of a photocycloadduct which reverts in the dark (Fig. 7.4) [56]. The pho- toreaction quantum yield increases in the presence of HgC12 and/or NaC104, showing that both metal ions preorganize the two anthracene units for photo- cycloaddition. The rate of the thermal dissociation reaction is much lower for the Na + adduct. Similar effects had previously been obtained for bis-

anthracenyl crown compounds [57]. These results can also be elaborated according to a logic view- point (AND logic, Section 9.7). For a spirobenzopyran unit linked to a crown ether thermally irreversible photo- chromism is observed only in the presence of a metal cation [58]. 7.4 Fluorescent Switches Several photochromic compounds have different fluorescence properties in their two forms. Occasionally on/off switching is observed. Two examples are shown

/iv + NaCIO4 Z4 Fluorescent Switches I 183 2 _x hv + HgCI2 � = 0.43 � = 0.23 Fig. 7.4. The quantum yield of photocycloaddition of com- pound 2 increases in the presence of HgCI2 or NaCIO4 [56]. 0.37 in Fig. 7.5. Compound 3, which consists of a fulgide photochromic unit with a binaphthol substituent attached, is colorless and does not emit in the open-ring form whereas its colored form, obtained by UV irradiation, fluoresces in toluene at room temperature [59]. Compound 42+ is strongly luminescent on excitation at a 3 C 3 -- Non-luminescent Luminescent b 42+ .F. R = 06H13 Luminescent F2 H3G'+ -- ...; %,.,n 3 Non-luminescent Fig. 7.5. On/offswitching of fluorescence in (a) fulgide derivative 3 [59] and (b) diarylethene derivative 42+ [60].

184 I 7 Bistable Systems 400-500 rim. Interestingly, such visible light excitation does not convert the open- ring to the closed-ring form [60]. Conversion can be performed by irradiation with UV light and the visible absorbing closed-ring species so obtained is not lumines- cent. This system can, therefore, be interrogated (the state of the compound is de- termined by "reading" the data) without destroying the information it contains. A recent example of luminescence switching exploits a [Ru(bpy)3] 2+ complex with a dianthryl moiety attached [61]. Excitation of the Ru(II) complex with visible light does not cause luminescence, because its triplet excited state is quenched by energy transfer to the lower-lying dianthryl triplet. When the system is excited with 390-nm light the dianthryl moiety undergoes cydization, with disappearance of the low-lying anthracene-type triplet, so that luminescence of the Ru(II) complex is switched on. Such behavior is observed both in (deaerated) solution and in poly- styrene matrix. Styryl compounds can undergo either trans-cis isomerization or [2+2]-cyclo- addition photoreactions [23]. Combination of a crown ether with a styryl compound yields molecular systems in which the styryl moiety has chromo- and fiuorogenic properties and

a switching function [62]. Several investigations have been performed on compounds of this family [63-65]. Two are shown in Fig. 7.6. The complexation capacity of compound 5 increases by a factor 11 on trans-cis photoisomerization [64], and compound 62+ has high affinity for Sr 2+ and Ba 2+, because it forms intramolecular sandwich complexes [65]. Metal ion complexation causes noticeable changes in the photophysical behavior of both compounds. (CH2)4S0' .--g./'O.-/ trans-[. Hg] 2+ by A, hv' o, _r'"'o",, o=S-o _, !..-0 cis-[5' Hg] 2+ Fig. 7.6. (H2)3 L.oO 62+ Fluorescent styryl compounds 5 [64] and 62+ [65] capable of coordinating metal ions.

Some metal complexes, e.g. those of Ni/II/, undergo high-spin/low-spin interconversion when the temperature is changed. This property has been exploited to obtain a fluorescent molecular thermometer [66]. The system investigated consists of the Ni/II / complex of a quadridentate macrocycle which carries a fluorescent naphthyl unit. The fluorescence of the naphthyl unit is much more efficiently quenched by the high-spin complex, which is more stable at low temperature. As a consequence, the fluorescence intensity increases with increasing temperature and can be used to measure temperature in the range between 25 and 75 °C. Another interesting report has described the guest-induced decrease in fluorescence quenching and molecule sensing ability of a cydodextrin-peptide conjugate [67]. Examples of fluorescence switching processes in which mechanical movement plays an important role, are discussed in Chapters 12 and 14. 7.5 Chiroptical Switches Chiral photobistable molecules are a particularly interesting class of photochromic compounds [36, 68-76]. In such molecules reversible photochemical transformation can lead to a change in chirality; this makes it possible to exploit the unique properties associated with the different stereoisomers. The importance of chiroptical switches is further emphasized since chirality controls most natural chemical processes, including molecular recognition, transport, information storage, catalysis, assembly, and replication. In a chiral photochromic system (Fig. 7.7a) the left-handed (S or M) and right-handed (R or P) forms of a chiral compound represent two distinct states in a molecular binary logic element (A or B). On excitation with light, the change of element is accompanied by a change in chiral state. Chiral switches based on photochromic molecules can be subdivided as follows (Fig. 7.7b) [36]: (i) Switching of enantiomers. Unless chiral light is used, irradiation of either enantiomer of a chiral photochromic molecule (R/S or P/M) leads to a race- mic mixture, because of the identical absorption characteristics of the two enantiomers. By use of left- or right-circularly-polarized light (CPL), enantio- selective switching is possible. (ii) Switching of diastereoisomers. In these systems two diastereoisomeric photo-bistable forms, e.g. P (right-handed) and M' (left-handed) helices, can undergo photoisomerization at two different wavelengths, ; and ;2. Alternatively, a system can be made of an achiral photochromic unit A and a chiral auxiliary X* which controls the change in chirality during the switching event. (iii) Functional chiral switches. In these systems, the change in chirality triggers the modulation of some function, e.g. fluorescence, molecular recognition, or motion.

186 I 7 Bistable Systems A (s or M) State 0 bY B (R or P) State I a /-CPL P - CPL M b (ii) hv P _ M' hv' AiX * by B-X* (iii) hv hv' bY A hv' Fig. 7.7. (a) A chiral photochromic system; (b) chiral switches [36]. (iv) Switching of macromolecules or supramolecular organization. Photobistable mole- cules (chiral or achiral) can, for example, be part of a host-guest system or covalently linked to a polymer. The photoisomerization process induces changes in some property such as the organization of the surrounding matrix or the helical structure of a chiral polymer. Besides the general requirements needed for photochromic switches, chiroptical switches must be stable towards thermal racemization. A few examples of chirop- tical switches are briefly discussed below. Comprehensive and thorough discussion can be found elsewhere [36]. 7.5.1 Overcrowded Alkenes The thermal and photochemical isomerization processes of the first chiroptical switch, based on the overcrowded alkene 7, are shown schematically in Fig. 7.8

(M)-cis-7 7.5 Chiroptical Switches by 300 nm bY' 250 nm (P)-trans-7 (P)-cis-7 (M)-trans-7 Fi�. 7.8. Thermal and photochemical isomerization processes of chiroptical switch 7 [72]. [72]. On heating a solution of enantiomerically pure (M)-cis-7 in p-xylene, race- mization was observed, with (P)-cis-7 being produced. No cis-trarrs isomerization was evident. Irradiation of (M)-cis-7 at 300 nm yielded a mixture of 64 % (M) -cis-7 and 36 % (P)-trarrs-7, as determined by chiral HPLC, NMR, and circular dichroism spectroscopy. Irradiation at 250 nm resulted in a photostationary state containing 68 % (M)-cis-7 and 32 % (P)-trarrs-7. Alternating irradiation at 250 and 300 nm resulted in a modulated circular dichroism signal which could readily be detected at

262 nm. In this switching process stereospecific interconversion of the M and P helices had indeed been achieved, although 10 % racemization was observed after 20 switching cydes. Successive structural modification improved the stability to- ward racemization, enhanced the stereoselectivity of the process, and shifted the photoisomerization wavelength into the visible region [73]. Further development of the chiroptical switching concept by using overcrowded alkenes has led to the construction of unidirectional rotary motors (Section 13.4.2). 7.5.2 Diarylethenes The open forms of the previously discussed diarylethenes consist of a dynamic system of helical conformers. Light induced, conrotatory ring-dosure of the sym- metric diarylethene 8a generates the (S,S)-Sb and (R,R)-Sb enantiomers (Fig. 7.9). Several of the dosed forms have been resolved by chiral HPLC, but the stereogenic centers are lost on ring-opening [74]. When chiral auxiliary groups are present, however, (see, e.g., compound 9 in Fig. 7.9), both the open and the closed forms are chiral and ring-dosure results in the formation of diastereomers. Because of

Bistable Systems Fe F2 Vis A--SS'A 8a 8b F2 F2 Fig. 7.9. Photochemical switching ofdiarylethenes 8 [27h, 74] and 9 [75] (* denotes stereogenic centers). their excellent reversibility and nondestructive readout, chiral photochromic diary- lethenes are promising systems for modulation of liquid crystalline phases [75]. 7.6 Photochemical Biomolecular Switches It is well known that many biological processes are triggered by light signals. Much effort has recently been devoted to the development of semisynthetic photo- biological switches [35, 77-80]. Such systems consist of a biological material or an environment the innate functions of which can be activated/deactivated by artificial photoresponsive units. Fig. 7.10 shows a biomaterial whose function has been blocked by chemical modification ("caged" biomaterial). If the deactivating group contains an appropriate photoactive moiety, it can be removed by light excitation, with release of the active biomaterial [35c]. More interesting are chemically engineered biomaterials that enable reversible switching of biological functions between inactive and active states. Fig. 7.11 shows schematically three possible procedures for photoregulating biomaterial activities such as binding, recognition, and catalysis [35c]: Biomaterial] h v Q + [Biomaterial Caged biomaterial Free biomaterial Fig. 7.10. Photochemical activation ofa biomaterial by light- induced cleavage of a photoprotective group [35c].

a 7.6 Photochemical Biomolecular Switches I 189 (Active site ON State OFF State b s s Np : h v ' ON State OFF State hv' ,.p Inactive Active biomatetal biomaterial Fig. 7.11. Three methods for switching the activity of a biomaterial [35c]: (a) tethering of photoisomerizable units to a protein; (b) integrating the biomaterial within a photosensitive environment; (c) use of photoisomerizable inhibitors,

190 I 7 Bistable Systems (a) Tethering of photoisomerizable units to a protein. When the photoisomerizable units are in state A, the tertiary structure of the protein is retained and the biomaterial can perform its function (e.g. substrate binding and catalysis). Photoisomerization of the photoactive groups from A to B distorts the tertiary structure and perturbs the function of the biomaterial. If the photoreaction is reversible, the biomaterial functions can be switched on and off. A variety of photoisomerizable groups can be used. (b) Integrating the biomaterial within a photosensitive environment. The biomaterial is immobilized in a matrix (e.g. polymer, monolayer) the properties of which (e.g. wettability, permeability) can be controlled by irradiation with light. In this way the transport of substrates towards the entrapped biomaterial can be reversibly photoregulated. (c) Use of photoisomerizable inhibitors or cofactors. A photoisomerizable, low molec- ular weight component, which can be recognized by the biomaterial, is applied. Such a component can play the role of either inhibitor or cofactor, but it will do that only in one of its two forms. For example, the added molecule A might be an inhibitor but it can lose this effect after photoisomerization to B. An example of type (a) is the lectin concanavalin A (Fig. 7.12a). This glob- ular protein has binding sites for Mn 2+ and Ca 2+ which act cooperatively when associating with 4)-mannopyranose. Chemical modification by tethering a photoisomerizable thiophene fulgide yields compound 10a and reversible pho- toisomerization yields the ring-dosed form 10b which has greater affinity for -)-mannopyranose [77]. ;N O UV ...O O -"JL--Lis-Con.A . ' N--'JL--Lis-Con.A Vis - / x O 10a 10b yy UV ,, Vis O=C C=O I I NH2 NH 11a Fig. 7.12. (a) The photoisomerizable thiophene fulgide derivative of concanavalin A (Con.A) 10 is capable of regulating anity for C-D-mannopyranose [77]; (b) the photoisomerizable azobenzeneacrylamide copolymer 11 is capable of regulating the activity of chymotrypsin [78]. O=C C=O I I NH2 NH 11b

7. 7 Electrochromic Systems I 191 Light-stimulated permeability and substrate

transport through photoisomer- izable polymers enables the use of polymer membranes as matrixes for photo- regulation of the functions of biomaterials (type (b) in Fig. 7.11). An example is photoregulation of the activity of chymotrypsin by immobilizing the biocatalyst in a photosensitive crosslinked, isomerizable polymer such as azobenzeneacylamide copolymer 11a (Fig. 7.12b) [78]. As an example of direct functionalization of the active site, type (c), we men- tion the reconstitution of flavoenzyme-glucose oxidase with a semisynthetic FAD cofactor (FAD = flavin adenine dinudeotide) [79]. The photoisomerizable nitro- spiropyran carboxylic acid 12 was covalently coupled to N6-(2-aminoethyl)-FAD 13 to yield the synthetic nitrospiropyran-FAD cofactor 14a that can be photoiso- merized to [14bH] + (Fig. 7.13a). The native FAD cofactor was removed from glu- cose oxidase and the synthetic photoisomerizable-FAD cofactor 14a was recon- stituted into the apo-glucose oxidase (apo-GOx), to yield the photoisomerizable enzyme 15a (Fig. 7.13b). The nitrospiropyran state of the reconstituted enzyme was inactive towards the bioelectrocatalytic oxidation of glucose, but photoisomer- ization to the protonated nitromerocyanine state [15b H] + activated the enzyme. Completely on/off behavior was observed. Comprehensive and thorough discussion of photoswitchable biomaterials and their promising applications in optobioelectronics can be found elsewhere [35, 37].

7.7 Electrochromic Systems

The term "electrochromic" is applied to compounds that can be interconverted, by reversible redox processes, between two (or more) forms with different absorption spectra [20]. As happens with photochromic systems (Section 7.2), the intercon- verting species differ from one another not only in their absorption spectra, but also in several other properties. It should be remarked that the similarity between photochromic and electro- chromic systems - the effect of the applied stimulus, i.e. the change in "color" - does not extend to the molecular-level mechanisms of the two phenomena. In photochromic systems the interconverting species are isomers, because the photo- reaction simply causes rearrangement of the electronic and nuclear structure of the molecule. In electrochromic systems the interconverting species are not isomers, because they have a different number of electrons. Photochromic systems usually involve two forms, A and B, of a molecule (Fig. 7.1) whereas in electrochromic systems several successive switching processes can often occur. For example, in a relatively simple compound such as [Ru(bpy)3] 2+ [81] as many as eight species, each with its own absorption spectrum, can be obtained on changing the value of the applied potential (Fig.

7.14). Other examples of species capable of exchanging a great number of electrons, at the same or different potentials, are discussed in Section 8.4.

192 7 Bistable SFstems I Z n- A E o

Ruil/Ru ii +1.0 0 DMF bpy-/bpy2- bpy/bpy- -1.0 -2.0 -3.0 E (V vs SCE) Fi�. 7.14. Redox states obtained on oxidation and reduction of [Ru(bpy)3] 2+. The redox couples of the involved subunits are indicated [81]. Z8 Redox Switches I 193 With regard to other criteria (e.g. fatigue), the requirements of photochromic and electrochromic compounds are similar. It should also be noted that light excitation can be switched on/off very rapidly (up to the femtosecond time scale), whereas electrochemical potentials can be changed only more slowly (sub- microsecond time scale). More details on electrochromic systems can be found in the literature [20, 31]. 7.8 Redox Switches Many redox switches have been reported in the last few years [14, 25]. Some are discussed in Section 12.4.3. Here we will describe a typical example only. Compound (R)-16 (Fig. 7.15) consists ofa chiral 1,1'-binaphthyl unit derivatized with two boron dipyrromethene moieties. This compound has very interesting spectroscopic and electrochemical properties [82] - an intense absorption band with a maximum at 495 nm, an intense ((I) = 0.69) fluorescence band with a max- imum at 509 nm, and a circular dichroism band with a maximum at 501 nm, a reversible two-electron reduction process (an electron per chromophoric unit) at -1.515 V (relative to the ferrocenium/ferrocene couple) and a quasi reversible two- electron oxidation process at +0.795 V. When oxidation and reduction are alter-

194 I 7 Bistable S)stems -,-BF2 Fig. 7.15. Compound (R)-16 is an example of redox switch with chiroptical signal [$2]. nated dectrochemiluminescence is observed. Spectroelectrochemistry studies have shown that both the absorption band at 495 nm and the circular dichroism band at 501 nm disappear on reduction of (R)-16 to its hisradical dianion form and that both bands are restored on oxidation to the neutral form. Thus (R)-16 combines optoelectronic properties and chirality. Such compounds can be useful for several applications, including chiral fluorescent sensors and light-emitting diodes with circularly polarized luminescence. 7.9 Other Systems A variety of other switching systems has been reported. A few peculiar examples are briefly mentioned. It has recently been shown that the dual cydodextrin compound 17

(Fig. 7.16) can catalyze the luminol chemiluminescent reaction, presumably by preorganiz- ing the chemiluminescent fuel (luminol) and the oxidant (Ce 4+) [83]. Magnetic- field stimulated on/off biochemiluminescence can be obtained by electrocatalyzed reduction of naphthoquinone functionalized magnetic particles in the presence of a biocatalytic peroxidase/luminol system [84]. Finally, the first example of a redox- switchable ceramic membrane was based on vanadium oxides [85]. Fig. 7.16. The dual cyclodextrin compound 17 is able to catalyze the luminol chemiluminescent reaction [83].

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2oo [8 M ultistate-M ultifunctional Systems 8.1 Introduction The switches discussed in the previous chapter are bistable species. When stimu- lated they switch from the initial form A to the final form B, and then revert either thermally or under the action of a second stimulus. In recent years a number of investigations has been performed on systems capable of existing in three or more forms that are interconverted by means of different stimuli. Systems which respond to a given combination of multiple stimuli open the way to more complex switches (logic gates) on the molecular scale. In this chapter we will discuss recent advances in the field of multistate- multifunctional systems and in the next we will describe systems that have been specifically constructed for, or discussed as, logic devices. It is important to note that the mechanisms of operation of most of the systems we will discuss are based on photoinduced conformational changes, acid-base reactions, redox processes, supramolecular associations, and other chemical events occurring in solution. Such mechanisms have little in common with the mechanisms that govern conventional electronics. In fact, information processing at the molecular level is based on principles more similar to those governing information transfer in living organisms. Some of the systems discussed have also been investigated in ordered arrays (e.g. self-assembled monolayers, Langmuir-Blodgett films, functionalized electrodes, the solid state). We will mainly concentrate on basic principles and molecular-level systems studied in solution. Reviews or leading papers on organized systems will be indicated. 8.2 Biphotochromic Supramolecular Systems As discussed in Section 7.2, photochromic molecules [1] have been extensively investigated because of their potential applications in several different fields, from information storage to smart windows, from imaging devices to ophthalmic lenses. In recent years attempts have been made to couple two photochromic units in the same supramolecular species. The objective of these studies was to obtain a syner- gistic effect between the properties of the two units to create materials with novel photokinetic properties. Molecular Devices and Machines -A Journey into the Nano World. V. Balzani, A. Credi, M. Venturi Copyright � 2003 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim ISBN: 3-527-30506-8

8.3 Photochemical Inputs Coupled with Other Stimuli [201 In a systematic investigation, several biphotochromic supermolecules have been synthesized in which two photochromic units of the spirooxazine and chromene families are linked through a coniugated or unconiugated spacer [2-4]. The colors of spirooxazine and chromene are in the 600 and 450 nm regions, respectivdy; in compounds containing both spirooxazine and chromene units, therefore, it might be expected that the color can be tuned. Some of the compounds examined are shown in Fig. 8.1. Compounds 1-3 contain two identical or different photo- chromes (naphthospirooxazine and benzo-[2H]-chromene moieties) linked by an ethenic bridge. The photochemical and dynamic properties of these compounds are different from those of the single components. For 1 colorability on UV irradi- ation increases, because thermal reversibfiity is lost [2]. Furthermore, excitation with visible light does not cause the reverse reaction, but slow photobleaching accompanied by degradation. UV irradiation of compounds 2 and 3 leads to colored intermediates that evolve in the dark leading to a thermal-stationary state which, for 2, partially returns to the original compound on visible irradiation. In these systems the reactivity of the central double bond [4] competes with the reactivity of the photochromic units and leads irreversibly to cyclic compounds. Compounds 4 and 5, in which the two photochromic units are linked by a rigid acetylenic bridge and a flexible ester bridge, respectively, behave as classical, ther- moreversible photochromic systems [3]. Photochemical reversibility, however, which is usually observed in single chromene molecules, does not occur. With compound 2, which contains both spirooxaxine and chromene moleties, colo- rability covers almost all the visible region. Compound 6 (Fig. 8.2) consists of two naphthopyran units linked at C(3) through a bis-thiophene, an electron rich substituent. On irradiation [5] response and coloration are rapid for one naphthopyran unit, because of the presence of the electron-rich substituent. Opening of the first naphthopyran is, however, accom- panied by a change in the hybridization of the spirocydic C(3) carbon from C(sp 3) to C(sp2), resulting in conjugation of the electron-deficient photomerocyanine to the bis-thiophene. Consequently, when the first unit is opened, the initial role of the bis-thiophene as an electron-donating substituent is considerably reduced. This change affects the properties of the second photochromophore. Opening of the second unit then leads to full conjugation of the two photochromophores, afford- ing a new bis-merocyanine with considerable bathochromism relative to the mon- omers. During fading, the effects are reversed - bleaching of the mono-opened form is slower [5]. Multiplexing optical systems based on mixtures of photochromic compounds have also been reported [6]. 8.3 Photochemical Inputs Coupled with Other Stimuli The photochemical inputs used to stimulate photochromic compounds can be coupled with several other types of stimulus. This coupling leads to a variety of interesting systems.

a hv A ,, "B]d- .... B 8.3 Photochemical Inputs Coupled with Other Stimuli [203 b c hv hv A., ---B A ' B hv' 1, hv' Read Erase -1(2) + 1(2) c Fig. 8.3. Schematic representation of the behavior of three types of photochromic system [17]. (a) The photochemical reaction of the form A reverts thermally in the dark. (b) The photochemical reaction of the form A can be reverted only by excitation of the form B with light. (c) Form B, which goes back to A when excited with light, can be transformed by a second stimulus 1(2) into another form C which is stable toward light excitation and, when necessary, can be reconverted to B. 8.3.1 Three-state Systems. Write-Lock-Read-Unlock-Erase

Cycles As illustrated in Section 7.2, most photochromic compounds change color on photoexcitation and revert more or less slowly to their initial state when kept in the dark (Fig. 8.3a). Compounds with this behavior (classified as T-type) are useless for information storage (or switching purposes) because the written information (switching state) is spontaneously erased (back converted) after a relatively short time. Other photochromic compounds do not return to the initial state thermally, but can undergo reversible photoconversion (Fig. 8.3b). Such compounds (classi- fied as P-type) have a severe problem - the light used to read the written data (i.e. to detect the switching state) causes back-conversion of the sampled molecules and, therefore, gradual loss of information (state definition). Several attempts have been made to overcome this difficulty, including the use of photochemically inac- tive infrared light to read the status of the system [7, 8]. A general approach to avoiding destructive reading is to combine two reversible processes that can be addressed by means of two different stimuli (dual-mode sys- tems) [9-15]. The additional stimulus can be another photon [9], heat [10], an electron [11-13], a proton [14], or even something more subtle such as forma- tion of a hydrogen bond [15]. In such systems (Fig. 8.3c) light is used to convert A to B (write); a second stimulus I(2) (e.g. a proton, an electron, etc.) is then used to transform B (which would be reconverted back to A by a direct photon-reading process) into C, another stable state of the system (lock) that can be optically detected without being destroyed (read). By use of this process the change caused by the writing photon is safeguarded. When the written information must be erased C is reconverted back to B by a stimulus opposite to I(2) (unlock; e.g. by a

:204 I $ Mulfisoe-MuluncfionM Systems F2 UV Vis F2 + 2e- ' - 2e- + 2H + - 2H + F2 Fi�, 8,4, Photochemical and electrochemical switchin� of a diarylethene derivative to perform a write-lock-read-unlock- erase cycle [16]. base, a hole, etc.) and B is then reconverted back to A (erase). Such a write-lock- read-unlock-erase cycle can constitute the basis for optical memory systems with multiple storage and nondestructive readout capacity. Several systems suitable for performing a write-lock-read-unlock-erase cycle have recently been reported. Compound 7 (Fig. 8.4) behaves such that states 7a, 7b, and 7c correspond to the species A, B, and C, respectively, in Fig. 8.3. Switching can occur in two independent ways, photochemically and electrochemically [16]. Exposure to visible light results in complete conversion of 7b to the ring-open iso- met 7a. The reaction can be reversed by exposure to UV light. Compounds 7a and 7b alone could not be used as a useful data-storage system, because any attempt to "read" the data could restfit in conversion to the alternate form, so the data could be erased by the attempt to read it. Chemical oxidation of 7b, however, gives the quinone 7c which is not light-sensitive and which can be converted back to 7b by reduction. This system can therefore operate in accordance with the write-lock- read-unlock-erase cycle illustrated in Fig. 8.3c. The write-lock-read-unlock-erase cyde can also be achieved with some fiavy- lium compounds [17-20]. In aqueous solutions the compounds of this family undergo a variety of structural transformations [20, 21] that can be driven by light excitation and pH changes (Fig. 8.5a) and are often accompanied by quite dramatic color changes or color disappearance. The Ct and Cc forms are the trans (more stable) and cis (less stable) isomers of the chalcone species, AH + is the fiavylium cation (which becomes the most stable species in strongly acid solution), and B2 is a hemiacetal species in rapid equilibrium with Cc (for the sake of simplicity, in the following text B2 + Cc will be simply indicated by Cc). The write-lock-read-

a 8.3 Photochemical Inputs Coupled with Other Stimuli [205 + OH- + H + i HOH OCH3 B4 Cc HO r'OCH3 + OH- + H + O- t""OCH3 Cc- b hv hv' + OH iT -OH i.'OCH3 0 + H+ E + H + A B Fig. 8.5. (a) Light- and pH-driven interconversion of the various forms of4Lmethoxyfiavylium. (b) Schematic representation of the write-lock-read-unlock-erase cycle of the 4-methoxyfiavylium ion [20]. + OH- *(AH +) C AH +

206 I $ Multistate-Mult;functionM Systems unlock-erase cyde of the 4t-methoxyfiavylium ion in aqueous solution can be described by making reference to Fig. 8.5b, with Ct, Cc, and AH + playing the role of species A, B, and C of Fig. 8.3c. 1. the stable form Ct can be photochemically converted, by irradiation with 365 nm light (write), into the Cc form that can be reconverted into the original form either thermally or on optical reading; 2. by use of a second stimulus (addition of acid, which can also be present from the beginning without disturbing the behavior of the system, pH _< 3.0), Cc can be converted into the kinetically inert form AH + (lock); 3. the AH + form has a spectrum dearly distinct from that of Ct and is photo- chemically inactive, so that it can be optically detected (read) without being erased; 4. by addition of base, AH + can be reconverted into Cc (unlock); 5. Cc can be thermally or

photochemically reconverted into the initial Ct form (erase). It should be noted that the locking time of the written information bit is not indefinite (at 25 �C and pH 3.0, the half-life of the back reaction from AH + to Ct is 8 days). Somewhat related to the topic discussed in this section are other systems in which a second stimulus intervenes to improve the performance of a photochromic or electrochromic compound. One example is electrochromic bis(dicyanovinyl)biphenyl derivatives, the reduced forms of which can be cyclized when writing must be avoided [22]. 8.3.2 Orthogonal Photochemical-Electrochemical Stimulation By using a single input on a chemical compound, one can play with two states. When more than one input is used, the number of available states increases, leading to systems capable of performing complex functions. On application of n independent stimuli, each related to a two states, 2 different states of the system become available in principle. It might happen, however, that some of the expected states cannot be obtained or are not stable. Several systems have been described in which photochemical and electrochemical inputs can be fully coupled - both photochemically interconvertible species can undergo reduction (or oxidation) and both reduced (or oxidized) species can be photochemically interconverted. Such systems, which usually consist of distinct photoreactive and redox units, can be represented by a square-type scheme such as that shown in Fig. 8.6a and, in principle, can be used as the basis for AND logic (Section 9.4.4). The scheme in Fig. 8.6a can be applied, for example, to compounds 8 and 9 (Fig. 8.6b). Compound 8 [23] consists of a photochromic azo group and an electrochromic anthraquinone group. The azo group can undergo trans-cis photoisomer-

a 8.3 Photochemical Inputs Coupled with Other Stimuli [207 Photoactive unit Redox-active unit Ox Red by Ox ! Red b HsCO .0. 0 8 C x = H, Me, MeO, CI, Br, F, CN [o .' ,oO:.Cx 10 Fig. 8.6. (a) Square-type scheme illustrating the behavior of a system containing photoactive and redox-active units. (b) Compounds 8 and 9 behave according to the square scheme shown in (a) [23]. (c) Compounds 10 [25] and 11 [26] can have up to eight states. 11 ization irrespective of the quinone/hydroquinone state of the redox moiety, and the latter can be electrochemically switched irrespective of the isomerization state of the azo unit. It is noteworthy that the rate of the cis - trans thermal isomerization of the quinone form is more than 30 times faster than that of the hydroquinone form. Compound 9 does not suffer from this drawback of an unstable state, because the four states obtained by independent electrochemical reaction of the quirtone moiety and valence photoisomerization of the aromatic ring are all stable [24]. For compounds 10 [25] and 11 [26] (Fig. 8.6c), which contain an anthraquinone moiety linked to photoisomerizable stilbene and dihydroazulene components, respectively, up to eight states have been obtained, taking advantage of the different reduction products formed by anthraquinone in aprotic and protic solvents. Another interesting example of combined photochemical and electrochemical stimulation is that of [Co(azo-bpy)3] "+ (n = 2,3; bpy = 2,2'-bipyridine; azo-bpy is a bpy ligand carrying a methylazobenzene unit in the 4-position), in which the fraction of cis-azobenzene in the photostationary state depends on the oxidation state of the metal [27]. Orthogonal photo- and electrochemical inputs can be used to control multi-stage recognition of guests. Compound trans-12 (Fig. 8.7a) consists of a photoisomerizable azobenzene unit and a moiety suitable for hydrogen bonding [28]. This compound can play the role of a host for naphthalene diimide guest 13, which has three stable oxidation states (13, 13-, 132-). Taken together this host-guest system features six possible binding states, as shown schematically in Fig. 8.7b. The 16-fold decrease in the association constant (measured by NMR in CDC13) for cs-12 relative to trans-12 arises from the loss of the favorable stacking interaction on isomerization. Electrochemical potentials were used to determine association constants for the various couples, which span a 70-fold range. Another interesting dass of multimode photochromic switch is the heteroaryl-functionalized dihydroazulene-vinylheptafulvene (DHA-VHF) systems such as those shown in Fig. 8.8 [29]. Photochromic behavior is observed for the DHA unit; the heterocydic units can be reversibly oxidized; and the DHA-VHF units can be irreversibly reduced. Bifunctional films with both electrooptical and photochromic properties have been prepared and investigated [30]. These films, which contain naphthospiroindolinooxazines and nitromethoxyspiropyran as photochromic species, can be used to modulate the light transmission by means of suitable electric fields, and to change their color under light irradiation.

8.3.3 Orthogonal Photochemical-(Acid-Base) Stimulation

Photochemical inputs have often been coupled with acid-base inputs to furnish systems with very special features. A generally overlooked difficulty with photochromic systems is that the starting form (e.g. Ct for the flavylium compounds, Fig. 8.5a) is the photoreactive species, so it cannot be read by absorption spectroscopy without writing. With the 4'-hydroxyflavylium ion, which can be deprotonated to yield the mono- and dianions of the cis and trans isomers (Fig. 8.9), this difficulty can be overcome by starting from AH +, which is the thermodynamically stable form at pH 1, and performing a write-lock-read-unlock-erase cycle as illustrate in Fig. 8.10a [17]. Because AH + is

a HN-I-I- -O1, 3 .0 HN-I-I- - /\ trans-12 8.3 Photochemical Inputs Coupled with Other Stimuli [209 uv Vis b Kas s = 9750 M '1 trans-12 -t-e- 13 UV Vis cis-12 -t-e- 13 Koss = 575 M '1 /(ass = 2054 M -1 trans-12 13 UV Vis cis-12 -t-e- 13 Koss = 228 M '1 Kas s = 591 M '1 13 2- UV trans-12 cis-12 132- Koss = 136 M '1 Fig. 8.7. A switchable host-guest system (a) and its six states (b) [25].

210 I $ Multistore- Multunctionl Systems Radical Radical cation cation -e- R DHA Radical anion Fig. S.S. by VHF I ' v -i1 T C3 +e- Radical anion Light- and redox-driven switching of the DHA-VHF system [29]. not photosensitive, it can be read by light excitation (i.e. by recording its absorption spectrum) without writing. It can then be unlocked by a jump to pH 12, which yields the metastable Cc 2- form. At this stage one can write the optical informa- tion obtaining the stable (locked) Ct 2- form that can then be read. When necessary the information stored into Ct 2- can be unlocked by means of a pH jump yielding Ct, and can then be erased by light excitation. The same performance can be obtained by starting from Ct 2-. The network of processes interconverting the vari- ous forms of the 4'-hydroxyflavylium ion (Fig. 8.9) enables the formation of shal- low and deep levels of memory [17], as happens in the human brain [31]. When the permanent (deep) AH + form of memory has been obtained (write and lock, Fig. 8.10b), a jump to pH 12 leads to the formation of a temporary (shallow) memory state, Cc 2-, the spontaneous slow erasure of which to give the deep Ct 2- memory can be accelerated by light. Reset can then be accomplished by a back pH jump. Multistate-multifunctional systems can give rise to intricate networks of reac- tions that have interesting features. With the unsubstituted flavylium compound [19], besides a cycle similar to that shown schematically in Fig. 8.5b, a cycle based on the anionic species present in basic media can also be performed (Fig. 8.11). The latter cycle starts at pH 11 with the Ct- form that, not being photosensitive, can be

read without writing. Two different paths can then be followed. The first begins with a jump to pH 6 which leads to �t and goes on as described above. The second path starts with a pH jump from 11 to 0, leading to Ct, which can be pho- tochemically written (and locked because of the low pH) to AH +. In this form, the information can be stored permanently and read without erasing, because AH + is thermally and photochemically stable. When necessary AH + can be unlocked by a pH jump to 11 and thermally erased to restore Ct-. An advantage of this cycle lies

A 8.3 Photochemical Inputs Coupled with Other Stimuli [211 + OH- + H + .+ r,r,OH + OH2 AH + - + U + + H + + OH- HOiH OH B4 HO r,l ,-OH B2 Cc Cc- Cc - + H + + H + hv hv ' ct- ct - + OH + OH + H + + H + 0 0 0 Fig. 8.9. Light- and pH-driven interconversions among the various Forms oF4Lhydroxyflav�1ium [17], in the possibility of reading the system in both the initial (non-written) and final (written) states without writing or erasing. Ct- is, moreover, more stable than so the durability of the system could be better. A disadvantage is that in this cyde auto-locking (and auto-unlocking) cannot occur, so two pH changes per cyde are needed. Other peculiar aspects of the multistate-multifunctional chemistry of fiavylium compounds have been extensively reviewed [20]. Compound 14 (Fig. 8.12) [32] consists of three independently addressable sub- units: � a tetraethynylethene (TEE) core, which can be reversibly photoisomerized between its cis and trans forms;

212 I 8 Multistate-MultunctionalSystems *AH + .Ct 2 - Abs., 435 nm Fluo., 515 nm AH + Irrad., 365 nm pH 1 Abs., 435 nm Ct Flue., 615 nm Ct 2- p H 12'. Cc 2- Inm b Abs., 435 nm Flue., 615 nm Deep Ct 2- memory .Cc 2 - Abs., 350 nm Irrad., 313 nm .Sh cc2 ..pH 12 allow memory *AH + Abs., 435 nrn Flue., 515 nm AH + Deep memory Irrad., 365 nm Ct)- Cc pH4 Fig. 8.10. 4LHydrexyflavylium networks [17]: (a) write-lock- read-unlock-erase cycle; (b) permanent and temporary memories. � the previously seen dihydroazulene (DHA) unit, which can be reversibly iso- merized to vinylheptafulvene (VHF); � a proton-sensitive N,N-dimethylanilino (DMA) group. With three possible switching processes this system can theoretically adopt eight interconvertible states which can be represented by a three dimensional (cubic) diagram like that shown in Fig. 8.12. Six states have been detected, and several individual interconversion processes cleanly addressed, providing three write- erase processes and one model for an AND logic gate (trans-14a/[trans-14aH]+/

[tras-14bH]+). Isomerization of the TEE moiety is fully light-driven but incomplete, and the VHF - DHA thermal isomerization is relatively rapid.

8.3 Photochemical Inputs Coupled with Other Stimuli [213 *Ct - Ct- pH Jump pH 11 Fi�. 8.11. pH Jump pH 0 hv *AH + Ct hv (zJ) Cc/B2 pH Jump AH + pH 0 pH6 pH6 / / zJ Cc- pH Jump / pH 11 The complex interconversion patterns of the unsubstituted fiavylium compound [19]. The symbols used for labeling the various forms are the same as those used in Fig. 8.9. 8.3.4 Molecular Shift Re�ister A shift register is a form of memory which in essence consists of a set of memory cells (registers) connected in series (Fig. 8.13a). Each cell stores one bit of informa- tion. During each dock cyde, the contents of each cell are shifted to the next ele- ment to the right, the bit that was in the last register (n) is transferred to (read by) the external circuit, and the first register (1) receives (is written with) a new bit of information. Electronic shift registers are used as circuit elements for a variety of applications. The first proposal for a molecular-level shift register appeared in 1988 and was based on photoinduced electron-transfer processes [33]. Macroscopically the regis- ter would consist (Fig. 8.13b) of a cathode (sending electrode, S) and an anode (receiving electrode, R) connected by many polymer chains (P). Each polymer chain should be made of the same number of identical monomer units (M). Each of these units constitutes a memory element and should consist of three different molecular components, an electron donor D, and primary and a secondary electron acceptors, A, and A2. A HOMO/LUMO scheme illustrating the basic principle of the proposed device is shown in Fig. 8.14. The clock cycle for the switching process begins with photo- excitation of every electron donor in each D-A-A2 monomer, forming the *D-A-A2 state which can undergo deactivation via three different routes: (1) radiative or radiationless decay directly to the ground state, (2) forward electron transfer to A, or (3) backward electron transfer to A2 in the adjacent mono- mer unit. The donor-terminated end of the polymer can decay only via the first

214 I $ Mulfisoe-Muluncfionol Systems z ILl + +Z

a 8.3 Photochemical Inputs Coupled with Other Stimuli [215 In Out 1 2 3 n b M1 M2 M3 D A1 A2 D A1 A2 D Fig. 8.13. (a) Schematic diagram of a shift register. (b) Schematic diagram of a molecular- based shift-register. S and R are the sending and receiving electrodes, P are polymer chains, M are the monomer units of the polymer, D is an electron donor, and A and A2 are a primary and a secondary electron acceptors [33]. two paths. If the forward dectron transfer from *D to A is the preferred process, spontaneous electron transfer from A- to A2 can follow (process 4), yielding D+-A-A2 - (Fig. 8.14b). At this stage, free electrons and holes are placed adjacent to one another on the neighboring monomers. The basis for switching is that electron transfer between monomer units is kinetically preferred over charge re- combination within a single D+-A-A2 - monomer. In such circumstances a single hole is left adjacent to the cathode. The next phase in the clock cycle is the data-writing process, which is performed electrochemically. If the oxidized donor is reduced by the electrode to its ground state configuration, photoinduced electron transfer can again occur in the next clock cyde. If, however, no reduction occurs, the next clock cycle will leave positive charge on the first two electron donors in the system. The electrons and holes are read out at the anode as i and 0. The system must register n cydes before data entered at the cathode are read at the anode. Clearly, the operation of such a system implies that several other requirements, besides those mentioned above, must be satisfied (an exhaustive discussion is given elsewhere [33]). For example, the D chromophore must be selectively excited, the light pulse must be sufficiently intense to allow >99.9 % probability of excita- tion of each D, but short enough to prevent the occurrence of two transitions to the right in one clock cyde, the chain length of each polymer should be long enough

� � �0 �� �� � �0 �� �� *D A1 A2 *D A1 A2 *D A1 A2 D + A A' D + A A- Fig. 8.14. A HOMO/LUMO scheme illustrating the principle of a molecular shift register based on hole transport: (a) the clock cycle is initiated by photoexcitation of the donor moiety in each triad; (b) electronic configurations resulting from successive forward electron-transfer steps [33]. D + A1 A to connect two electrodes, and a large number of polymer chains of exactly the same length should be used if the signal is to be detectable with sufficient accuracy. Although many triads have been designed which undergo highly efficient long-lived charge separation appropriate for a molecular shift register based on photo- induced electron transfer [34] (Section 6.3.3), formidable technical difficulties have yet prevented the construction of a working system. In the proposal described above for a molecular shift register, data transmis- sion occurs by hole transport. Alternatively, one could use this system to transport

� � �� D- A1 A2 D A1 A2 D A1 A2 b � � �� D A1 *A- D A1 A2 D A1 A2 Fig. 8.15. A HOMO/LUMO scheme illustrating the basic principle o� a molecular shift register in which bits are encoded and propagated as electrons: (a) data are encoded by electrochemical reduction of the donor moiety adjacent the cathode; (b) excited doublet state resulting from photoexcitation of the reduced species [35]. negative charge along the polymer [35]. In the latter scheme (Fig. 8.15) the clock cyde begins with electrochemical encoding of data into the polymer. Reduction (or lack of reduction) of the ground electronic state of the donor adjacent to the electrode places (or does not place) a free electron into its LUMO. This reduced species undergoes spontaneous stepwise thermal electron transfer until the negative charge is localized on the last acceptor group in the first monomer (Fig. 8.15a). Radical artions of many organic chromophores have distinct spectral signatures with large absorption coefficients [36]. Selective photoexcitation of the D-A1-A2-

state gives an excited (doublet) state, with the electronic configuration shown in Fig. 8.15b. Optical switching is achieved by preferential charge shift from this excited state to the LUMO of the donor in the next toohomer unit. Competitive charge shift to the adjacent acceptor would result in switching errors. Some studies on photoinduced electron transfer involving excitation of radical anions, which might be relevant for this kind of device, have been reported [37] (Section 4.2.1.2). Even in this version, however, the system appears too complex to be constructed. The proposal of a molecular shift register based on photoinduced energy transfer, instead of photoinduced electron transfer, has also been advanced [38]. The shift register should have the same configuration as that discussed above (Fig. 8.14), except that each triad should be composed of three chromophoric units (A-B-C) with triplet energies that decrease sequentially, A > B > C. The system should be entirely optically coupled with the macroscopic world. A unique chromophore, L, attached to the first A chromophore, should absorb in a spectral region where the other chromophores are transparent. After efficient intersystem crossing energy transfer should occur to populate the triplet excited state of A, 3A, thereby writing a "1" bit. Efficient triplet-triplet energy transfer in the triad should form the triplet of C, 3C. At this stage, because further energy transfer is uphill, the information bit is stored (for a short time only). Shifting of this triplet energy ("1" bit) into the next triad should be achieved by photoexcitation of 3C to an upper energy level with an energy greater than that of 3A. By coupling each shift step with a write operation (writing a "1" or a "0" bit), an entire data string could be stored. Finally, reading could also be performed optically at the opposite end of the chain, by transferring the energy to a chromophore E that has: � a lower triplet energy than 3C, � a unique triplet-triplet absorption spectrum, � the possibility of converting an upper triplet state to the fluorescent singlet E. Energy transfer from upper triplet excited states has occasionally been observed and studies on possible model compounds have been reported [38-40]. It is clear, however, that construction of a system of this type is no easier than that based on photoinduced electron transfer. 8.4 Multielectron Redox Processes As mentioned in Section 7.7, dectrochemical stimulation can cause several, simultaneous and/or successive, switching processes even in simple compounds. In addition to the metal complex cited there (Figure 7.14), we would like to recall well known organic molecules like methylviologen (MV 2+, 1,1'-dimethyl-4,4'- bipyridinium dication) which can undergo two successive reversible one-electron reductions [41], tetrathiafulvalene (TTF) which can be reversibly oxidized to the TTF + and TTF 2+ forms [42], and fullerene (C60) whose voltammogram is indica- tive of six equally separated reversible reduction steps (Fig. 8.16) [43].

C6o cOo- C62o-/3 - C-/4 - 8.4 Multielectron Redox Processes I 219 10pA 0 Fig. 8.16. - 1.0 - 2.0 - 3.0 E (V vs SCE) Cyclic voltammogram For reduction of C60 (acetonitrile-toluene, 1:5; -10 �C) [43]. In the last few years the development of supramolecular chemistry has enabled the design and construction of compounds, e.g. polynudear metal complexes [44] and dendrimers [45-58], capable of exchanging many electrons. Such multiredox systems can contain: � equivalent, noninteracting redox units, each capable of undergoing a one- electron redox process at the same potential, and/or � nonequivalent redox units which exchange electrons at different potential values giving rise to complex redox patterns. Both types of system can find applications in catalysis, molecular recognition, energy conversion, and information processing. 8.4.1 Systems with Equivalent Redox Units It is well known that polymers containing suitable redox active substituents, e.g. ferrocene, exchange many electrons at the same potential [59]. Polymers, however, are not well defined species. In the last few years several dendrimers containing a well defined number of equivalent, noninteracting redox active units have been prepared. Ferrocene, one-electron acetonitrile), a well known and simple compound which undergoes a reversible oxidation at an accessible potential (+0.390 V relative to the SCE in has been extensively used for functionalizing the periphery of dendrimers [60, 61]. Dendrimers containing 27 (Fig. 8.17, [61d]), 54, 81, and 243 ferrocenyl units have been synthesized and their electrochemical behavior has been investigated. In these compounds the ferrocene units are reversibly oxidized at

Fe Fe Fe Fe Fe Fo + 27e- - 27e- Fe + Fe + Fe+ Fe+ Fe+ Fe+ Fe + Fe + Fe+ Fe + Fe+ Fe+ Fe+ Fig. 8.17. Simultaneous oxidation of 27 ferrocene units in a dendrimer [61d].

the same potential, with a number of exchanged electrons which is equal (within experimental error) to the number of peripheral ferrocene units (250 _+ 30 exchanged electrons for the dendrimer containing nominally 243 units). The potential value for ferrocene oxidation shows little or no dependence on dendrimer generation. These results indicate that the ferrocene units behave independently from one another. The oxidized products are insoluble in the solvent used (CH2C12) and are deposited on the electrode surface. It has recently been reported that a 64-ferrocene dendrimer can reduce C60 stoichiometrically (64 C60 per dendrimer) in toluene at -30 �C [61e]. Such multielectronic redox-stable compounds can be regarded as molecular batteries [61d, e] for molecular-electronic circuits. They can, furthermore, be useful for multielectron transfer catalysis and for sensory purposes, either directly or after electrode deposition [61a, 62, 63]. Dendrimers functionalized at the periphery with cobaltocenium [64] and with both ferrocene and cobaltocenium [65] units have also been studied. For both ferrocene- and cobaltocenium-based dendrimers, inclusion complexation with cydodextrins have been investigated [60b, 64a]. Tetrathiafulvalene (TTF), which can be reversibly mono- and dioxidized (+0.34 and +0.78 V relative to Ag/AgC1), has been extensively used to prepare redox-active dendrimers. Compounds containing 12 [66a, b], 21 [66c], 24, 48, and 96 [67] TTF units at the periphery have been synthesized. Oxidation of the 96-TTF dendrimer leads to a generation of polycationic species bearing up to 192 positive charges on the srrrface. Functionalization with crown ether-TTF units enables the prepara- tion of dendrimer-modified electrodes for metal cation sensing [67]. In dendrimers containing TTF units both in the core and along the branches (e.g. 15, Fig. 8.18), all the TTF units are oxidized simultaneously, irrespective of their topological position [68]. Dendrimers have also been synthesized (e.g. 16, Fig. 8.18) that con- tain two branches terminated with the electron-donor TTF units and one branch terminated with electron-acceptor anthraquinone (AQ) units [69]. Donor-acceptor intradendrimer interactions are very small. Cyclic voltammetric studies in acetoni- trile revealed two waves on oxidation (TTF) and two on reduction (AQ), all revers- ible in nature and with the number of exchanged electrons corresponding to the redox-active units contained in the dendrimer. Thus, these compounds can be switched reversibly between cationic and anionic states; for compound 16 the +16, +8, -4, and -8 states were clearly observed. Polycationic dendrimers containing up 21 [70] and 45 [71] 4,4'-bipyridinium units have been prepared (see, e.g., compound 1742+ in Fig. 8.19) and their elec- trochemical behavior has been investigated. All the bipyridinium units are reduced at the same potential, although there is evidence of electronic interaction between the radical cations which increases with dendrimer generation. In an attempt to achieve charge trapping, compounds consisting of a phenyl bipyridinium core (which is easier to reduce) surrounded by benzyl bipyridinium units (which are more difficult to reduce) have also been investigated (e.g. 1826+ in Fig. 8.20) [72]. Examples of small dendrimers functionalized at the periphery with fullerenes have also been reported [73, 74].

222 I 8 Multistate-Multifunctional Systems s' s s__s ' s o o '? '�-o 0o (e- s Ss s s Fig. 8.38. Dendrimer 35 contains] 3 electrochemically equivalent F units [68]. Dendrimer 36 carries o branches terminated with electron-donor F units and one branch terminated with electron-acceptor anthraquinone (AQ) units [69].

8.4 Multielectron Redox Processes I 223 /.71 1742+ Fig. .9. Dendrimer 74a+ contains 2] electrochemically equivalent 4,4-bipyridinium units [70]. 8.4.2 Systems with Nonequivalent Redox Units In complex systems there may be different and/or equal but interacting redox units which exchange electrons at different potentials giving rise to characteristic redox patterns. Particularly interesting in this regard are the oligonuclear metal complexes of bipyridine-type ligands [44, 47, 75, 76]. The compounds of this type most exten- sively investigated are those already discussed as light-harvesting antennae (Sec- tion 5.5.1.2), based on the metals and ligands represented in Figure 5.11. In these

224 8 Multistate-MultfunctionalSystems + -- k + Fig. 8.20. Dendrimer g26+ consists of a phenyl bipyridinium core surrounded by benzyl bipyridinium units [72]. compounds, each metal center can undergo one or two oxidation processes, and each ligand can undergo two or three reduction processes. Because the bridging ligands enable electronic interactions between the connected metal centers, even chemically and topologically equivalent units have different redox behavior; this restfits in very complex redox patterns. Fig. 8.21 shows the cyclic voltsmmetric (CV) patterns obtained in N,N-dime- thylformamide at -55 �C for the reduction of the dinudear [(bpy)2Ru(2,3-dpp) Ru(bpy)2] 4+ and hexanuclear [{(bpy)2Ru(2,3-dpp)}2Ru(2,3-dpp)Ru{(2,3-dpp) Ru(bpy)2}2] 2+ complexes [77]. Even for the hexanudear complex, which ex- changes as many as twenty-six electrons, all processes can be assigned on the basis of the patterns observed for the reduction of mono-, hi-, tri-, and tetra-nuclear model compounds. The components shown in Figure 5.11 have also been used to construct den- drimers containing 10, 13, and 22 metal centers that, in addition to working as light-harvesting antennae (Section 5.5.1.2), participate in many redox processes. On reduction, many overlapping waves, difficult to assign, are observed. Such compounds, however, have relatively simple oxidation patterns that can be pre- determined by made-to-order synthetic control of the component units. Reversible exchange of a controlled number of electrons at defined potentials can thus be achieved [78-80]. One example is the decanudear dendrimers shown in Fig. 8.22. In the [Ru{(2,3-dpp)Ru[(2,3-dpp)Ru(bpy)2]2}3] 2�+ dendrimer (Ru0 in Fig. 8.22), the first oxidation process involves the exchange of six electrons at the same potential (+1.53 V relative to the SCE), corresponding to the simultaneous oxida- tion of the six peripheral Ru(II) ions, whereas in the [Os{(2,3-dpp)Ru[(2,3- dpp)Ru(bpy)2]2}3] 2�+ dendrimer (Ru9Os in Fig. 8.22), the Os(II) ion is oxidized

7 3 2 9// 4 8 8.4 Multielectron Redox Processes I 225 8 56 7 10 Ru 2,3-dpp bpy /5 23 20 12 3 4... 26 10 9 / - 1.0 4 17 - 2.0 - 3.0 E (V vs SCE) 25 21 24126 5r, -1.0 Fig. 8.21. CV patterns for the reduction of the dinuclear [(bpy)2Ru(2,3-dpp)Ru(bpy)2] 4+ and hexanuclear [{(bpy) 2 Ru (2,3-d pp)}2

Ru (2,3-d pp) Ru {(2,3-d pp) Ru (bpy) 2}2] 12+ complexes (N,N-dimethylformamide, -55 �C) [77]. - 2.0 E (V vs SGE) -3.0

226 I 8 Multistate-Multifunctional Systems 10 FcFc 6e- +0.4 +0.8 +1.2 +1.6 Rulo FcFc 6e- +0.4 +0.8 +1.2 +1.6 FcFc 6e- Ru90s +014 +0.8 +1.2 +1.6 E (V vs SCE) Fig. 8.22. Redox patterns (differential pulse voltammetric peaks) for three decanuclear dendrimers [75-$0]. Peak Fc+/Fc indicates oxidation of ferrocene as internal standard. The symbols used to represent the dendrimers are the same as those displayed in Fig. 5.11. Iu30s 7 before the six peripheral Ru(II) ions, with a 1:6 pattern of exchanged electrons (one-electron oxidation at +1.35 V followed by a six-electron oxidation at +1.55 V). Finally, in the [Os{(2,3-dpp)Ru[(2,3-dpp)Os(bpy)2]2}3] 2�+ dendrimer (Ru3Os7 in Fig. 8.22), which has an Os(II)-based core, three Ru(II)-based units in the inter-

8.4 Multielectron Redox Processes I 227 mediate positions, and six Os(II)-based units in the peripheral positions, oxidation involves first the six peripheral Os(II) ions, and then the central Os(II) ion, yield- ing for the electron exchange a 6:1 pattern (a six-electron process at +1.05 V and a one-electron process at +1.39 V) instead of the 1:6 pattern observed for Ru9Os. In liquid sulfur dioxide at -70 �C all the metal ions can be oxidized [81]. In larger dendrimers, the number of equivalent units becomes huge and a variety of electron-exchange patterns can be expected. In the docosanudear dendrimer made of an Os(II)-based core and 21 Ru(II)-based units, a one-electron process at +1.42 V (relative to the SCE), assigned to the oxidation of the Os(II) ion, is followed by a 12-electron process at +1.54 V, because of the simultaneous oxidation of the 12 equivalent and noninteracting peripheral Ru(II)-based units [80]. Electronic interaction is also observed between ferrocene units in dendrimers containing silicon-bridged biferrocene moieties [82]. Complex redox patterns are sometimes observed for multinudear grid-type compounds of oligopyridine ligands. In a tetranuclear Co(II) species of 4,6- bis(2',2"-piryd-6'-yl)-2-phenylpyrimidine ligands, 11 electrons are exchanged in 10 reversible steps [83]. Other suitable candidates for multibit information storage by redox processes are porphyrin compounds [84]. A systematic investigation has been performed on porphyrin [85] and ferrocene-porphyrin [86] compounds with the aim of con- structing self-assembled monolayers (SAM) on gold surfaces suitable for practical applications [87, 88]. Several compounds have been synthesized and characterized, including europium porphyrinic triple-decker sandwich complexes (see, e.g., Fig. 8.23) [88]. Electrochemically robust SAM of such compounds have been obtained which show three well resolved, reversible oxidation waves at accessible potentials. Fig. 8.23. An europium porphyrinic triple-decker sandwich complex used to prepare multiredox SAM [$$].

a HN-H- --0. N-. ' "/3--H HN-H---O 21 2O 21 2O 19 19 Fig. 8.24. A three-component, two-pole molecular switch: electrochemical control of a molecular recognition process [99]. 2O

8.5 Electrochemical Inputs Coupled with Chemical Inputs Electrochemical inputs can be coupled not only with photochemical inputs (Section 8.3.2), but also with chemical stimuli [89-94]. Systems of this kind mimic biological processes where interplay between redox and molecular recognition is used to regulate a wide variety of transformations. Flavoproteins containing the flavin cofactors FAD (flavin adenine dinucleotide) and FMN (flavin mononucleotide) are frequently encountered redox enzymes that have to vary their redox potentials over a range of more than 500 mV [95]. Such changes are caused by a variety of interactions including hydrogen bonding, aromatic stacking, steric effects, and dipole interactions. Model systems have been prepared and investigated to enable better understanding of these modulation effects [96-98]. Starting from such investigations, the system illustrated in Fig. 8.24a has been designed [99]. Receptor 19 consists of the previously seen (Fig. 8.7) hydrogen-bonding moiety, linked to an anthracene unit, and receptor 20 is an acylated diaminopyridine. Both hosts can participate in three-point hydrogen-bonding interactions with naphthalene diimide guest 21, either in its oxidized (21) or one-electron reduced (21-) form. In addition, host 19 is capable of forming aromatic stacking interactions. Owing to such stacking interactions, in $CHCl_3$ solution 19 binds 21 more than an order of magnitude more strongly than 20, although 21- has greater affinity for 20. Compound 21-, in fact, forms stronger hydrogen bonds with both 19 and 20, but does not participate in stacking interactions with 19. The behavior of this three-component, two-pole molecular switch, in which the recognition process can be controlled electrochemically, is shown schematically in Fig. 8.24b. Control of one- or two-electron reduction of ubiquinone by redox-dependent recognition [100] and a three-pole redox-controlled hydrogen-bonding switch [101] have also been reported.

a Fe + 23+ 8.6 Multiple Chemical Inputs I 229 b Na + [22 � Na] + Zn 2+ 23 + 22 + [22- Na] + _ e- e 23 [23. Zn2] 5+ [L'Zn] 2+ 22 + L [23'Zn2] 4+ Na + Fi�. 8.25. An artificial re�ulatory system for sodium ions [102], (a) The redox-active li�ands based on ferrocenes; (b) the various steps of the cycle, An artificial regulatory system for sodium ions has been described [102]. The principal components of such a system are two types of redox-active ligands based on ferrocenes, the ferrocenecryptand 22 and the ferrocenium ligand 23 + (Fig. 8.25a). As schematically illustrated in Fig. 8.25b, starting from equimolar amounts of 23 + and the sodium complex of 22 in acetonitrile solution, the addition of two equivalents of Zn 2+ leads to complexation of Zn 2+ by 23 +. The aminoferrocenium ion 23 + is thus converted into a strong oxidant, which is capable of oxidizing [22.Na] + quantitatively. The oxidized oxaferrocenium cryptand has drastically decreased affinity for Na + ions, which are released. The capacity to bind Na + ions by the ferrocene cryptand can be re-established by adding to the reaction mixture a strong ligand (L, e.g. cydam) capable of removing Zn 2+ ions from the [23.Zn2] 4+ complex. 8.6 Multiple Chemical Inputs Systems have also been constructed that switch under the action of multiple chemical inputs. An interesting example is shown in Fig. 8.26 [103]. The supra-

230 I $ Mulfisoe-MuluncfionM Systems o o o o Co 02 H+ /',..-(0..) 24 o [H] 0 Compound 2 acts as a cesium sensor in acidic Fig. 8.26. �� C O o) environment and as a potassium sensor in alkaline environment [103], molecular system 24 consists of an anthracene unit linked to an azacrown ether, which has a large affinity for K + and can be protonated on the amine group, and a calixarene-type crown ether which has a large affinity for Cs +. In 24 the anthracene fluorescence is substantially quenched by photoinduced electron transfer from the amine unit and Cs + complexation has no effect. Protonation of the amine unit of 24 is not followed by a strong increase in intensity, because of photoinduced elec- tron transfer quenching by the diaryloxybenzene moiety of the calixarene com- partment (Fig. 8.26). Addition of Cs + to [24H] + causes a fourfold increase of the fluorescence emission. In contrast, K + causes a sevenfold enhancement in the fluorescence intensity of 24 and has no effect on that of [24H] +. This compound thus switches from performing as a cesium sensor in an acidic environment to a potassium sensor in an alkaline environment. References (a) Photochromism: Molecules and Systems (Eds.: H. DORR, H. BOUAS- LAURENT), Elsevier, Amsterdam, 1990. (b) Chem. Rev.,

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235 9 Logic Gates 9.1 Introduction In current computer networks data are processed electronically by microprocessor systems and are exchanged optically between remote locations. Data processing and communication require the encoding of information in electrical and optical signals in the form of binary digits [1]. A threshold value and a logic convention are established for each signal. In a positive logic convention, a 0 is used to repre- sent a signal that is below the threshold voltage and a i is employed to indicate a signal that is above. For example, a threshold voltage of 2 V and a positive logic convention can be established for a certain electrical signal. In such a case, a value of 3 V would be above the threshold and would correspond to a 1, whereas a value of i V would be below the threshold and would correspond to a 0. In a negative logic convention, the assignment is reversed. By use of similar assumptions the logic circuits of microprocessor systems process binary data through sequences of logic gates. Although it is not necessarily true that the components of a molecular computer [2-4] will have to operate in ways analogous with those of conventional silicon- based computers, much effort has been devoted to the design, synthesis, and characterization of molecular systems in which silicon-based logic can, in princi- ple, be mimicked [5]. It is worth recalling another aspect of information processing [6, 7]. In commu- nication networks bundles of optical fibers can transmit hundreds of gigabits per second because propagating light beams of different wavelengths do not interfere. The routes of the optical signals traveling through these networks are determined by optoelectronic devices that, at the receiving

end of each optical fiber, convert the incident optical inputs into electrical signals. The electrical signals are then reconverted into optical outputs which are routed along another optical fiber. The noninteracting properties of optical signals, however, do not apply to electrical sig- nals, because only one electric signal can be transported through a single electric wire. This means that the electronic part of the optoelectronic devices cannot handle the immense parallelism potentially offered by optical signals. Strategies must be developed to switch the propagating optical signals with optical, rather than electrical, stimulation [8]. Molecular Devices and Machines -A Journey into the Nano World. V. Balzani, A. Credi, M. Venturi Copyright � 2003 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim ISBN: 3-527-30506-8

236 I 9 Logic Gates In.Out NOT Inl,_ . In2 Uu! OR In1 t _ . In2 , UU AND In Out In1 In2 Out 0 1 0 0 0 1 0 0 I 1 I 0 1 1 1 1 Fig. 9.1. In 1 In2 Out o o o o 1 o 1 o o 1 1 I Symbols and truth tables of the NOT, OR, and AND logic gates. 9.2 Fundamental Concepts of Logic Gates The three basic types of logic gate [1, 9] are the NOT, AND, and OR gates. Each has been designed to perform according to a set of rules delineated in a so-called truth table, which is a list of outputs that the gate should give, on the basis of certain inputs. The symbols used to indicate these three logic gates and their truth tables are shown in Fig. 9.1. The NOT gate converts the input signal I into the output signal 0, and vice versa. Because of the inverse relationship between the input and output values, the NOT gate is often called an inverter. The OR gate combines two input signals [10], In and In2: when In and/or In2 is 1, Out is 1; when In and In2 are 0, Out is 0. The AND gate also combines two inputs [10] into one output. In this instance, however, Out is 1 only when both inputs In and In2 are 1; in the other three cases, Out is 0. Because these three gates alone are not sufficient to perform all the necessary logic functions, combinational logic circuits that obey different truth tables can be assembled connecting NOT, OR, and AND gates. The NOR gate (Fig. 9.2) corre- sponds to the inverted functions of the OR gate and can therefore be indicated by connecting the output of an OR gate with the input of a NOT gate. As a conse- quence, the two inputs In and In2 are converted into the output after two consec- utive logic operations. In a similar fashion, the NAND gate (Fig. 9.2) is assembled connecting the output of an AND gate to the input of a NOT gate. The NOR and NAND operations are termed universal functions because any conceivable logic operation can be implemented by relying on one of these two gates only. In fact, digital circuits

are fabricated routinely interconnecting exclusively NOR or exclu- sively NAND operators. Other important combinational logic circuits are the XOR and XNOR gates (Fig. 9.3), which introduce the exclusive function. The XOR logic gate has exactly the same truth table as that of an OR function, except when both inputs are equal to 1, in which case the output is 0. The XNOR logic gate is the inverse function of

In1 Out In2 9.3 Molecular Switches as Logic Gates I 237 Inn; O-, NOR NAND In In= Out In In= Out 0 0 1 0 0 1 0 1 0 0 1 1 1 0 0 1 0 1 1 1 0 1 1 0 Fig. 9.2. Symbols and truth tables of the NOR and NAND logic gates. XOR, so that if both inputs have the same value the output is equal to 1 and when the inputs are different the output is O. Other combinational logic circuits can of course be constructed. The logic gates of microprocessor systems are assembled by interconnecting transistors, and their input and output signals are electrical [1]. The concept of binary logic is, however, general and can thus be extended to any type of signal, including chemical, optical, and mechanical. Of course, devices are needed that respond to such signals according to the logic gate rules. 9.3 Molecular Switches as Logic Gates The analogy between molecular switches and logic gates is obvious. As we have seen above, molecular switches convert input stimulation into output signals. Therefore, the principles of binary logic can be applied to the signal transduction In1 Out In1 Out Ina Ina In1 XOR XNOR In2 Out In In2 Out 0 0 0 0 0 1 0 1 1 0 1 0 1 0 1 1 0 0 1 1 0 1 1 1 Fig. 9.3. Symbols and truth tables of the XOR and XNOR logic gates.

238 I 9 Logic Gates operated by molecular switches. It should be noted that there is no need to have systems with a full yes-no change in the relevant signals, because analysis of the logic behavior can be based on the assignment of appropriate threshold values to the input and output signals. Interestingly, the inputs and outputs do not need to share the same logic convention and different conventions applied to the same molecular device can lead to different logic functions, in the same way as for semiconductor devices [1]. In the molecular-level switches discussed in previous chapters stimulation is usually performed by optical, electrical, or chemical inputs. The outputs produced are again optical, electrical, or chemical, but most often the input and output sig- nals do not belong to the same category. For example, in photochromic systems an optical (photochemical) input produces an optical (change in color) output, whereas in other systems an optical (photochemical) input causes an electrical

(change in the redox potential) output. The different categories of input and output do not compromise the use of the switch as a logic gate, because the result of a logic operation is controlled only by the values of the encoded binary digits, irre- spective of the nature of the input and output signals. It should be pointed out that input/output molecular-level processes are very common, but their logic aspects have been recognized only recently. For example, the fluorescence (optical output) of hundreds of compounds is quenched by addi- tion of a quencher (chemical input) [11], but the "NOT logic gate" behavior of these systems was not noticed. The first proposal to execute a logic operation at the molecular level goes back to 1988 [12], but the field began to develop only five years later when the analogy between molecular switches and logic gates was experi- mentally demonstrated [13]. In the last few years molecular-level logic functions of several types have been reported and discussed [4, 13-21]. As mentioned above, any kind of input or output signal can be used, but most of the examples described are based on fluorescence switching caused by photo- induced electron-transfer (PET) processes, as illustrated schematically in Fig. 9.4 [14]. In this figure, F is a potentially fluorescent unit (e.g. an anthracene molecule) the fluorescent excited state of which is quenched by PET from the HOMO orbital of an appended electron-donor receptor, D (e.g. an amine unit). When the HOMO orbital of the electron donor is engaged by a suitable added molecule or ion (for an amine, e.g., by protonation), fluorescence can be observed because the HOMO of the donor is reduced in energy and electron transfer can no longer occur. Fluorescence is an ideal output because of its ease of detection even at the single- molecule limit [22]. Another remarkable feature of fluorescent signals is that they do not need to be wired to operate. Light can indeed bridge the gap between the world of molecules and our macroscopic world. In the following sections illustrative examples will be presented in order of increasing logical complexity. For more detailed discussions, excellent review articles are available [13-21]. We would also like to mention that chemical wave logic gates [23], logic operations based on optical transitions [24], and combina- tional logic representation and sequential machine interpretation of the two- photon dissociation of nitric acid [25] have been reported.

E LUMO HOMO HOMO E LUMO HOMO 9.4 Basic Logic Gates I :239 HOMO Excited fiuorophore Free receptor Excited Bound fiuorophore receptor Fig. 9.4. Schematic illustration of fluorescence switching by photoinduced electron transfer (PET) [14]. 9.4 Basic Logic Gates As we have pointed out, any logic function can be implemented connecting the appropriate combination of simple NOT, OR, and AND gates, although often it is more convenient to use the NOR, NAND, XOR, and XNOR gates as basic logic operators. In the following text, therefore, we will consider a basic set of eight functions - YES, NOT, OR, AND, NOR, NAND, XOR, and XNOR. 9.4.1 YES Gate The YES logic gate has a single input and a single output - when the input is 0 the output is 0, and when the input is i the output is 1 (Fig. 9.5a). Such an operation is so trivial that it is not considered in an electronic context, where it simply represents an electrical conductor (PASS logic). In a more general context of inputs and outputs of different categories, however, it is not trivial. On a molecular basis, hundreds of examples of YES-type behavior are known, most of which have been developed for other applications and have not been recognized from a logical viewpoint. For example, the triggering of a light output on stimulation by a chem- ical input forms the basis of many fluorescent molecular sensors [11]. One of the

240 I 9 Logic Gates YES In � Out b c o o 0'0-'0-- 0-0 0- In Out N N (Ca +) (Fluo) 0 0 15- Cl-O 1 1 Fi�. 9.5. Symbolic representation (a), molecular implementa- tion (b), and truth table (c) of a YES Io�ic �ate based on compound 15- [17, 26]. most interesting examples of a sensor that can be viewed as a YES logic gate is compound 15- shown in Fig. 9.5b [17]. In this system, Ca 2+ is the chemical input, the tetracarboxylate unit plays the role of a Ca 2+ receptor, and the aromatic tricydic unit fluoresces (output) only in the presence of the chemical input [26]. In the absence of Ca 2+, the fluorescent excited state of the aromatic moiety of 15- is quenched by electron transfer from the alkoxyaniline electron-donor moiety. On Ca 2+ coordination molecular rearrangements and the presence of the positive metal ion cause a strong reduction of the electron-donor power of the amine unit, making the PET process much slower and increasing the fluorescence quantum yield. Compound 15- is an excellent sensor for monitoring intracellular Ca 2+ concentration [26]. 9.4.2 NOT Gate The NOT gate inverts any signal received (Fig. 9.6a) and is therefore very important in electronic equipment. In chemical systems NOT logic behavior is very common because of the ease with which luminescence (output) can be quenched by a chemical input. Sensors based on this principle can find applications in a variety of fields (e.g. wind tunnel research in aerodynamic engineering [27]). A simple example of a NOT

chemical gate is shown in Fig. 9.6b. In a 1:4 (v/v) mixture of CH3OH and H20 the fluorescence quantum yield of compound 2- is 0.13, but it drops to 0.003 in the presence of 1000 equivalents of acid [28]. The quenching process is related to the occurrence of PET from the central pyrazoline unit to the benzoic acid. The inverse relationship between the chemical input and the optical output translates into the truth table of the NOT operation (Fig. 9.6c). An example of NOT logic based on oligonudeotides is given in Ref. [4].

a NOT In Out 9.4 Basic Logic Gates I 241 b c oo Out (H +) (Fluo) o 1 2- 1 0 Fig. 9.6. Symbolic representation (a), molecular implementa- tion (b), and truth table (c) of a NOT logic gate based on compound 2- [25]. 9.4.3 OR Gate The OR gate has two inputs and one output (Fig. 9.7a). In electrical terms it can be viewed as a circuit with two switches in parallel. In chemical systems the OR logic was first recognized in nonselective Na+/K + sensors [13]. Other examples based on the same principle have been reported [29-32]. A well-behaved OR gate should have the same high level of output when switched on. The example shown in Fig. 9.7b refers to cryptand 3 which bears three anthracene units. In THF the fluorescence quantum yield of 3 (10 -s mol L -) is very low (0.001, including some exciplex fluorescence) because of PET from the tertiary nitrogen atoms to anthracene. In the presence of 10 -2 mol L - Cu 2+ or Ni 2+, the quantum yield increases approximately 100-fold [30, 31]. A completely different example of a molecular-level OR gate is given [33] by triad 4 (Fig. 9.7d); excitation of 4 at 640 nm leads to the C-ZnP-*P excited state, whereas excitation at 550 nm leads to the C-*ZnP-P excited state. In both cases the system evolves towards the charge- separated excited state C+-ZnP-P - which can be detected optically by a large absorption change at 960 nm where the carotenoid cation has an intense band. Alternatively, the readout could be achieved in principle by detection of a photo- voltage in an appropriate assembly. 9.4.4 AN D Gate The AND operator again has two inputs and one output (Fig. 9.8a) and in a simple electrical scheme it can be represented by two switches in series. On the molecular scale AND logic is followed by a number of fluorescent sensors investigated long ago [34] when their logic aspect had not yet been recognized. The best examples of

242 I 9 Logic Gates b -N N a OR In In2 Out C In1 In2 Out (Cu 2+) (Ni 2+) (Fluo) 0 0 0 0 I 1 1 0 1 1 1 1 e In1 In2 Out (640nm) a (550nm) a (960nm) b 0 0 0 0 1 1 1 0 1 1 1 1 aExcitation bAbsorption Fig. 9.7. Symbolic representation

(a), molecular implementa- tion and truth tables of OR logic gates based on compounds 3 (b and c) [30, 31] and 4 (d and e) [33]. molecular levd AND gates are those based on two chemical inputs and an optical (fluorescence) output [13, 34-38], but examples of molecular systems able to process chemical and optical inputs [39-48] or two optical inputs [49] with AND functions are also known. Fig. 9.8 illustrates the anthracene derivative 5 that pro- duces a virtually perfect true table [37]. In methanol the fluorescence quantum yield of 5 in the presence of 10 -3 mol L - H + and 10 -2 mol L - Na + is 0.22 (output state 1, fourth line of the truth table, Fig. 9.8c) whereas none of the three output states 0 has quantum yield higher than 0.009. The PET quenching process involves

9.4 Basic Logic Gates I 14t AND Inl[_ . in2 Iuut b kN-N 5 In1 In2 Out (H*) (Na +) (Fluo) 0 0 0 0 1 0 1 0 0 1 1 1 Fig. 9.8. Symbolic representation (a), molecular implementa- tion (b), and truth table (c) of an AND gate based on compound 5 [37]. the amine moiety in the first two states of the truth table and, of course, the crown ether in the third. Interestingly, the crown ether alone could not quench the anthracene fluorescence, but when the amine is protonated the process becomes thermodynamically allowed and does occur. Features of AND logic are also observed for the so-called "off-on-off" (or "on- off-off') systems [44, 45, 46, 47]. Typical examples are fluorescent sensors which are able to detect a metal ion only in a well defined pH range. AND gates based on electrochemical [48] and spectroscopic [50-52] experiments have also been reported. An example of AND logic based on oligonudeotides is given Ref. [4]. 9.4.5 NOR Gate The NOR operation is the inverse of the OR operation and can thus be represented by a simple combinational circuit (Fig. 9.9a). At the molecular scale integration of the NOT and OR operations can be achieved within one supramolecular (two- component) species such as compound 6 shown in Fig. 9.9b [53]. This compound consists of a fluorescent anthracene unit and a 2,2'-bipyridine moiety which can be a receptor for H + or Zn 2+. When this happens the 2,2'-bipyridine unit becomes easy to reduce and it quenches the fluorescent excited state of anthracene by PET. 9.4.6 NAND Gate This operator results from the combination of an AND and a NOT gate (Fig. 9.10a). An early example of NAND logic was discussed by the authors [35] in a logical

244 I 9 Logic Gates a Inl In2 NOR Out b c Inl In2 Out Ni6 (H +) (Zn 2+)

(Fluo) 0 0 1 I[O 0 1 0 1 0 0 1 1 0 Fig. 9.9. Symbolic representation (a), molecular implementa- tion (b), and truth table (c) of a NOR gate based on compound 6 [53]. AND context. A more recent example is illustrated in Fig. 9.10. Compound 7 con- sists of a Tb 3+ complex connected to a phenanthridine moiety [54]. On excitation in the phenanthridine absorption band at 304 nm, strong Tb 3+ phosphorescence is not observed (output) only when both acid (which protonates the phenanthridine unit) and oxygen (which quenches the phenanthridine triplet donor) are present. NAND logic is also observed for a fluorescent ATP sensor [55]. a NAND In2 Out b c CH3 Inl In2 Out O=P--O H ,- -N I /x,/'- //N (H +) (02) (Phos) i...N, .N.., n - - J o- -Tb- I-O 0 0 1 I H3cPv l ,_./N 7 0 1 1 O--I- O 1 0 1 CH3 1 1 0 Fig. 9.30. Symbolic representation (a), molecular implementa- tion (b), and truth table (c) oFa NAND gate based on compound 7 [54].

9.4 Basic Logic Gates I 145 9.4.7 XOR Gate The exclusive OR gate is particularly important because it can compare the digital state of two signals. If they are different the output is 1, whereas if they are the same the output is 0. This type of logic has proven to be difficult to emulate on the molecular scale, but some examples are now available [56, 57]. The first reported molecular-level XOR gate is illustrated in Figs. 9.11 and 9.12 [56]. The electron-rich macrocyde 8 can be threaded by an electron-deficient wire- type molecule such as 92+. The resulting pseudorotaxane complex [8.9] 2+ is held together by a charge-transfer (CT) interaction. Complexation is signaled by as many as three different optical channels: � appearance of a red color, because of the presence of a CT absorption band in the visible region; � disappearance of the blue-green fluorescence of 92+; � disappearance of the UV fluorescence of 8 with 'truax = 343 nm (the disappear- ance of the two fluorescent signals is because of the presence of the lower lying CT state in the complex). For the XOR function protons and n-Bu3N are the inputs and the fluorescence of 8 at 343 nm is the output. The working mechanism of this system is illus- a XOR Inl Out In2 b C In In2 Out (H +) (n-Bu3N) (Fluo) Fig. 9.11. Symbolic representation (a), molecular implementa- tion (b), and truth table (c) of an XOR logic gate based on compounds 8 and 92+ [56]. The working mechanism of the systems is fully illustrated in Fig. 9.12. o o o o 1 1 I o I 1 o

246 I 9 Logic Gates -I- Dethreading B [9- B2] 2+ + Rethreading -I- Dethreading a [8-9] 2+ [8-9] 2* [8H]* 9 2+ + + Rethreading Fig. 9.12.

Working mechanism of the XOR logic gate based on compounds 8 and 92+ [56], the formulas of which are shown in Fig. 9.11. trated schematically in Fig. 9.12. As mentioned above, in the absence of the two inputs the fluorescence of 8 is quenched in the pseudorotaxane (output 0). When Bu3N input alone is applied the complex dethreads because of the formation of a stronger CT interaction between the amine and 9 2+. Under such conditions 8 is free and its fluorescence is not quenched (amine input 1, output 1). Application of the H + input causes protonation of 8 and, again, dethreading of the pseudorotax- ane. Because protonation of 8 (presumably at the aliphatic ether oxygen atoms) does not perturb its emission compared with that of the neutral form, the H + input 1 causes an output 1. Therefore the output achieves logic state 1 in the two situations in which exclusively one of the two inputs is present. However, when both inputs are applied in stoichiometric amounts, acid-base neutralization results, the complex remains intact and the 343-nm emission is quenched (output 0). An example of XOR logic based on oligonucleotides is given Ref. [4]. 9.4.8 XNOR Gate Exclusive NOR logic corresponds to an XOR gate feeding into a NOT gate (Fig. 9.13a). An example of this type of logic is a pseudorotaxane (Fig. 9.13b) con- sisting of an electron rich tetrathiafulvalene derivative (10) inserted in the cavity of an electron-deficient bipyridinium cydophane (114+) [58]. In CH3CN, an absorp- tion band associated with the CT interaction is observed at 830 nm. This absorp- tion is taken as the output signal. The two inputs are the application of positive

XNOR In1 Out In2 9.5 Combinational Logic I 247 b c In 1 In 2 Out 040,41 == (....0/44 O (+0.5 V) (-0.3 V)(830 nm) a H H 10 0 0 1 0 1 0 1 0 0 1 a Absorption Fi�. 9.13. Symbolic representation (a), molecular implementa- tion (b), and truth table (c) of an XNOR Io�ic �ate based on compounds 30 and 334+ (+0.5 V) and negative (-0.3 V) potentials sufficient to cause one-electron oxidation and reduction of 10 and 114+, respectively. In either circumstance the complex dissociates and the CT absorption disappears. In summary, electrical stimulation controls the CT absorption (output). A positive logic convention (low = 0, high = 1) was applied to the potential input that controls the redox state of 10, and a negative logic convention (low = 1, high = 0) was applied to the potential input that governs the redox state of 114+. The resulting truth table corresponds to that of a XNOR gate (Fig. 9.13c). It has been remarked [21] that the input string with In and In2 equal to 1 implies that input potentials +0.5 V and -0.3 V are applied simultaneously to a solution containing the pseudorotaxane compound and not to an individual complex. Of course, the concomitant oxidation of 10 and reduction of 114+ in the same pseudorotaxane would be unrealistic. The XNOR operation exe- cuted by the supramolecular system is, therefore, a consequence of bulk properties and not a result ofunimolecular signal transduction. 9.5 Combinational Logic 9.5.1 INH Function Inhibit (INH) gates are basically AND gates with one of the inputs inverted through a NOT function (Fig. 9.14a). At the molecular scale physical "wiring"

248 I 9 Logic Gates a In1 In INH Out b c CH3 In1 O=P--O H I �- � CH3 1 FiB. 9.4. Combinational Ioic scheme (a), molecular implementation (b), and truth table (c) oan Inhibit (INH) Ioic ate based on compound 2 In2 Out (02) (Phos) 0 0 0 0 1 0 1 0 1 1 0 between two gates can be avoided by suitable functionalization. Fig. 9.14 illustrates the behavior of compound 12 which consists of a Tb 3+ complex with an appended quinoline moiety [59]. This compound has a weak Tb 3+ emission band at 548 nm (2exc = 330 nm) in either aerated or degassed alkaline solution (pH 11). A 50-fold increase in the emission intensity is observed under acid conditions (pH 2.9) if oxygen is absent. The protonation of the quinoline nitrogen atom affects the mechanism of energy transfer from the quinoline excited state to the lanthanide excited state, enhancing the emission intensity. Oxygen, however, quenches the quinoline triplet excited state thereby reducing the efficiency of energy transfer to the Tb 3+ complex. A three-input INH gate has also been reported in which a PET quenching pro- cess is blocked by Ca 2+ and fi-cyclodextrin inputs, with oxygen as a third input that disables the device [53]. 9.5.2 EnOR Function The enabled OR (EnOR) gate is a three-input system corresponding to a two-input OR function which is activated only in the presence of the third input, and can be represented by an OR gate feeding into an AND gate (Fig. 9.15a). An example of such a behavior is given by the fiavylium compound 13 (Fig. 9.15) which is con-

a EnOR 9.5 Combinational Logic I 249 In1 In2 In3 Out b o 13 365-nm light and H + C In1 In2 In3 Out (365 nm) a (H +) (SDS) (434 nm) b 0 0 0 0 0 0 1 0 0 1 0 0 0 1 1 0 1 0 0 0 I 0 1 1 I 1 0 1 I 1 1 1 a Excitation bAbsorption Fig. 9.15. Combinational logic scheme (a), molecular implementation (b), and truth table (c) oFan Enabled OR (EnOR) logic gate based on compounds 13 and 14 + [60]. verted into compound 14-- (output - change in the absorption spectrum) by the action of light (In) and protons (In2) [60]. Such an AND gate can be expanded to an EnOR gate by a third input (In3), sodium dodecyl sulfate (SDS), which traps 13 and concentrates protons locally. Thus, SDS above its critical miceliar concentration serves as an enabler for protons, even at relatively high bulk pH, by concentrating these sufficiently to activate the transformation. This behavior corresponds to an OR operation between In2 (H^+) and In3 (SDS), which is activated only in the presence of In (irradiation with 365-nm light).

9.5.3 Half Adder

We have seen above that specific sequences of NOT, OR, and AND operations can be programmed in a single molecular switch. Clearly, the complexity that can be achieved with only one molecular switch is limited. Combination of molecular independent NOT, OR, and AND operators would afford the possibility of obtaining any combinational logic circuit. If such systems operate in parallel there is no need for digital communication between them. A step along combination of molecular independent operators has led to a system capable of performing as a half-adder. A half-adder is the basic component of computational arithmetic in semiconductor technology. Its function is to add two one-digit binary numbers together. A half-adder consists of an AND gate and an XOR gate working in parallel (Fig. 9.16a). The output from the AND gate gives the carry digit of the addition and the output from the XOR gate gives the sum digit. To transfer the concept of parallel connectivity to the molecular world one must envisage two logic-displaying molecules that share common stimuli and have different outputs. The compounds 154- and 164- shown in Fig. 9.16 have been designed with this purpose [61]. Compound 154- combines well known receptors for Ca^{2+} and H^+ with a push-pull chromophoric moiety the absorption spectrum of which is sensitive to the presence of the two cations. Taking the transmittance at 390 nm as an output and an appropriate threshold value, the molecule behaves as a XOR logic gate in aqueous solution, as is apparent from the truth table shown in Fig. 9.16b. Compound 164- was then designed which shows AND logic (Fig. 9.16c), because both its Ca^{2+} and H^+ receptors must be occupied if fluorescence (419 nm) is to be observed. Because compounds 154- and 164- do not interfere with each other and are fully compatible in terms of chemical inputs and power supply, their XOR and AND logic can be operated in parallel for the purpose of binary addition (Fig. 9.16d). The first binary number is coded for by the presence (1) or absence (0) of the H + input. The second binary number is coded for by the presence (1) or absence (0) of the Ca 2+ input. The sum digit is coded for by the transmitted light intensity output at 390 nm when high (1) or low (0). The carry digit is coded for by the emitted light intensity output at 419 nm when high (1) or low (0). The table in Fig. 9.16d shows that the molecular system is capable of performing the binary additions: 0 + 0 = 00, 0 + 1 = 01, 1 + 0 = 01, and 1 + 1 = 10. In the decimal number system these operations become 0 + 0 = 0, 0 + 1 = 1, 1 + 0 = 1, 1 + 1 = 2. It should be pointed out [61] that such a system: � is based on general principles and can therefore be extended to a larger number of inputs; � operates in wireless mode; � can be reset by washing if it is polymer bound. It is also worthwhile recalling that if a binary number longer than two digits must be added, a full adder must be constructed [62]. The electronic representation

a In1 Out1 [Carry digit 9.5 Combinational Logic I 251 Out2 Sum digit b N N -/ In1 In2 Out (H +) (Ca 2+) (390 nm) a 0 0 0 0 1 1 1 0 1 1 1 0 Transmittance C -N 164- In1 In2 Out (H +) (Ca 2+) (Fluo) 0 0 0 0 1 0 1 0 0 1 1 1 d Added number In1 In2 (H +) (Ca 2+) 0 0 0 1 1 0 1 1 a Transmittance Fi�. 9.16. Combinational Io�ic scheme Ca), molecular implementation and truth table oFthe XOR 154- (b) and AND 164- (c) components oFa halF adder (d)

252 I 9 Logic Gates Half Adder $ In1 Half C2 In2 Adder C Fi�. 9.17. Scheme of a full adder, In and In2 are the digits to be added, C is the carry digit from the previous pair of inputs, and C2 are the final sum and carry digit. of such a device is shown schematically in Fig. 9.17. The three inputs are Inl, In2 (the digits to be added) and C1 (the carry digit from the previous pair of inputs). Through a combination of two half adders and a further XOR gate, connected both in series and in parallel, the sum and carry outputs of the addition are produced. Clearly it is not easy to implement such a complex circuit with a molecular or supramolecular species. 9.5.4 A Three-state, Three-input, Two-output Molecular Switch A very interesting three-state molecular switch that responds to two optical inputs (Inl, UV light, and In2, visible light) and one chemical input (In3, H +) producing two optical outputs (Ouh, absorbance at 401 nm, and Out2, absorbance at 563 nm) is illustrated in Fig. 9.18 [63]. Binary digits can be encoded on each signal by applying positive logic convention (low = O, high = 1). In the antidockwise cycle shown in Fig. 9.18a, the colorless spiropyran derivative SP in acetonitrile solution switches to the

merocyanine form ME (which absorbs at 563 nm) on irradiation with UV light; ME switches to the protonated MEH + form (which absorbs at 401 nm) when treated with H +, and MEH + switches back to the colorless SP form on excitation with visible light. Alternatively (clockwise cycle), SP switches to MEH + when treated with H +, MEH + switches to ME after removal of H +, and ME switches back to SP on excitation with visible light. Thus, the optical Ouh is high (1) when only input In3 is applied (Inl = O, In2 = O, In3 = 1), when only input In2 is not applied (Inl = 1, In2 = O, In3 = 1), or when all the inputs are applied (Inl = 1, In2 = 1, In3 = 1). The optical Out2 is high (1) when only input Inl is applied (Inl = 1, In2 = O, In3 = 0), or when only input In3 is not applied (Inl = 1, In2 = 1, In3 = 0). The corresponding truth table and equivalent logic circuit are illustrated in Fig. 9.18. One portion of this complex logic circuit converts the three inputs Inl, In2, and In3 into Ouh through AND, NOT, and OR operations whereas the other part transduces the same inputs into Out2 through AND and NOT operations.

Vis UV OH SP d+ ME OH + H + - H + Vis 1 + H+ I /+[/H NO 2 OH MEH+ b 9. 6 Neural-type Systems I 253 In1 In2 In3 Outl Out2 (UV) (VIs) (H +) (401 nm) a (563 nm) a 0 0 0 0 0 0 0 I 1 0 0 1 0 0 0 1 0 0 0 1 0 1 I 0 0 1 0 I 1 0 1 1 0 0 1 1 1 I 1 0 Absorption Out2 Inl In Ina Fig. 9.18. A three-state, three-input, two-output molecular switch: (a) molecular basis; (b) truth table; (c) combinational logic scheme [63]. Out1 9.6 Neural-type Systems 9.6.1 An XOR Logic System Under the Control of an Intrinsic Threshold Mechanism The neuron processes signals in a fashion which resembles the working of a tiny logic device, relying on the behavior of ions in solutions [64, 65]. The neuron is quiescent unless the sum of the input signals over a period of time rises above a critical value. When such a threshold value is reached, the neuron is switched on and an output signal is generated. Some elementary properties of neurons can be mimicked by simple chemical systems [48, 57, 66]. Particularly interesting is a photochemical system which performs as a threshold device and integrates the effects of two inputs into a single output [57]. Such a system consists of an aqueous solution containing the trans-chalcone form (Ct, Fig. 9.19a) of the 4'-methoxyflavylium ion (AH+), and the [Co(CN)6] 3- complex ion (as the potassium salt). Excitation by 365-nm light of Ct, which is the thermodynamically stable form of the flavylium species in the pH range 3-7, causes trans - cis photoisomerization ($ = 0.04). If the solution is sufficiently acid (pH < 4), the Cc a 254 I 9 Logic Gates hv HO I)CH3 + H+ + OH- Cc AH + [C0(CN)613-+ H3 O+ + hv [CO(CN)5(H20)] 2- + HCN d XOR n1 . .Out n2 Fig. 9.19. An XOR logic system under the control of an intrinsic threshold mechanism: the two photoreactions involved (a and b); absorbance change (tmax - 434 nm) under continuous and (inset) pulsed irradiation (c); truth table and symbolic representation of the XOR behavior (d) [57]. In 1 In 2 Out (Flash 1) (Flash 2) (434 nm) a o o 0 o 1 1 1 o 1 1 1 0 Absorption isomer is rapidly protonated with conversion to the 4'-methoxyflavylium ion AH +, which is kinetically stable under such pH conditions and has an intense absorp- tion band with a maximum at 434 nm and an emission band with a maximum at 530 nm. At higher pH, however, protonation does not occur and the Cc photo- product is back converted to Ct. As far as [Co(CN)6] 3- is concerned, excitation by 254- or 365-nm light in acid or neutral aqueous solution causes dissociation of a CN- ligand from the metal coordination sphere ((I) = 0.31), with a consequent increase in pH (Fig. 9.19b). When an acid solution (pH 3.6) containing 2.5 x 10 -s mol L - Ct and 2.0 x 10 -2 mol L - [Co(CN)6] 3- is irradiated at 365 nm, most of the incident light is absorbed by Ct, which undergoes photoisomerization to Cc. Because the pH of the solution is sufficiently acid, Cc is rapidly protonated (Fig. 9.19a), with the consequent

9. 6 Neural-type Systems I 255 appearance of the absorption band with a maximum at 434 nm and of the emis- sion band with a maximum at 530 nm characteristic of the AH + species. If irradi- ation is continued it is observed that these absorption (Fig. 9.19c) and emission (not shown) bands increase in intensity, reach a maximum value, and then decrease up to complete disappearance. In other words, AH + first forms and then disappears with increasing irradiation time. The reason for the off-on-off behavior of AH + under continuous light excitation is related to the effect of the [Co(CN)6] 3- photoreaction (Fig. 9.19b) on the Ct photoreaction (Fig. 9.19a). As Ct is consumed, with formation of AH +, an increasing fraction of the incident light is absorbed by [Co(CN)6] 3-, the photoreaction of which causes an increase in the pH of the solu- tion. This change in pH not only prevents further formation of AH +, which would imply protonation of Cc molecules that continue to be formed by light excitation of Ct, but also causes back reaction to Cc (and, then, to Ct) of the previously formed AH + molecules. Clearly, the examined solution performs like a threshold device as far as the input (light)-output (spectroscopic properties of AH +) relationship is concerned. Instead of a

continuous light source, pulsed (flash) irradiation can be used (Fig. 9.19c, inset) [57]. Under the action of one flash only, a strong change in absorbance at 434 nm is observed, because of the formation of AH^+. After two flashes, how- ever, the change in absorbance almost disappears. In other words, an output (434 nm absorption) can be obtained only when either input 1 (flash 1) or input 2 (flash 2) are used, whereas there is no output under the action of none or both inputs. This finding shows that the system described above behaves according to XOR logic, under the control of an intrinsic threshold mechanism (Fig. 9.19d). A very important aspect of the system described above should be emphasized. In view of the inherent difficulty in establishing electrical communication between different molecules, other procedures for processing and transmitting signals at the molecular level must be developed to achieve integration of molecular-level devices into complete electronic circuits. In the system described above intermolecular communication occurs in the form of H^+ ions. Another noteworthy aspect of the system is that the input and output signals have the same nature (light) and that the fluorescence output could be fed, in principle, into another device. 9.6.2 A Perceptron-type Scheme Further elaboration of the concept illustrated in the previous Section can lead to the design of more complex, but also more flexible, artificial chemical networks. The scheme shown in Fig. 9.20 [57] resembles a minimum array of perceptrons, the artificial intelligence units used to mimic the behavior of neurons [65, 67, 68]. In such a system, Inl and In2 are two equally intense (I �) pulses of UV light at 266 nm emitted by two independent light sources (flash i and flash 2). Each light pulse is subdivided into two beams of equal intensity (I�/2). One beam of each pulse is sent to cell B containing a solution of a fiuorophore (e.g. naphthalene) in which absorption of 266 nm light causes emission at approximately 365 nm. This emitted light is used to excite an appropriate

Ou! Change in absorbance or emission intensity I � Tr Inl In2 Fi�. 9.20. A minimal perceptron-type scheme based on the system illustrated in Fi�, 9,19, In and In2 are two equally intense pulsed li�ht beams at 266 nm �enerated by flash sources (flash 1 and flash 2), Cell A contains an aqueous solution of �t and $[Co(CN)_6]^{3-}$, Cell B contains a solution of naphthalene in cyclohexane, and cell C contains an aqueous solution of $[Co(CN)_6]^{3-}$. The output is the absorption (,tmax - 434 nm) or the emission (,tmax - 530 nm) bands of the AH^+ species formed in cell A. The truth table is the same as that in Fig. 9.19d [57].

Ct-[Co(CN)6] 3- aqueous solution (see previ- ous section) contained in cell A. The other beam of each pulse, before arriving at cell A, must cross a cell C containing a solution that absorbs, and can be bleached by, 266-nm light (e.g. an aqueous solution of [Co(CN)6] 3-). In such a system, when only one input (i.e. one of the two flashes) is used, a beam of 266-nm light is completely absorbed by cell C, whereas the other beam excites the fiuorophore contained in cell B. This excitation leads to the generation of 365-nm light that, absorbed by Ct contained in cell A (Fig. 9.20), causes its conversion into AH + (Fig. 9.19a), with a consequent increase in absorbance at 434 nm and emission at 530 nm. When both flashes are consecutively fired the intensity of the 365-nm light incident on cell A, originating from cell B, doubles, which would imply con- sequent doubling of the amount of Ct converted into AH +. At the same time in cell C the first pulse bleaches the [Co(CN)6] 3- solution, so that the second pulse of the 266-nm light is transmitted to cell A. This causes the photoreaction of [Co(CN)6] 3- (Fig. 9.19b), with a consequent increase in pH and back conversion of the previously formed ^H + molecules to Cc and then to Ct. Clearly, this system also performs as a threshold device and as an XOR logic gate (Fig. 9.19c). Further- more, in this case the input-output relationship can be changed at will by chang- ing the "weights" of the connecting signals (e.g. the splitting ratio of each incident light pulse or the composition of the solutions contained in the cells). In conclu-

H3c'N AZ + H + - H + 9. 7 Signal Communication Between Molecular Switches I 257 -I- .3�. H3c-N X-_ -N AZH + b c In I In 2 Out (UV) (Vis) (556nm) a 0 0 0 or1 0 1 1 1 0 0 1 1 0 Absorption In2 Fig. 9.21. Reversible interconversion (two-state molecular switch) between the orange azopyridine AZ and the red-purple AZH + (a). Truth table (b) and combinational logic circuit Out (c) illustrating the signal transduction behavior of the two-state AZ-AZH + molecular switch and the three-state molecular switch shown in Fig. 9.18 [71]. sion, the system illustrates the concept of digital communication through inter- molecular light signals and can also be adapted to fuzzy logic [69]. 9.7 Signal Communication Between Molecular Switches As mentioned at the end of Section 9.6.1, the inherent difficulty in establish- ing electrical communication between different molecules points to the need to develop other procedures to transmit signals. In the system illustrated in Fig. 9.19, intermolecular communication was achieved by means of H + ions [57]. Another example is based on the system shown in Fig. 9.18, in which switching of light absorption is used to modulate the fluorescence of pyrene [70]. Communication of chemical signals between two independent molecular switches can also be established by exploiting photoinduced proton-transfer pro- cesses [71]. Reversible interconversion (two-state molecular switch) between the orange azopyridine AZ and the red-purple AZH + (Fig. 9.21a) can be achieved in acetonitrile solution by addition of CF3CO2H or Et3N. As we have seen in Section 9.5.4 (Fig. 9.18), stimulation with UV and visible light induces interconversion between the three states SP, ME, and MEH + controlling the uptake and release of H +. When the two-state molecular switch and the three-state molecular switch are combined in solution, photoregulation of the concentration of H + can be exploited to modulate the switching between the two states AZ and AZH +. The photo- generated base ME can deprotonate the acid AZH +, promoting the formation of AZ; on irradiation with visible light the acid MEH-- can protonate the base AZ inducing the formation of AZH--. The logic behavior of the two communicating molecular switches is summarized in the truth table shown in Fig. 9.21b. The two inputs are ultraviolet light (In) and visible light (In2), and the output is the absorption of AZH + at 556 nm (Out). It can be noticed that the output digit Out has only one value for the input strings 01, 10, and 11, whereas it can be either 0 or 1 for the input digit 00. It can, in fact, be seen that its value depends on the sequence of events leading to the O0 input string. More precisely, when the two inputs are O, the output signal is 0 if the sys- tem comes from the state 100, changing In from 1 to O, whereas the output signal is 1 if the system comes from the state 011, changing In2 from 1 to O. In other words, the system has a memory effect. The sequential logic circuit equivalent to the truth table is illustrated in Fig. 9.21c. In this circuit, the input data In and In2 are combined through NOT, OR, and AND operators. The output of the AND gate, Out, is also an input of the OR gate and controls, together with In and In2, the signal transduction behavior. An alternative strategy for digital transmission between molecules is based on the communication of optical signals [72]. As illustrated in Fig. 9.22a, the investigated system consists of an optical network in which three optical signals travel from an excitation source to a detector after passing through two quartz cells. Cell A contains an equimolar acetonitrile solution of naphthalene (N), anthracene (An), and tetracene (T). Cell B contains an acetonitrile solution of the three-state molec- ular switch SP, MEH +, and ME shown in Fig. 9.18. The excitation source sends three monochromatic light beams to cell A, stimulating the emission of the three fluorophores. The light emitted in the direction perpendicular to the exciting beam reaches cell B. When the molecular switch is in state SP, naphthalene emission at 365 nm is absorbed and a low intensity output (Out = O) reaches the detector. The anthracene and tetracene emissions at 401 and 544 nm, respectively, pass unaffected and high-intensity outputs (Out2, Out3 = 1) reach the detector. When the molecular switch is in the MEH + state, the naphthalene and anthracene emis- sions are absorbed and only the tetracene emission reaches the detector (Out = O, Out2 = O, Out3 = 1). When the molecular switch is in the ME state, the emission of all three fluorophores is absorbed (Out = O, Out2 = O, Out3 = 0). The inter- conversion of the molecular switch between three states is induced by addressing cell B with UV light (In), visible light (In2), or H + (In3) inputs. Thus, three inde- pendent optical outputs (Out, Out2, Out3) can be modulated by stimulating the molecular switch with two optical inputs and one chemical input. The relationship between the three inputs and the three outputs is illustrated by the truth table shown in Fig. 9.22b. The equivalent logic circuit (Fig. 9.22c) shows that all three inputs control the anthracene channel Out2, but only In and In3 influence the tetracene channel Out3. Instead, the intensity of the naphthalene channel Out is always low and it is not affected by the three inputs [72]. The operating principle ofgating optical signals with optical signals might lead to the development of all-optical switches based on molecular components, although current systems are very far from any kind of application.

9. 7 Signal Communication Between Molecular Switches I 259 si In3 Out2 Out I In1 In2 b In1 In2 In3 Out1 Out2 Out3 (UV) (Vis) (H +) (365nm) a (401 nm) a (544nm) a 0 0 0 0 1 1 0 0 1 0 0 1 0 1 0 0 1 1 1 0 0 0 0 0 0 1 1 0 1 1 1 0 1 0 0 1 1 1 0 0 0 0 1 1 1 0 0 1 Transmittance C Out3 In1 In 2 In3 Fig. 9.22. Arrangement (a) �or the experiment on communication o�optical signals between the three-state molecular switch shown in Fig. 9.] $ and three fluorescent compounds (see text). Truth table (b) and combinational logic Out2 circuit (c) illustrating the signal transduction [72]. Note that Out is always low and is, therefore, neglected in the electronic representation.

260 I 9 Logic Gates In 1 In 2 I I I Deoxyribozyrne logic gate Catalyst S Fluorescent Non fluorescent I Out Fig. 9.23. Schematic representation of a deoxyribozyme-based logic gate. The two circles attached to substrate S

represent a fluorophore and a quencher units [4]. 9.8 Computation Based on Oligonucleotides In the last decade it has been demonstrated that biochemical methods based on oligonudeotides can be successfully employed for computational purposes [4, 73- 75]. Oligonudeotides and DNA have been used not only to implement logic oper- ations [4, 74], but also to solve hard computational problems [73, 75]. The potential of such methodology relies on the inherently high parallelism afforded by base- pairing reactions of DNA molecules. A detailed discussion of these complex sys- tems is available elsewhere [73-75]. A rational, modular approach for the construction of oligonucleotide-based logic gates has been devised very recently [4]. The system (Fig. 9.23) comprises: � two input oligonucleotides, In and In2, � an oligonucleotide substrate, S, labeled at its ends with a fiuorophore and a quencher, � a specifically designed deoxyribozyme molecule, which performs the logic oper- ation. The deoxyribozyme species contains a catalytic region that can deave S, allosteri- cally coupled with controlling elements capable of recognizing input oligonudeo- tides In and In2, such that the catalytic activity of the deoxyribozyme can be pro- moted or inhibited by binding of In and/or In2. When the correct set(s) of inputs is supplied, the catalytic activity of the deoxyribozyme is switched on, thereby cut- ting S into two fragments, one of which - the fluorophore-labeled fragment - constitutes the output (Out) of the gate. Consequently, the emission of the fluo- rophore, which was initially quenched in S by energy transfer to the attached quencher, increases as a result of separation of the fluorophore from the quencher.

9. 9 Molecule-based Electronic Circuits I 261 By appropriate combination of the controlling elements with the catalytic region, deox'yribozyme logic gates could be obtained that can perform one-input YES and NOT unctions and two-input AND and XOR operations [4]. Both the inputs and the output of this type of logic gate are o]igonuc]eotides, and detection of the state of the gate can be achieved by measuring the fluorescence intensity. 9.9 Molecule-based Electronic Circuits A completely different approach to molecular logic is that based on the use of molecules as wires and diodes to construct miniaturized electric circuits that would be much smaller than the corresponding micron-scale digital logic circuits fab- ricated on conventional solid-state semiconductor computer chips [62, 76]. As mentioned in Chapters 3, 4, 15, and 16, many investigations have been performed on the electrical conductivity and electrical switching properties of molecules and supramolecular systems

[77]. A schematic diagram for an AND logic gate based on diodes, and its molecular implementation, are shown in Fig. 9.24 [62]. Such a A B O () C=N /CH3 .s/=X _ SH � C=N Fig. 9.24. Electronic circuit scheme (a) and molecular implementation (b) of a diode-diode AND logic gate [62].

gate would measure only approximately 3 nm x 4 rim, an area one million times smaller than the corresponding logic element fabricated on a semiconductor chip using transistor-based circuits. OR and XOR gates and a half adder have also been designed. Much remains to be learned about the mechanisms of conductance of molecular wires and switches, however, and about the means of manipulating, bonding, and ordering these in extended circuit-like structures. If this approach is successful it will be possible to construct ultrahigh-density molecular circuitry that would have great impact in computer science (a Pentlure on a pinhead) [62]. It can be noted that the AND molecular-level logic gates shown in Figures 9.8 and 9.24 are completely different, not only because of the chemical structures of the molecules on which they are based, but also because of the chemical environ- ments (solution and solid state, respectively) and the input and output signals. They are, in fact, different philosophically - whereas the AND gate of Fig. 9.24 is a device for solid-state electronics, that of Fig. 9.8 and, more generally, most of the systems described in this chapter, work on chemical principles that are more similar to those controlling information transfer in living organisms. The approach to molecular-scale logic shown in Fig. 9.24, in which molecules are used as simple circuit components, has the potential advantage of being strictly related to the paradigms of current microelectronics technology [78]. On the other hand, the "chemical" approach to molecular logic gives the opportunity of implementing even complex logic operations with one molecule or supramolecular species. It is difficult, at present, to predict which of these two strategies will have the greater technological impact. These and other questions about the advent of molecular computers (e.g. serial or parallel architectures, solid-state or "wet") are one of the big challenges of nanotechnology. 9.10 Conclusions Most of the logic gates described in this chapter are based on simple chemical compounds and well documented chemical, electrochemical, photochemical, and photophysical processes occurring in solution, and the methods used to obtain the illustrated results rely on the simultaneous stimulation of large numbers of mole- cules. From this viewpoint, one could argue that we have simply illustrated some types of chemical reactions. We have tried to stress, however, the novel conceptual interpretation of the observed processes. We believe that research in this field is interesting for several reasons: � at least in principle, some of the described effects can be scaled down to single molecules; � synthetic multistate-multi functional systems might play the role of models to begin understanding the chemical basis of complex biological processes;

References 1263 � integration of molecular-level devices might be successfully achieved by inter- molecular communication based on chemical and light signals, thereby over- coming the difficulty of establishing electrical communication between different molecules; � digital communication through intermolecular light signals can be extended to the field of fuzzy logic; and, last, but not least � these studies introduce new concepts to the "old" field of chemistry and stimu- late the ingenuity of research workers engaged in the "bottom-up" approach to nanotechnology.

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267 Part III Molecular-scale Machines Molecular Devices and Machines - A Journe into the Nano World. V. Ba]zani, A. Credi, M. Venmri Copyright � 2003 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim ISBN: 3-527-30506-8

259 10 Basic Principles of' Molecular Machines 10.1 Introduction Movement is one of life's central attributes [1, 2]. Nature provides living systems with complex molecules called motor proteins which work inside a cell like ordinary machines built for everyday needs. These proteins ceaselessly perform duties such as transporting molecular materials, copying and translating the genetic code into proteins, communicating with other cells, adapting the cell shape to the external environment, and reorganizing its interior to enable complex processes such as cell division and locomotion. The same molecules can be collectively organized in such a way as to enable bacteria and spermatozoids to swim or pro- duce forces by musde contractions in more complex organisms, from insects, through humans, to whales, the largest living animals. Because of these biological engines we can walk, talk, and even think. At the root of existence lies movement at the molecular level [3]. The development of civilization has always been strictly related to the design and

construction of devices, from the wheel to the jet engine, capable of facilitating man movement and traveling. Nowadays the miniaturization race leads scientists to investigate the possibility of designing and constructing machines on the nano- meter scale, i.e. at the molecular level [4-6]. Natural molecular-level machines and motors are extremely complex systems; their structures and detailed working mechanisms have been elucidated in a few instances only and any attempt to con- struct systems of such complexity by use of the bottom-up molecular approach would be hopeless. What can be done, at present, in the field of molecular-levd machines is to construct simple prototypes consisting of a few molecular compo- nents capable of moving in a controllable way, and to investigate the challenging problems posed by interfacing artificial molecular machines with the macroscopic word, particularly as far as energy supply and information exchange are concerned. Certainly the study of motion at the molecular level is a fascinating topic from the viewpoint of basic research and a promising field for novel applications. In Part III of this book we try to illustrate the most important aspects of move- ment at the molecular level by discussion of several examples of natural and arti- ficial molecular machines. Because this topic is very broad, we cannot be exhaus- tive. In particular, the illustration of natural molecular machines will be limited to a few typical examples, with suggestions for further reading. Molecular Devices and Machines - A Journe into the Nano World. V. Balzani, A. Credi, M. Venturi Copyright � 2003 WILIY-VCH Verlag GmbH & Co. KGaA, Weinheim ISBN: 3-527-30506-8

2701 10 Basic Principles of Molecular Machines 10.2 The Concept of a Molecular Machine A macroscopic machine is any combination of mechanisms for utilizing, modify- ing, applying, or transmitting energy [7]. The movements of the mobile parts of a macroscopic machine can be described by Newtoffs equations of motion which determine the coordinates and speed of each part of the machine relative to a given origin. Going down to very small dimensions, questions arise [8-10] about whether the macroscopic concept of movement can be maintained because, as we have seen in Chapter 1, there are already problems in the quantum mechanical description of the shape of a molecule. The concept of movement, in fact, is not intuitive in quantum mechanical language, because the Schr6dinger equation of motion indicates correspondence between forces and quantum eigenstates only. These problems do not, however, seem to be relevant to nanoscale size molecular machines, because the structure and even the movement of single molecules with a diameter of approximately 1 nm can clearly be seen by use of modern techniques. A good example is that of single-molecule rotors, surrounded by like molecules that form a supramolecular bearing on a surface, studied by scanning tunneling microscopy (STM) in ultrahigh vacuum [11]. Such molecular rotors are propeller- shaped hexa-tert-butyldecacydene (HBD) molecules of l.S nm diameter (Fig. 10.1a), deposited on an atomically clean Cu(100) surface. For surface coverage of slightly less than one monolayer, a close-packed supramolecular layer with nano- meter-sized holes is formed by the molecules. As a result of robust intermolecular interactions the packed HBD molecules cannot rotate on the plane of the Cu(100) surface and they appear in the STM images as six-lobed objects (Fig. 10. lb). Some of these molecules can, however, dissociate from the supramolecular assembly to enter one of the nanometer-sized voids in which they are free to rotate. The rate of rotation is greater than the scan rate of imaging at ambient temperature and, as a result, the molecules in motion (Fig. 10.1c) look like toroidal objects. Interestingly, a single rotating molecule can be translated, with the aid of the STM tip, to a position where it is immobilized by the surrounding molecular layer. It should be noticed that, although this system represents an impressive example of real-space observation of molecular motion, it cannot be considered a molecular machine because thermal (fluctuation) energy cannot be used to do work (ide infra). Supported by experiments of this kind and, even more so, by the existence of a wealth of nanometer-scale natural machines [1, 12-14], it seems reasonable to extend the macroscopic concept of artificial machines to the molecular level [15- 17]. Caution, however, must be exercised because molecular machines, particularly natural ones, must operate at energies only marginally higher than that of the thermal bath and hence can be subjected to large fluctuations (Section 10.3.1). Molecular-level machines operate as a result of nuclear movements caused by chemical reactions. Any kind of chemical reaction involves, of course, some nuclear displacement. The term "molecular machine",

Fig. 10.1. (a) Molecular structure ofhexa-tert- butyldecacyclene (HBD); (b) and (c): SIM images of HBD molecules on an atomically clean Cu(100) surface [11]. Notice that in (c) for a molecule in the center of the picture the six lobes are not well defined and the molecule looks like a toroidal object. Reproduced, with permission, from Reft [11].

however, is used only for chemical systems performing reactions that can cause motions of large amplitude, leading to real translocation of some component pats of the system. As we will see in subsequent chapters, particularly interesting nuclear motions, from the view- point of artificial molecular machines, are those related to: � isomerization reactions involving -N=N-, -C=N-, and -C=C- double bonds in covalent supramolecular structures; � acid-base or redox reactions causing making or breaking of intermolecular bonds (including hydrogen bonds); � metal-ligand reactions causing the formation or disruption of coordination bonds. Molecular-level machines must contain a motor, which in principle consists of a mobile and a stationary part. An external operator should be able, by means of a given input, to induce the displacement of the movable component from the sta- tionary one. When the system is investigated in solution, in which both compo- nents are in motion, the bulkiest is considered motionless and the other is said to move relative to it. In addition to a motor, macroscopic machines contain a great variety of auxiliary components such as fasteners, bearings, drive shafts, gears, brakes, rotors, etc. The concepts of machine components can also be extended to the molecular scale. For example, the role of molecular-level fasteners can be played by covalent bonds linking distinct subunits of the system, or by strong intermolecular interactions such as those originating from multiple hydrogen bonds; star-shaped molecules can play the role of gears; steric crowding caused by a substituent placed in a selected position of a moving subunit can play the role of a brake. Such auxiliary components will be dealt with in Chapter 11. Like macroscopic machines, molecular-level machines are characterized by: � the kind of energy supplied to make them work; � the kind of movement performed by their components; � the manner in which their operation can be controlled and monitored;

� the possibility of repeating the operation at will; � the time scale needed to complete a cycle of operation; � the function performed. Each of these features will be discussed briefly. 10.3 Energy Supply Under equilibrium conditions, Brownian motion arising from thermal energy cannot be exploited to drive a motor, even if anisotropy features are embedded in the system [18, 19]. Such a result would in fact violate the second law of thermo- dynamics (work cannot be extracted from background noise) and the principle of microscopic reversibility (the rate of passage across a free energy surface between isoenergetic states must be equal in both directions). To make a molecular machine work, energy must be supplied to its motor. By following an original model proposed by Feynman for a mechanical "ratchet and pawl" engine [20], it has been shown [21-23] that under BrownJan motion condi- tions fluctuations brought about by an energy-releasing process can be used to perform chemical or mechanical work by an energy-requiring process. The most obvious way of supplying energy to a chemical system is by using some kind of fuel capable of causing a chemical reaction. There are, however, alternative, more convenient, ways of powering artificial molecular machines. 10.3.1 Chemical Energy In his famous address "There is Plenty of Room at the Bottom" to the American Physical Society R.P. Feynman discussed the possibility of constructing molecular- level machines and observed [24]: "An internal combustion engine of molecular size is impossible. Other chemical reactions, liberating energy when cold, can be used instead". This is exactly what happens in our body, in which chemical energy, ultimately derived from food and oxygen, is used in a long series of slightly exergonic reac- tions to power the biological machines that sustain life. Theoretical discussions on natural molecular motors can be found elsewhere [3, 14, 21, 22]. We will only consider, in simple terms [21, 22], what happens in plants, where energy is supplied by degradation of adenosine triphosphate (ATP). (A dis- cussion of the ATP synthase molecular motor is given in Section 13.2). The energy (approximately 12 leT) is stored in a phosphate bond and it is released when this bond is broken to form adenosine diphosphate (ADP) and inorganic phosphate (Pi). Natural motors continuously "break" ATP molecules in a never ending cycle, somewhat like a machine gun "breaking" bullets [21]. If we indicate the motor by M, we can say that first ATP is bound to the motor, MATP; ATP is then hydro- lyzed to give MADPPi; the phosphate is then released, to give MADP, and,

10.3 Energy Supply [273 finally, ADP is also released, so we return to the initial state, M. Although the chemical reactions are reversible, the cycle goes one way because the quotient of the rate of the forward reaction over the rate of the back reaction equals the Gibbs free energy gained in the reaction (12 kT) divided by the thermal energy (kT). The reaction proceeds because the photosynthetic process (Section 6.2) makes use of the solar energy flux to supply fresh new ATP, while all the used ADP and Pi is removed. The chemical cycle loops one way as a direct consequence of far-from equilibrium concentrations of the reactants involved; it loops in the direction in which the reaction proceeds towards equilibrium [22]. The natural motor can thus be compared with a ratchet that eats nonequilibrium fluctuations and walks. The nonequilibrium fluctuations are generated by the chemical cycle that eats chemical energy. The molecular machine can be viewed as a BrownJan version of an internal combustion engine which burns one molecule of fuel at a time [22]. Molecular motor operation has recently been described as biased diffusion on a potential energy surface defined by the interactions of the motor with its track and its fuel [14]. In the same way, if an artificial molecular-level machine must work by input of chemical energy, it will need addition of fresh reactants ("fuel") at any step of its working cycle, with the concomitant formation of waste products. It should be noticed that even cycling between two forms of a molecular-level system under the action of chemical inputs implies formation of waste products. For example, if the forward reaction is caused by an acid input, successive addition of a base will return the system to its original form, but the acid-base reaction generates waste products. Accumulation of waste products will inevitably compromise the opera- tion of the machine, unless they are removed from the system, as happens both in natural machines and in macroscopic internal combustion engines. The need to remove waste products introduces noticeable limitations in the design and construction of artificial molecular-level machines based on "chemical fuel" inputs. As we will see later, all proposed artificial machines operating by use of chemical energy become increasingly less efficient on increasing the number of cycles, and finally stop working. 10.3.2 Light Energy In green plants the energy needed to sustain the machinery of life is provided by sunlight [25]; in general, light energy is not used as such to produce mechani- cal movements, but it is used to produce a chemical fuel, namely ATP, suitable for feeding natural molecular machines. Light energy, however, can directly cause photochemical reactions involving large nudear movements. A simple example is a photoinduced isomerization from the lower energy trans to the higher energy cis form of a molecule containing -C=C- or -N=N- double bonds; this is followed by a spontaneous or light-induced back reaction [26, 27]. Such photoisomeriza- tion reactions have indeed been used to make molecular machines driven by light energy inputs [28]. In supramolecular species photoinduced electron-transfer

2741 10 Basic Principles of Molecular Machines reactions can often cause large displacement of molecular components [29]. Indeed, working with suitable systems, an endless sequence of cyclic molecular- level movements can in principle be performed making use of light-energy inputs without generating waste products. Mechanical work cannot, however, be gen- erated unless anisotropy features are embedded in the system [30]. Compared with chemical energy inputs, photochemical energy inputs have other advantages, besides the fundamental one of not generating waste products: � light can be switched on and off easily and rapidly; � lasers provide the opportunity of working in a very small space and very short time domains; � photons, besides supplying the energy needed to make a machine work, can also be useful to "read" the state of the system and thus to control and monitor the operation of the machine. 10.3.3 Electrochemical Energy Man has invented a great variety of macroscopic machines powered by electrical energy. By analogy, one can wonder whether it is possible to use electrical energy also in molecular machines. If we consider molecular machines operating via chemical reactions in solution, the answer is "yes" because electrical potential can be used to cause redox reactions involving large structural changes in supra- molecular systems [31, 32]. By working on a reversible redox couple it is possible to fuel the forward reaction and, reversing the potential, to return to the reactant, i.e. to cause a switching process without formation of waste products [33]. As for input of light energy, such reversible reactions cannot generate mechanical work unless anisotropy features are embedded in the system [30]. The use of electrochemical energy inputs in the place of chemical redox inputs has the advantage that it can be switched on and off easily and rapidly. Electrochemical techniques can, further- more, also be a useful means of monitoring the operation of the machine, and electrodes are one of the best ways of interfacing molecular-level systems with the macroscopic world. 10.4 Other Requirements 10.4.1 Types of Motion The movements performed by the component parts of artificial molecular-level machines can be of a variety of types. For practical applications, the most impor- tant are linear movements (e.g. of a ring along a wire) [6, 34], rotary motions (e.g. of subunits around a covalent bond) [35], changes in molecular structure (e.g. al- losteric processes) [36], assembly and disassembly (e.g. of host-guest species) [37],

10.4 Other Requirements I 275 translocations of components (e.g. of metal ions) [38], and contractions and exten- sions (e.g. of artificial "muscles") [39]. Several examples of these kinds of move- ments will be illustrated in Chapters 12-16. 10.4.2 Control and Monitoring To enable control and monitoring of the operation of a machine, changes in the positions of the moving components should cause readable changes in properties of the system. In this regard, any kind of chemical or physical technique can be useful. Most frequently control of the state of the system is performed by a spec- troscopic method (in particular, NMR, UV-visible absorption, luminescence) [6, 16, 34-37]. For systems based on donor-acceptor interactions, electrochemistry can profitably be used [6, 16, 31, 32, 34, 37-39]. Information on rate constants can be obtained by conventional kinetic methods for slow processes, by electrochemistry and stopped flow techniques for relatively rapid processes, and by flash spectroscopy (on different time scales) for very fast processes. 10.4.3 Reset Because a machine must work by repeating cydes, reset is an important require- ment. This means that any chemical reaction related to the movements performed by the component parts must be reversible. Although no chemical reaction is fully reversible, this requirement is reasonably well met by many proton-transfer (acid- base) and electron-transfer (redox) reactions, by photoinduced isomerization reactions (particularly, those involving -N=N- double bonds), and by some metal- ligand coordination reactions. 10.4.4 Time Scale The operation time scale of a molecular machine can range from less than pico- seconds to days, depending on the nature of the reactions involved. Electron- transfer, proton-transfer, and photoisomerization reactions can be very fast, but complex movements of component parts, on which the function of the machine is based, can be much slower because of both mechanical and chemical friction [40, 41]. 10.4.5 Functions The functions that can be performed by exploiting the movements of the compo- nent parts in artificial molecular-level machines are various and, to a large extent,

10 Basic Principles of Molecular Machines still unpredictable. As we will see in Chapters 12-16, they might be related not only to mechanical-like aspects (e.g. transportation of a cargo through a mem- brane), but also to information processing (e.g. logic gates). References 1 Science, 2000, 288(5463), Spedal issue (Eds.: L. CHONO, E. CULOTTA, A. SUDOEN) on Movement: Molecular to Robotic. 2 For autonomous movements in inanimate systems, see: R.F. ISMAGILOV, A. SCHWARTZ, N. BOWDEI'I, G.M. WHItESIDES, Artget. Chem. Int. Ed., 2002, 41,652, and references therein. 3 For a recent, interesting discussion on molecular motors, see: E. FRE�, ChemPhysChem, 2002, 3, 270. 4 H. KUH, H.-D. F6RStERLI6, Principles of Physical Chemistry: Understanding Molecules, Molecular Assemblies, Supramolecular

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11 Spontaneous Mechanical-like Motions 11.1 Introduction The most important part of a macroscopic machine is, of course, a motor. Without a motor, i.e. a device that supplies motive power under the action of external inputs, a machine cannot operate. In addition to a motor, macroscopic machines contain a great variety of auxiliary components that might be involved in mechanical motion, but do not produce it. Before examining molecular-scale machines, it is interesting to make a short survey of molecular and supramolecular compounds that exhibit spontaneous mechanical-like movements under the action of thermal energy. 11.2 Rotors The direct observation of a single

molecular rotor [1] has already been described in Section 10.2. Spontaneous rotation of their component parts is observed for many molecules and supramolecular species. Free rotation around single bonds occurs in all chemical compounds unless it is prevented by steric crowding. Rotation also occurs in metal complexes such as ferrocene. Particularly interesting rotors are the metal bis-(porphyrinate) double-decker compounds [2-6]. Two examples of such compounds are shown in Fig. 11.1. Viewed from the top of a porphyrin ring such double-decker compounds can be regarded as two overlapped wheels rotating around a molecular axle. The speed of rotation is rapid, unless the meso positions have particularly bulky substituents. For compound la the rate constant for rota- tion is 63 s - at 273 K [3]. Compound lb, which bears a flexible oligoether strap between the two porphyrin ligands, does not undergo complete rotation and can therefore be regarded as a molecular oscillator [4]. As we will see in Section 12.2, systems of this kind can be designed to achieve a positive allosteric effect [6] that can, mechanically, be regarded as a "braking" effect. Other examples of rotors have been reported [7]. 113 Cogwheels By synthetic design it is possible to obtain propeller-shaped molecules in which the motions of two or more internal rotors (blades) may be so strongly coupled that

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la 11.4 Gears 1:279 %,0 lb Fig. 11.1. Cerium bis(5,15-diarylporphyrinate) double-decker complexes which behave as a molecular rotor (la) [3] and as a molecular oscillator (lb) [4]. correlated rotation becomes energetically preferred over the independent rotation of the individual groups. For example [8], the diarylacetic acid derivative 2 (Fig. 11.2a) incorporates two identical aryl rings linked to the same atom. Rotation of one ring in one direction around the single bond linking it to the "focal" methine carbon atom forces the other ring to rotate in the opposite direction. Thus, when one ring rotates clockwise, the other must rotate antidockwise and vice versa. The mechanism of this coupled conformational motion, involving concerted dis- rotation, has been termed "cogwheeling" [9] because of the formal analogy be- tween the pair of chemical rotors and their mechanical counterpart, a pair of cog- wheels. In appropriately structured molecules this phenomenon can result in the formation of stereoisomers (called "phase isomers") [10] that can be separated by substantial energy barriers; the diastereomeric triarylmethanes, for example, are stable at room temperature and their interconversion (slippage) requires 30.5 kcal mol - [11]. Many two- and three-bladed molecular propellers have been investigated [8-12]. A computer simulation of the interconversion of the energy of a gas flow and the rotational energy of a molecular-sized propeller [13] and a dynamic study of a molecular dipolar rotor in a rotating electric field [14] have also been reported. 11.4 Gears Further elaboration of the propeller concept has led to the design of systems in which the rotors are tightly intermeshed so that correlated rotation is rendered more likely and the system bears an obvious resemblance to bevel gears. Triptycene, a rigid molecular unit with three blades, each comprising a benzene ring, is a molecular mimic of a gearing element and has therefore been used as a building block to obtain molecular gears [11, 15-18]. For example, molecular gear 3 (Fig. 11.2b) incorporates [15c] two 9-triptycyl ring systems bridged by a methylene group. The aryl rings of the two 9-triptycyl ring systems interdigitate in a manner clearly reminiscent of the notches of a pair of meshed gears. As a result, the rotations of the two 9-triptycyl ring systems about the single bonds linking them to the

H3C 3 2 b H3C H3 Fig. 11.2. (a) A macroscopic and a molecular [$] propeller-shaped entity; (b) a macroscopic and a molecular [15c] gear; (c) a macroscopic and a molecular [18] gear train; (d) a macroscopic and a molecular [19] bevel gear. "focal" methylene group are coupled, so that when one 9-triptycyl ring system rotates dockwise, the other rotates antidockwise and vice versa. Two diastereomers of 3 can be isolated at ambient temperature, showing that gear slippage is slow on the laboratory timescale. The smooth cogwheeling of molecular gears is disrupted by methyl groups in the 1-position of the two triptycyl units (a molecular "monkey wrendY') [11]. In the course of gearing a benzene ring bearing a 1-methyl group is

forced into the notch between the two arene rings in the other rotor. Accommodation of this group in an already overcrowded space substantially increases the steric strain of the molecule and profoundly affects the gearing behavior. More complex triptycene molecular gears have also been synthesized. Molecular gear train 4 (Fig. 11.2c), consisting of two labeled triptycenes connected by an additional triptycene unit, has been constructed [18]. The meso and dl isomers of this doubly geared molecule were separated and identified. On the basis of these results it seems possible that in large molecules information can be transferred from one end to the other via cooperativity of the torsional motions of the chain. It should be noted that in a gear train the motion of the two terminal gears, which in a machine would constitute the interface of the motor with the function to be per- formed, is disrotatory if the number of gears is even, and conrotatory if the num- ber is odd. In metallocene compounds, rotation of the organic rings about the metal can be regarded as analogous with rotation about a low-friction ball-bearing. Such a structure has been used to construct the triptycene-based molecular bevel gear 5 (Fig. 11.2d) in which an acetylene-substituted triptycene is linked to a four-toothed tetraphenyl cydobutadiene containing cobaltocene [19]. NMR spectroscopic data show that rotation about the metal and about the phenylbutadiene bonds is rapid at 203 K, suggesting a correlated gearing mechanism between the two intermesh- ing cogs of the four and three toothed metallocene gear, as expected on the basis of a space filling model. Correlated rotation in other organometallic compounds has been investigated [20] and simpler "two-toothed" molecular gears have also been reported [21]. 11.5 Paddle Wheels Triptycene has also been used to construct paddle-wheel-like systems [17, 22] (sometimes called paddlanes [23]), e.g. those shown in Fig. 11.3 [17]. In com- pounds containing only one triptycene unit rotation of the triptycene relative to the ring ("rope skipping") can occur when the ring is sufficiently large as in 6, but it does not occur if the ring is small (e.g. in 7). Metal ion complexation by the crown ether of 6 slows the rotation only slightly, presumably because of the poor binding properties of the triptycenocrown ether [17]. In the bis-triptycenocrown ethers 8 and 9 the triptycene gears undergo rapid rotation on the NMR timescale at temperatures above 333 K, whereas resolution into sets of individual NMR signals occurs at low temperature (<233 K). 11.6 Turnstiles Macrobicydic molecules 10-12 (Fig. 11.4) comprising a hexa(phenylacetylene) macrocyclic frame with a diethynylarene bridge constitute another interesting dass of chemical rotor [24]. The central p-phenylene ring of 10 can rotate about its axis.

2821 Spontaneous Mechanical-like Motions 6 X= (CH2CH2)20 1 7 X = CH2CH 2 Fig. 11.3. 8 X=O] X = OCH2CH20 Macroscopic and molecular [17] paddle wheels. This conformational motion is reminiscent of the movement of the spindle of a turnstile [25] and, as a result, this compound has been called a molecular turn- stile. The motion corresponds to a double-well potential energy surface so that the system has conformational bistability. The dynamic process associated with the molecular turnstile is affected considerably by the size of the R groups attached to the central p-phenylene ring. Indeed, two degenerate conformations of 11 can be identified by low-temperature H NMR spectroscopy. At ambient temperature, however, rotation about the axis of the central ring of 11 is fast on the H NMR timescale and a free energy barrier of 13.4 kcal mol - is associated with this dynamic process. In contrast, this rotation does not occur in 12, even when a solution of this compound is heated to high temperatures. In this instance the substituents attached to the central p-phenylene ring are far too bulky to be able to pass through the cavities of the macrobicyclic ring system. 11.7 Brakes Spontaneous (thermally induced) mechanical-like movements on the molecular scale can be controlled not only by changing the temperature, but also by suitable modification of the molecular structure and by use of external inputs. Mechanically the motion-controlling systems can be viewed as brakes. An example of a chemically-controllable three-toothed molecular gear [26] is given by compound 13

Fig. Macroscopic and molecular [24] turnstiles. 11.8 Ratchets I 283 10 R=H 11 R = --XOCH 3 in Fig. 11.5. Perhaps it would have been more appropriate to discuss this system in the next chapter, because it works under the action of an external input. We have chosen to describe it here, however, because of its dose relation with the ratchets illustrated in the next section. Compound 13 incorporates a 9-triptycyl ring system attached to a 2,2'-bipyridine unit. In this compound, the brake is activated by a change in the conformation of the bipyridine unit (noncoplanar to coplanar) on complexation with a metal ion. The rotation about the single bond connecting the triptycyl and bipyridine units is rapid in acetone at 303 K on the H NMR time- scale. As a result, only four sets of resonances are observed in the H NMR spec- trum for the aromatic protons of the 9-triptycyl ring system. To slow down this dynamic process the solution must be cooled to 193 K. Under these conditions the twelve aromatic protons of the 9-triptycyl unit became nonequivalent. On addition of Hg(II) trifiuoroacetate to an acetone solution of 13 the metal ion is coordinated by the 2,2'-bipyridine ligand yielding [13-Hg] 2+ (Fig. 11.5). As a result the conformation of the unit is locked and the H NMR spectra (303 K) recorded before and after addition of the metal ion are markedly different. On chelation the singlet associated with the protons of the methoxy group attached to the disubstituted pyridine ring is shifted downfield by +2.02 ppm and the resonances of the aro- matic protons of the 9-triptycyl ring system broaden significantly. At 243 K rotation about the single bond connecting the 9-triptycyl ring system to the 2,2'-bipyridine unit is already slow enough to render some of the aromatic protons of the 9- triptycyl ring system nonequivalent. These observations indicate that the locked conformation of the 2,2'-bipyridine unit brakes the rotation of the 9-triptycyl ring system. The molecular brake can be released by adding EDTA to the acetone solu- tion of [13-Hg] 2+. Indeed, removal of the coordinated metal unlocks the confor- mation of the 2,2'-bipyridine unit, disengaging the brake. Several other examples of brakes will be reported in Chapter 13. 11.8 Ratchets Ratchets are devices that allow motion in one direction only; in its simplest form a ratchet contains three components (Fig. 11.6a) - a toothed ratchet wheel, a pawl

284 I 11 Spontaneous Mechanical-like Motions Release H3 + EDTA / .CH3 13 [13- Hg] 2+ Fi�, 11,$, Macroscopic and molecular [26] brakes, that prevents unintended rotation of the ratchet wheel, and a spring that holds the pawl in place. To obtain a molecular ratchet [27] the 2,2'-bipyridine unit of the previously described brake [26] was replaced by helicenes of appropriate lengths (Fig. 11.6a). The helicene unit of compounds 14 and 15 has a helical conformation. Rotation of the triptycene forces the helicene increasingly further out of planarity until an energy maximum is reached. Molecular modeling calculations (AM1) on compound 14 yielded an asymmetric peak (Fig. 11.6b) for the rotational energy around the triptycene-helicene bond. Because of the chiral helical structure, as the triptycene rotates clockwise, resistance builds up steadily, while for antidockwise rotation the barrier rises much more steeply. Although the situation bears a dose resemblance to that in a macroscopic ratchet, NMR results have shown that the triptycene in 14 rotates equally in both directions. This result, which might appear counterintuitive, is the only one to be expected on the basis of the principle of microscopic reversibility, which states that the rates of passage across a free energy surface between isoenergetic states must be equal in both directions [28]. If this were not true, the second law of thermodynamics would be violated. 11.9 Gyroscanes and Gyroscopes Rotational movements of molecules hosted in hemicarcerands have been exten- sively investigated [29], also because of their relevance to catalytic processes [30]. Novel, molecular-level rotation movements have recently been observed in other suitably designed systems

[31]. Cucurbiturils are macrocyclic compounds capable of hosting suitable guests in their cavity [32]. A supramolecular species in which a smaller macrocycle (cucurbit[S]uril) is located inside a larger macrocyde (cucurbit[10]uril) has been isolated and characterized [33]. On crystallization from concentrated hydrochloric

a R 14 R=H 15 R = CH 3 1 I. 9 Gyroscanes and Gyroscopes I 285 24O 230 22O � � � � � � � � � 0 30 60 90 120 Dihedral angle (degrees) Fig. 11.6. (a) Macroscopic and molecular [27] ratchets; (b) calculated (AM]) energetics for rotation around the triptycene/ helicene bond in compound 14; clockwise rotation of the triptycene corresponds to leA-to-right progression on the x axis [27]. acid the inner cavities of these complexes are filled with a chloride ion, while water molecules or H30 + ions cover the two portals of the inner cucurbituril and bridge the rims of the two macrocycles by hydrogen bonding. The plane of the inner ring is tilted significantly (64 �) against that of the outer macrocyde. In solution both macrocyclic rings rotate freely relative to each other, suggesting the name gyro- scane for this new dass of supramolecular system. Conceptually different systems are the molecular compasses and gyroscopes [34], which consist of a central aromatic group coupled to two axially positioned ethynyltriptycenes (Fig. 11.7). In such systems, which are somewhat related to turnstiles, the central aromatic unit is sterically shielded from contact with other molecules in the environment by a triply bridged framework, and thus it should rotate freely. If the rotating moiety carries polar or polarizable substituents, it can respond to external fields. The aim of these studies is to explore new concepts for the fabrication of photonics materials based on dipolaf units that can reorient rap- idly under the influence of electric, magnetic, and optical stimuli. Semiempirical calculations with the AM1 method indicate that rotation about triptycene-alkyne

2861 Spontaneous Mechanical-like Motions Fig. 11.7. Formula of a 1,4-bis[(9-triptycyl)ethynyl]-2,3- difluorobenzene and schematic illustration of its shape and functional similarity with a macroscopic gyroscope [34]. and aryl-alkyne single bonds should be essentially frictionless in the gas phase. Rapid rotation in solution is apparent from NMR spectra, whereas in the solid state rotation is prevented by interdigitation of adjacent molecules and by dose contact with the solvent of crystallization. This drawback can probably be avoided by placing bulky substituents in selected positions. References J.K.

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,881 12 Movements Related to Opening, Closing, and Translocation Functions 12.1 Introduction In biological systems, molecular functions such as recognition, transport, cataly- sis, signal transfer, etc., are precisely regulated by structural changes caused by exchange of information at the molecular level. Structural changes are at the basis of mechanisms such as allostery, cooperativity, feedback, etc. [1, 2]. Information transfer and modulation are performed by exchange of chemical species (e.g. pro- tons, metal ions) or as a result of external energy input (e.g. photons) that usually involve more or less extensive conformational changes. In living organisms con- formational changes are often very complicated. It has, for example, long been known that vision is the result of conformational changes triggered by photoexci- tation of rhodopsin, but, despite great progress recently made in the elucidation of the structure [3] and function [4, 5] of this transmembrane protein, the number of unanswered questions and unsolved problems concerning the mechanism of con- version of absorbed light into biological signals is still increasing [6]. In the last ten years mechanical experiments with single molecules have become possible and fundamental intramolecular and intermolecular interactions have been investigated. Several techniques differing in force and dynamic range are now available; the most prominent of these are magnetic beads [7], optical tweezers [8], and atomic force microscopy (AFM) [9-14]. Molecular dynamics simulations of biomolecules have also undergone explosive development [15]. In this chapter we will illustrate some examples of conformational changes in natural and artificial systems, mostly connected with opening, closing, and trans- location functions. 12.2 AIlosteric Movements 12.2.1 AIlosteric Enzymes In living organisms, if every enzyme were active at all times a mad rush of chem- ical change would result. Enzymes that build nudeotides or amino acids would be Molecular Devices and Machines -A Journey into the Nano World. V. Balzani, A. Credi, M. Venturi Copyright � 2003 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim ISBN: 3-527-30506-8

Active site 12.2 AIIostefi� Movements [289 b CTP Fig. 12.1. An allosteric enzyme: aspartate carbamoyltransferase [16, 17]. The catalytic and regulatory subunits are shown as white and shaded regions, respectively. (a) The active site is available; (b) cytidine triphosphate (CTP) binds to a regulatory domain, shutting ofTthe active site. active at the same time as those that digest them, resulting in a futile cyde of syn- thesis and destruction. To avoid this problem, key enzymes are carefully regulated. They are activated only when their products are needed, and shut down otherwise. A typical example is aspartate carbamoyltransferase (also known as aspartate transcarbamoylase or ATCase) [16, 17], an enzyme that in bacteria determines when thymine and cytosine will be made. Because of its remarkable changes in shape it is known as an allosteric enzyme (the term allosteric is derived from the Greek for "other shape"). The enzyme, as shown schematically in Fig. 12.1, is composed of six large catalytic subunits and six smaller regulatory subunits. The active site of the enzyme is located where two individual catalytic subunits touch, so the position of the two subunits relative to each other is critical. If the two sub- units are in tight contact, an amino acid from one extends into the active site of the other, blocking its action. If the two are pulled slightly apart, however, the active site is revealed, allowing molecules to enter and the reaction to be performed. This is the job of the regulatory subunits - they pull the central catalytic subunits apart, turning the enzyme on, or let them stick together, turning the entire com- plex off. When the proper raw materials are in plentiful supply, they bind to the active sites and force the molecule into the open, active shape. The regulatory

29o I 12 Movements Related to Opening, Closing, and Translocation Functions subunits, however, bind one of the final products of the enzyme chain, cytidine triphosphate (CTP). When there is plenty of CTP, therefore, it binds to a regulatory domain, triggering it to close the enzyme down, shutting each active site off. In conclusion, when raw materials are more plentiful, the enzyme is turned on; when there is enough of the ultimate product, the enzyme is turned off. The molecular- level mechanisms of these processes are very complicated and must involve strong amplification of the input signal [18]. In Nature the allosteric effect usually provides a mechanism by which the activ- ity of an enzyme can be regulated, and also a means of obtaining chemical feed- back, which is a necessary step towards achieving total control over molecular-scale chemical processes. Interesting examples of allosteric regulation of enzymes have recently appeared. It has, for instance, been shown that Zn 2+ ions can, by complexation, control the conformation, and thus the activity, of an HIV-1 protease inhibitor [19]. 12.2.2 Artificial Allosteric Systems The design of artificial allosteric systems [20-22] is of great significance not only for regulating the catalytic activity and complexation properties of artificial receptors, but also for controlling molecular-scale mechanical-like movements. One of the earliest examples of artificial chemically-induced conformational motion is that related to the construction of molecules such as the ditopic receptors I and 2 (Fig. 12.2a) [20, 23]. Such molecules are characterized by an active site, a remote site, and a conformational mechanism which transmits binding informa- tion from one site to the other. In I and 2, the 2,2'-bipyridine and crown ether binding sites, although separated and electronically insulated, cannot behave independently. Chelation of metals with the 2,2'-bipyridine unit forces the aromatic rings toward coplanarity and brings the groups in the 3- and 3'-positions of the bipyridyl close together. This binding restricts the conformational freedom of the crown ether and thereby alters its receptivity to metal ions. In compound 2, which contains a larger crown ether macrocycle, the capability of the macrocycle to coordinate Hg(CF3)2 in a pseudo- rotaxane-like structure is dramatically increased by coordination of Pd 2+ at the bipyridyl site (positive allosteric effect). Many other examples of artificial systems with positive allostery have been reported [24]. Examples of negative allosteric effects are also known. One interest- ing case [25] is that illustrated in Fig. 12.2b. Receptor 3 is based on the triamino- triazine scaffold, which has a donor-acceptor-donor hydrogen-bond surface well suited to act as a host for imide guests such as uracil. When 3 is exposed to Cu + the two bipyridine arms swing toward each other to coordinate the metal ion. This process forces the rotation of the exocyclic C-N bonds of the triazine, distorting the hydrogen-bonding surface. When the metal ion is extracted from the coordi- nation pocket the original hydrogen-bonding surface is reconstructed. More recently, this system has been modified to exploit the Cu(I)/Cu(II) coordination a b l n=l] 2 n=2 12.2 AIIostedc Movements [291 [3.Uracil] [3.Cu] + + Zn 2+ Fig. 12.2. (a) Ditopic receptors capable of an allosteric effect [23]; (b) negative allosteric effect in a ditopic receptor [25]; (c) control of the distance between two pyrenyl units by means of a chelation-induced conformational change [27]. [4.Zn]2+ 001 chemistry extensively used to cause motions in rotaxanes and catenanes (Chapters 15 and 16). A tridentate terpyridine ligand appended to the triazine ring gives the copper ion the possibility of choosing between a tetracoordinated bis-bipyridine (preferred by Cu +) or a pentacoordinated terpyridine-bipyridine (preferred by Cu 2+) coordination environment. As discussed above, the former does not have the hydrogen-bonding surface; the latter, however, does. The allosteric effect can therefore be switched off and on by electrochemical or chemical redox reactions [26]. The system shown in Fig. 12.2c is an interesting example of the control of fluorescence properties by means of a &elation-induced conformational change [27]. Compound 4 consists of two bipyridine and two pyrene units linked to a perhy- droanthracene moiety. The two pyrene units are dose together, giving rise to excimer emission on photoexcitation. On addition of Zn 2+ ions chelation by the two bipyridine receptor units causes an axial-to-equatorial change of the bipyridine substituents which, in turn, causes a triple ring flip of the perhydroanthracene system. This conformational switch transduces the signal to the effector site, where

,,21 12 Movements Related to Opening, Closing, and Translocation Functions ,CH2 H N. N (2) + Zn 2+ + [H3N(CH2)nNH3] 2+ n=4-9 H2C ,n [5' H3N(CH2)nNH3] 2+ [5 .Zn] 2+ CH2 I + Zn 2+ + [H3N(CH2)nNH3] 2+ n=4-9 Fig. 1:2.3. AIlosteric effects in compounds 5 and 6 [28]. H2C ,Zn (CH2)n N i_i'H [6 .Zn. H3N(CH2)nNH3] 4+ an equatorial-to-axial change of the pyrene substituents results in a change in the fluorescence (from excimer to monomer emission). Inspection of molecular models shows the signal is transduced over a receptor-effector distance of 2 nm. Positive and negative allosteric effects have been obtained by means of the dever design exemplified by compounds 5 and 6 (Fig. 12.3) [28], which consist of two crown ethers linked by heteroaromatic rings. The two crown ethers can interact cooperatively with a suitable alkyldiammonium ion, whereas the two pyr- azole rings can interact with a metal ion such as Zn 2+. Depending on the relative arrangement of the crown ethers relative to the pyrazole nitrogen atoms, the com- pounds afford negative (5) or positive (6) allosteric effects of the metal toward diammonium complexation. Particularly interesting is a recent report on a podand that has a dual response to external stimuli, with intramolecular chirality transfer. Coordination of Cu(I) by two bipyridine-type moieties of the podand causes distortion of the molecular structure with formation of a cyclic binding site for an alkali metal ion which can have a helical or nonhelical structure [29]. Coordination of Cu(I) is also a necessary condition for a double-calix[S]arene receptor to bind strongly with C70 [30]. Several other investigations have been performed on allosteric systems [31] and on conformational switching processes related to a variety of functions [32], including folding [33], sensing [34], and molecular beacon applications [35].

12.3 Tweezers and Harpoons 12.3 Tweezers and Harpoons [293 12.3.1 Tweezers Molecular tweezers were perhaps the first examples of molecular-level machines reported in the literature [36, 37]. A classical case is that shown in Fig. 12.4 [36]. In the trans configuration the azobenzene compound 7 has weak coordinating capacity for large cations. Excitation with light causes trans - cis isomerization [38, 39] yielding a supramolecular configuration suitable for enclosing large metal ions between the two crown ethers, with a strong increase in the coordination capacity. The trans form extracts Na + 5.6 times more efficiently than the cis form, whereas the cis form extracts K + 42.5 times more efficiently than the trans form. Such devices offer a means of controlling the rate of ion transport through membranes a b /, .N--Oo_ UV 6--'� o? e_o.? ....6---o- Fi�. 12.4. (a) A macroscopic tweezer; (b) a molecular-level phototweezer based on azobenzene [36].

12 Movements Related to Opening, Closing, and Translocation Functions [40]. Several years ago it was predicted [41] that this kind of photoinduced movement could be useful for the photocontrol of catalytic activity. Recently the coupling reaction of aminoadenosine and an adenosine active ester has indeed been shown to be catalyzed by suitably functionalized azobenzene derivatives [42]. Change in selectivity from K + to La 3+ has been observed on photoexcitation of a bis(spirobenzopyran) azacrown ether, as a result of the availability of a phenolate coordinating site in the merocyanine form of the photochromic units [43, 44]. Several other kinds of photoresponsive host molecule have been reported [45, 46]. Because all are thermally reversible, it is impossible to keep the guest hosted in the dark; most such systems also lose their performance on repeating cycles. Recently, however, new types of

photochromic compounds have been developed which undergo thermally irreversible photochromic reactions and have fatigue- resistant performance [47] (see also Section 7.2). By using the dithienylethene photochromic unit linked to crown ether moieties new phototweezers have been constructed (e.g. compound 8, Fig. 12.5 [48]) which have excellent properties for switching metal ion coordination. The concept of phototweezers has been extended to saccharides by use of diarylethene or azobenzene units linked to two boronic acids (Chapter 7, Fig. 7.3) [49]. The photoinduced trans-cis isomerization of azobenzene can also be exploited to induce intramolecular complexation in self-complementary molecules such as 9 + (Fig. 12.6) [50]. This compound incorporates a macrocyclic polyether head bridged by a photoactive azobenzene unit to a linear tail with a terminal ammonium group. In the trans isomer the ammonium recognition site is positioned away from the complementary macrocyclic head. On irradiation in o-dichlorobenzene, however, trans- cis isomerization occurs, bringing the ammonium recognition site into dose proximity with the crown ether head and enabling their intramolecular asso- \ F2/F2 / uv """ ""-0 _) Antiparallel conformation S S Parallel conformation Fig. 1:1.5. A dithienylethene-based molecular-level phototweezer [48].

4- NH3 UV vis, Fi�. 12.6. The photoinduced isomerization of the azobenzene unit of 9 + is accompanied by the motion of the cationic tail which can interact with its macrocyclic head only in the isomer [50]. 12.3 Tweezers and Harpoons [295 ciation. Thus, whereas the trans isomer of 9 + has strong affinity for metal cations, the binding capacity of the cis isomer toward metal cations is almost completely suppressed by the photoinduced self-complexation [50, 51]. Another kind of molecular-level tweezer has recently been reported [52]. The y4 conformer of a strapped chiroporphyrin free base with two 8-methylene chains linking two adjacent meso substituents has been found to undergo complete and reversible conversion to the yfiyfi complex on addition of Ni 2+. Very interesting synthetic receptors in the shape of a pair of tweezers or of a clip (e.g. 10-12 in Fig. 12.7) have been prepared [53]. Because their cavity has electron-donor properties, in non polar solvents these compounds give rise to charge-transfer (CT) host-guest species with a variety of electron acceptors, similar to what happens with the CT-based pseudorotaxanes discussed in Section 14.2.3. For example, on mixing 10 with tetracyanobenzene (TCB) in CHC13 solution, the fluorescence bands of 10

(&max = 344 nm) and TCB (&max = 332 nm) are quenched and a CT absorption band appears with &max = 417 nm. The association constant of the 1:1 complex was found to be 7.3 x 105 L mol-L On excitation at 417 nm the complex shows an emission band with &max = 570 nm, assigned to the CT excited state. Formation of the complex can also be followed by electrochemical measure- ments, and it has been shown that dissociation occurs when the TCB unit is re- duced [54]. 10 11 12 Fig. 12.7. Tweezers 10 and 11, and clip 12 [53].

2961 12 Movements Related to Opening, Closing, and Translocation Functions NC CN 4 _ Ar,., Ar OCH3 0 + Ar Ar OC O 15 2' I Ar = 3,5-di-t-buyphenyl I CH3 Fig. 12.8. The harpooning effe is observed for molecules 13, 14, and 152+ [56-59]. A tubeilike species made of four anthracene units with correlated pincer-like movements has been reported [55]. On suitable modification this molecular framework could also prove useful for studying cooperative effects. 12.3.2 Harpoons and Related Systems Somewhat related to tweezer-like movements are the conformational changes caused by electrostatic attraction forces generated by photoinduced electron trans- fer in dyads with semiflexible bridges, e.g. compound 13 in Fig. 12.8 [56]. Because the donor and the acceptor components are neutral, photoinduced electron trans- fer causes, at the two ends of the molecule, the formation of charges of opposite sign. As a consequence of the resulting electrostatic attraction, conformational distortion occurs (in competition with charge recombination) and the two ends of the molecule approach each other (harpooning effect). Crucial to the observation of this harpooning motion is that both the extended and folded charge-separated states have characteristic fluorescence. Conformational changes are also expected from calculations [57], and have been observed experimentally [58], for supposedly rigid donor-acceptor systems such as compound 14 (Fig. 12.8). Even for the syn, syn U-shaped isomer of the giant tetrad 152+ (Fig. 12.8), photoinduced electron- transfer and charge-recombination processes are expected to cause electrostatically- driven conformational changes [59]. Initially the uncharged porphyrin molecule lies dose to the methylviologen group, which has a double positive charge. After the porphyrin-to-viologen photoinduced electron-transfer process both end groups carry a single positive charge that opens the molecular jaws. Such changes of con- formation are expected to have marked influence on the interpretation of the observed electron-transfer rate constants [57-59].

Interestingly, another U-shaped porphyrin-based molecule has been reported to host C60 or C70 in its jaw-like trap [60].

12.4 Controlled Assembly and Disassembly of Host-Guest Systems I 297 H2 14+ //--X/Nx/--,N--Zn'.. JJ [16H2 .Zn] Fig. 2.9. 352 nm Light-induced processes in complex [16H2.Zn] 4+ [62]. Light excitation in suitably designed supramolecular species can cause mechan- ical movements related to excimer or exciplex formation. An interesting ex- ample is the so-called "photoinduced crown ethers" [61], which comprise linear oligooxyethylenes terminated at both ends with pyrenyl units. On excitation with UV light the pyrenyl units form an intramolecular excimer which stabilizes a folded conformation analogous to that of crown ethers. This structure exists for fractions of microseconds, i.e. for a period of time corresponding to the lifetime of the excimer. Another example is given by compound [16H2] 2+ [62], a phenanthro- line-based azacrown ether with a pendant anthracene unit (Fig. 12.9). In the ground state of the Zn(II) complex [16H2-Zn] 4+ there is no z-stacking between the anthracene and phenanthroline units; on excitation with light, however, an exciplex is formed; this implies substantial molecular rearrangement. Exciplex formation can also be switched on and off by pH changes. Similar behavior has been ob- served with compounds constructed by linking methylnaphthalene units at both ends of a polyamine chain [63]. This structure can lead to the formation of an excimer whose appearance, fluorescence intensity, and decay time are strongly dependent on the protonation state of the polyamine spacer. The use of these and related systems as fluorescence chemosensors has been reviewed [64]. 12.4 Controlled Assembly and Disassembly of Host-Guest Systems 12.4.1 Introduction Molecular stir-assembly, a concept central to Nature's forms and functions [65], is an important route towards the construction of artificial molecular-level machines [66-69]. The challenge for chemists engaged in this field resides in the "program- ming" [69, 70] of the system, i.e. in the design and synthesis of components which carry, within their structures, the pieces of information necessary not only for construction of the desired supramolecular architecture, but also for the perfor- mance of the required function. In systems based on self-assembly the machine- like function to be performed is often related to the occurrence of a reversible assembly-disassembly process. The system must therefore be programmed to

Self-assembly I ' _ or Fig. 1:2.10. Schematic representation of a self-assembly- induced-disassembly-reset process that can be used to design molecular-level devices [69]. be able not only to self-assemble under thermodynamic control (Process 1 in Fig. 12.10), but also to disassemble under the action of a suitable energy input (Process 2 in Fig. 12.10). Disassembly implies, of course, chemical transformation of one of the assembled partners. To repeat the self-assembly-induced-disassembly process at will (cyclic process), reset of the system is needed after induced disassembly (Process 3 in Fig. 12.10) [69]. For practical purposes, the state of the system must be well defined. This means that the self-assembly equilibrium (Fig. 12.10, Process 1) must be strongly dis- placed towards the assembled species. The interaction driving the assembly must, therefore, be relatively strong. The designing principles include: � choice of molecular components that can give rise to an intimate supramolecular structure, usually in the form of a host-guest system; � presence of complementary, strongly interacting (electron donor-electron acceptor, acid-base, etc.) units; � multipoint interactions; � choice of a suitable, weakly interacting solvent. Disassembly of a thermodynamically stable supramolecular structure requires the destruction of the interaction responsible for the association process. This can be achieved by means of an appropriate chemical reaction that transforms one of the assembled partners (Fig. 12.10, Process 2). For example, when the interaction responsible for complexation is donor-acceptor in nature, it can be destroyed by oxidation of the electron-donor unit or reduction of the electron-acceptor unit. When the association is based on hydrogen bonding involving an ammonium center, [N+-H --- O], it can easily be destroyed by addition of a base. Once again, disassembly must be complete to avoid loss of definition of the system. The reac- tion needed to cause disassembly can be promoted by chemical, photochemical, or electrochemical stimulation [66, 71].

12.4 Controlled Assembl) and Disossembl) of Host-Guest S)stems I 299 Reset of the system implies reassembly, which can occur only after the occur- rence of a chemical reaction opposite to that responsible for disassembly (Fig. 12.10, Process 3). For example, if disassembly was achieved by reduction of an electron-acceptor unit, oxidation of such a unit must be performed to restore the donor-acceptor interaction and achieve reassembly. In this section we will illustrate some examples of self-assembly-induced- disassembly-induced-reassembly processes in systems that can be viewed as sim- ple molecular-level machines. Similar systems, which are more interesting as switches or memories, rather than as machines, have already been discussed in Chapters 4 and 7. Finally, the peculiar case of host-guest systems with pseudo- rotaxane structure will be discussed in Chapter 14. Although the examples described refer to bulk solutions, it should be remarked that binding or folding energies at the single-molecule level can be investigated by atomic force microscopy (AFM) [9-14]. 12.4.2 Photoinduced Processes 12.4.2.1 Inclusion Complexes Formation of host-guest species can be accompanied by extensive rearrangement of the structure of the receptor, a phenomenon (induced fit) well known in natural [72] and artificial [73, 74] systems. Such rearrangements can often cause changes in the fluorescence of the host and/or guest and can thus be exploited for fluo- rescence sensing [34, 75, 76]. In other systems conformational changes may be induced by light excitation [45, 46]. When two macrocydic ligands are linked together by two (or more) pillars, cylindrical structures are obtained which are suitable for linear recognition or as ditopic coreceptors. The binding selectivity is governed not only by the size of the macrocyclic ligands, but also by the length of the pillars. Insertion of azobenzene- photoisomerizable components in the pillars yields "photoelastic" cylindrical structures the binding selectivity of which can be photocontrolled [40]. Compound 17 (Fig. 12.11a), for example, undergoes extensive rearrangement on photoexcita- tion and can be viewed as a photoswit&able molecular-level gate [77]. Other cylindrical macrotricyclic compounds consisting of two azamacrocyclic rings connected by two azobenzene pillars have recently been studied [78, 79]. At pH < 5.5 in the dark, compound 18 is present only as the trars, trars-18 species (Fig. 12.11b) [79] whereas at higher pH an increasing number of azobenzene units assume the cl, s form. trars - cl, s Photoisomerization and back cl, s - trars thermal isomerization occur, leading to photostationary state compositions that are pri- dependent. Interestingly, the fully protonated form trars, trars-[18H2] 42+ gives rise to a stable inclusion complex with [Co(CN)6] 3-. Cydodextrins (CD) and their derivatives are quite effective host species for a variety of guest molecules in aqueous solution [80]. As for crown ethers, their binding capacity might be controlled by photoinduced structural changes of a component of the supramolecular structure [81-83]. A dassical example is shown

a trans, trans-17 Fi�. 12.11. uv Vis, cis, cis- 17 (a) A molecular-level photocontrolled gate based on azobenzene photoisomerization [77]; (b) structural formula of macrotricyclic compound trans, trans-IS [79]. trans, trans-18 in Fig. 12.12 [84]. In aqueous solution, the azobenzene-capped fi-CD 19 does not bind 4,4'-bipyridine when the azobenzene group is in the trans form. On isomer- ization of the azobenzene unit from the trans to cis conformation, however, 4,4L bipyridine can be hosted. When the compound goes back to the trans isomer the guest compound is ejected from the CD cavity. Photocontrol can also be exerted on the guest component. For example, in aqueous solution, the trans form of p- (phenylazo)benzoate is bound more strongly than the cis isomer by fi-CD [85]. The different affinity has been ascribed to the fact that the stretched, thread-like struc- ture of the trans-azobenzene group fits the cavity of fi-CD better than the elbow- shaped cis isomer. This observation has been exploited to trigger the catalytic activity of fi-CD in ester hydrolysis, because the cydodextrin cavity can be made available to the substrate upon light-driven expulsion of the azobenzene guest. An extensive review of these processes has been published [81]. Photochemical control of a cavity has been achieved by introducing two uv + Vis, trans-19 Fi�. 12.12. Photoinduced inclusion of 4,4Lbipyridine inside the cavity of the azobenzene-capped fl-CD 19 [84].

anthracene units near the metal-binding site of a calix[4]arene [86]. Such a com- pound has poor metal-ion affinity and poor selectivity. On excitation with light, photodimerization of the anthracene units occurs, with formation of an ionophoric cavity with much better ion affinity and sharp Na + selectivity. Hemicarceplexes that release guests upon irradiation have also been reported [87]. The recently developed multibranched molecules called dendrimers are poten- tial hosts of great interest [88]. A variety of dendrimers functionalized with trans- azobenzene units have been prepared [89-92]. Irradiation of compound 20 (Fig. 12.13) at 365 nm leads to a photostationary state less rich in the d,s isomer (87 %) than is expected from the behavior of the separated model azobenzene units (93 %) [90b]. This result suggests that photoisomerization causes steric crowding at the periphery of the dendrimer. It has also been found that photoexcitation of the naphthalene units of 20 sensitizes the cis - trans, but not the trans - cis, isomer- ization reaction of the azobenzene units. When dissolved in dichloromethane 20 extracts eosin molecules from aqueous solutions, with the hosting capacity being somewhat larger for the all-trans isomer (nine eosin molecules per dendrimer) compared with the dendrimer obtained in the photostationary state upon irradia- tion at 365 nm (seven eosin molecules per dendrimer) [93]. Irradiation of both these dendrimer-eosin host-guest species in dichloromethane causes ejection of the eosin molecules leading to species that contain only four eosin molecules per dendrimer. When the light is switched off the thermal cis - trans isomerization occurs and, if shaken again with eosin-containing water, the trans form of the dendrimer extracts eosin molecules forming the initial host-guest species (nine eosin molecules per all-trans dendrimer). These results show that 20 behaves like a photopump, because it hosts eosin molecules in the dark and ejects them on photoexcitation. Formation and dissociation of DNA triplex are reversibly photoregulated by the els-trans isomerization of the azobenzene tethered to the third strand [94]. When the azobenzene is in the trans form a stable triplex is formed but on isomerization to the cis form the modified nucleotide is removed from the target duplex. 12.4.2.2 Metal-ion Ejection Many physiological functions, such as neurosynaptic transmission and musde contraction, are controlled by brief, localized fluctuations of intracellular free Ca 2+ concentration. Release or uptake of cations is possible as a result of photoinduced alteration of the chemical structure of a receptor [95-102]. One example is the photodeavable cryptand 21 (Fig. 12.14a) [98]. This photoreaction is, however, irre- versible whereas that shown in Fig. 12.14b is reversible [99]. Light excitation of compound [22-Ca] 2+ causes rapid photoejection (picosecond time-scale) of the metal ion. The electronic transition responsible for photoejection is a charge transfer from the nitrogen atom of the crown unit to the merocyanine unit. The stability constants of the complex in the excited state is estimated to be two orders of magnitude lower than in the ground state. Photochemically controlled binding and release of other metal ions, e.g. Mg(II), Ba(II), Zn(II), Cu(II), Pb(II), Hg(II), Fe(II), Co(II), and Cd(II) have also been achieved [101, 102].

12 Movements Related to Opening, Closing, and Translocation Functions 2O Fi�. 11.13. A dendrimer bearing 32 trans-azobenzene units on the periphery that upon photoisomerization ejects some of the hosted eosin molecules [90, 93]. 12.4.3 Redox-induced Processes Disulfide linkages of cysteine residues maintain the tertiary structure of enzymes and regulate enzymatic activity [1]. For example, a native ribonudease can be reversibly reduced to the corresponding thiol derivative which does not have any activity. A redox

regulation mechanism involving conformational changes can also be applied to artificial systems [103]. An interesting example is compound 23 (Fig.

a Co2 Co ..N N [21 � K]* b hv ./XO NC 3 /)-CN t,,.u O-CH3 [22-Ca] 2' Fig. 12.14. 12.4 Controlled Assembly and Disassembly of Host-Guest Systems J 303 ,. 0 NO hv (a) Photocleavable cryptand 21 [98]; (b) photoejection of Ca 2+ from [22.Ca] 2+ [99]. 12.15a) with two thiol groups inside the binding cavity [104]. When dissolved in 1,2-dichloroethane solution, 23 can extract several soft metal ions from water, with strong selectivity for Ag(I). Disulfide 24, obtained by oxidation of 23 with H202, does not have any extraction capacity, as expected, because its cavity is dosed by the disulfide linkage. The oxidation reaction can be fully reversed by using NaBH4 as reductant. The concept of switching between open and dosed cavity discussed above is relevant to gating of ion channels. Calixarenes, in the same way as cyclodextrins, are electrochemically inactive receptors that can form indusion complexes with a variety of redox-active guests. It has been found [105] that the water-soluble calixarene hexasulfonate 258- forms (Fig. 12.15b) stable complexes with ferrocene and cobaltocene derivatives [106] and with bipyridinium-based compounds [107]. In contrast with cydodextrins, however, binding to calixarenes such as 258- becomes stronger when the guest is positively charged. This result has been exploited [106] in the design of a three- component supramolecular system in which an electroactive guest can choose reversibly between two macrocyclic hosts, depending on its oxidation state. The cobaltocenium cation forms a strong 2:1 complex with 258-, even in the presence of excess fi-CD. Reduction of the cobaltocenium guests, however, leads (Fig. 12.15b) to their indusion in fi-CD and subsequent oxidation back to the mono- cation affords the original complex. Unlike cydodextrins, calixarenes, and cucurbituril, cydophane 262- (Fig. 12.15c) is electroactive and was an early example of redox-switchable macrocyclic receptors [108]. Interestingly, this host in its oxidized form interacts with naphthalene in an "alongside" fashion; on two-electron reduction of its isoalloxazine moiety, however, the binding mode of naphthalene changes and an inclusion complex is formed. Interesting examples of redox-controlled three-pole switches have been reported [109, 110]. A three-component supramolecular system composed of tetrathiaa C\ H HS- H202 23 oo J NaBH4 24 Go -o3s_ so; '1, OH_ OH SOs so; Co]]z +2 + 2e- - 2e- -o3s_ so; --I 8- ',k 8.. OH_ OH 258- Co II c - 2e- 26 - H+ Fig. 12.15. (a)The capacity of compound :23 to extract metal ions from water is switched off.on oxidation to :24 [104]; (b) selection of either calixarene 25 s- or fl-cyclodextrin hosts by changing the oxidation state of the cobaltocenium ions [106]; (c) switching of the binding mode of naphthalene with cyclophane :262- on reduction-oxidation of the latter [105]. fulvalene (TTF), which can exist in three stable forms (TTF, TTF--, and TTF 2--) and two hosts, specifically the x-electron-accepting cydophane cydobis(paraquat-p-phenylene) 274+ and the x-electron-donating crown ether 28, has been investigated (Fig. 12.16) [109]. In its role as an electron donor TTF forms, in acetonitrile solu- tion, a 1:1 inclusion complex with 274+ which can be dissociated-reassociated reversibly by cyclic oxidation-reduction of TTF, whereas TTF 2+ acts as a x-electron acceptor, giving a 1:1 inclusion complex with 28. In contrast, TTF + is not bound by either of the two hosts. When the electrochemical potential applied to the solution becomes more positive than +0.4 V (relative to the SCE) TTF is oxidized to the monocation form and the complex disassembles to give three essentially non- interacting species. Further one-electron oxidation to TTF 2+ at potentials more positive than +0.7 V (relative to the SCE) leads to the insertion of the dication into the cavity of 28. Because both oxidized forms of TTF are stable, the initial state can be restored by subsequent reduction. This system can therefore be switched

Fig. 12.16. A supramolecular switch in which selection of either cyclophane :274+ or crown ether 28 hosts is achieved by changing the oxidation state of the TTF guest [109].

reversibly between three distinct states by exercising electrochemical control on the guest behavior of TTF (Fig. 12.16). The fact that the three states have different colors, coupled with the ease of their electrochemical interconversion, renders this supramolecular system suitable for electrochromic applications (Section 7.7); the system could, moreover, form the basis for the construction of molecular devices in which energy- or electron-transfer processes between selected components can be controlled (see also Section 4.2.2) [109]. This investigation, with others dis- cussed in this book, suggests that carefully designed molecular machines could be employed to perform a variety of valuable functions that go far beyond their char- acteristic molecular motion. The supramolecular complex composed of an "enlarged" version of the tetraca- tionic cyclophane 274+, namely cyclobis(paraquat-p-biphenylene), and a polyether- type thread containing a ferrocene unit in the center has been studied recently with the aim of developing new dual-mode switchable systems [111]. By means of spectroscopic and electrochemical experiments it has been found that such a complex, which does not adopt a pseudorotaxane geometry, can be dissociated reversibly either by oxidation-reduction of the ferrocene unit of the guest or by reduction-oxidation of the bipyridinium units of the host. Redox-driven processes involving metal complexes have been investigated [112]. Particularly interesting is the redox-driven intramolecular anion hopping between coordinated metal centers that occurs in compound 296+ (Fig. 12.17) [113]. This compound consists of two tetraazamacrocyclic (cyclam) moieties, each bearing a 2,2'-bipyridine (bpy) unit; the cyclam rings can host Ni(II) whereas the bpy units,

Fig. 12.17. Redox-controlled anion (A-) translocation in the trinuclear metal complex 296+ []] 3]. pointing outwards, are available for coordination of a Cu(II) ion according to a 2:1 stoichiometry. The resulting species 296+ is, therefore, a trinudear metal complex in which the Cu(II) ion, which prefers a five-coordination sphere, has a solvent molecule or an anion, A-, in the fifth coordination position. In aqueous solution the Cu(II) center of 296+ has particularly large affinity for trinudear anions such as N3-, NCO-, and NCS-, presumably because of its high positive charge (6+). Each proximate Ni(II) center, which has a low-spin d 8 electronic configuration, does not compete with the Cu(II) cation for the A- anion. Thus, in a solution containing 296+ and A- in 1:1 stoichiometry the anion stays on the copper center. On electrochemical oxidation, the Ni(II) metal ions hosted in the cydam units are oxidized to Ni(III), which prefer an octahedral coordination environment. The A- ion therefore translocates on an oxidized Ni(III) center, as pictorially illustrated in Fig. 12.17. On Ni(III)-to-Ni(II) reduction A- returns to the central copper ion. The translocation distance is estimated to be ca 1 nm. More or less pronounced redox-induced structural changes occur in a variety of sensing processes [112, 114-116]. Redox-driven translocation of metal ions is discussed in Section 12.7.1. 12.5 Conformational Changes in Proteins and DNA 12.5.1 Protein Folding-Unfolding Processes The specific function of a protein is determined by its three-dimensional structure and the capacity of this tertiary

structure to evolve with time. The functional conformation of a protein is determined by its amino acid sequence, and understanding how the one-dimensional primary sequence folds into the functional three-dimensional tertiary structure is a central problem in structural biology [117-120]. The folding of a protein is a complex molecular motion which results from a sequence of simple processes, starting from rotations about single bonds, strongly conditioned by cofactors [121], and often assisted by other polypeptides (molecular chaperones) that enable the functional state of the protein to be maintained under conditions in which it would normally unfold and aggregate [122]. In the search for kinetic methods of experimental investigation, means of triggering the folding and unfolding processes have been developed [123]. One approach consists in reduction or oxidation of a component of the protein to shift the folded-unfolded equilibrium. Large-amplitude motion can be controlled by light, by means of a photoinduced electron-transfer reaction on the heme group of cytochromes [124] or by redox stimulation of methionine units in the amino acid chain [125]. Such systems could serve as a basis for the construction of controllable devices based on proteins [126]. Different, but somewhat related, processes are the dynamic exchange between single and double artificial molecular helices in solution, by spiral sliding of their synthetic oligomer strands [127], and the modulation of contraction-extension of polyheterocydic strands by coupled ion binding-pH change [128]. In the last few years several mechanochemical experiments have been performed on single protein molecules. These techniques can give important information on protein-folding mechanisms, but fundamental differences must be considered when forced unfolding by mechanical manipulation is compared with the classical experiment in which a protein is unfolded by means of chemical denaturants or exposure to heat. For example, mechanical forced unfolding might proceed by a different path along the proteiffs configurational landscape than thermal unfolding. For a discussion of these and related problems the reader can refer to recent reviews [9, 10, 11a, 12, 13].

12.5.2 Molecular Machines Based on DNA

The DNA molecule is not only the repository of genetic heritage, but also a very interesting molecule for nanotechnology [129, 130] and logical computation [131]. Interesting mechanical movements, based on conformational changes in DNA molecules, have been recently described

[132-135]. In DNA double-crossover molecules (DX), two DNA double helices are joined to each other twice, yielding rigid molecules. By attaching two DX molecules to one end of a longer DNA strand, a structure (Fig. 12.18) consisting of two short double helices, anchored to a longer double helix, has been obtained [132]. The segment separating the two DX units consists of a special sequence that can switch conformation. Depending on the solution conditions this segment can assume either the B conformation, in which DNA twists to the right, or the Z conformation, which has a left-handed twist. The two DX molecules lie on the same side of the longer DNA strand when the middle segment is in the B form and on opposite sides when that segment assumes the Z form. The B-Z transition results in a rotary displacement of up to 6 nm and 0.6-nm lengthening of the segment. The motion is monitored by means of changes in the fluorescence of dyes attached to the free ends of the DX molecules. When the segment is in the B form the two dyes are on

B-DNA Fig. 12.18. Schematic representation of a mechanical device based on the B-Z transition in DNA [132]. The open and filled circles represent dyes whose separation distance changes upon the change in conformation of the middle DNA segment. Adapted, with permission, from Ref. [132b]. the same side and closer to each other than when the segment is in the Z form. Thus energy transfer is higher in the B form than in the Z form. A nanomechanical device in which the DNA is used not only as a structural material but also as fuel is depicted in Fig. 12.19 [133]. The device has the form of a tweezer and results from the base-pairing (hybridization) of three oligonucleotide strands, A, B, and C (open state, Fig. 12.19). Strand A is labeled at the 5'and 3' ends with two different dyes. When a suitable "closing" strand F is added it hybridizes with the dangling ends of strands B and C, pulling the tweezer closed. Re-opening of the tweezer is achieved by adding strand G, which is a complement to the entire length of the closing strand F. Therefore, G starts hybridization with the overhang section of F and eventually removes it, forming a double-stranded waste product, FG. The overall cycle, which can be repeated many times, is again monitored by measurement of fluorescence intensity, which drops by a factor of six when going from the open to closed state. This corresponds to a difference of 6 nm in the distance between the two ends, and to an angle of 50 � between the open tweezer arms. Not surprisingly, given the complex hybridization processes associated with switching, the time scale of the operation is rather slow (13 s under the experimental conditions employed). More recently a DNA-based, DNA-fuelled mechanical device has been developed in which both stable states correspond to fully paired structures, and are expected to be more robust [134]. Extensive investigations have been performed on single-molecule manipulation of DNA [136], including direct microscopic observation of the time course of DNA restriction reactions [137].

Open Closed 'i. ' Fi�. 12.19. Schematic representation of a DNA-based tweezer operated by hybridization of complementary DNA strands. The open and filled circles attached to strand A represent 12.6 Molecular Locks J 309 dyes whose separation distance changes upon switching between the open and closed forms of the tweezer. Adapted, with permission, from Ref. [13 3]. 12.6 Molecular Locks Many self-assembly systems capable of generating geometrical figures (squares, triangles, boxes, etc.) have been reported in the last few years [138]. Particularly interesting mechanically is the system shown in Fig. 12.20a, which behaves as a molecular lock. This function, which is somewhat related to that of the molecular brake (Sections 11.7 and 13.4), has been obtained [139] by use of a platinum(II)- pyridine bond which is irreversible under ordinary conditions but can be disrupted in highly polar media and at elevated temperature. Macrocycle 304+ is obtained by self-assembly on mixing the ethylenediamine-platinum(II) nitrate complex 31

12 Movements Related to Opening, Closing, and Translocation Functions a H2N.]]/--'N H 2 --4+ .,. ,NH2 6NO2 31 H2N"_N H2 304+ 32 H2N.._/.N H2 --8+ ,'N'[Pt"N',. HaN._' NH2 i'- pt n' pt 1' H2N" 'NH2 H2N',NH 2 -- 338+ b Release + Salt, heating Locking - Salt, cooling Self- assembly Fig. 12.20. A molecular lock [139]. (a) Structural formulae of the compounds employed; (b) schematic representation of the molecular lock principle. with the pyridine-based ligand 32. The formation of 3{) 4+ is kinetically controlled, because dissociation of the Pt-pyridine bond is negligible under the reaction conditions. In the presence of 5 mol L - NO3- at 100 �C, however, catenane 338+ is formed which can be locked by removing the salt and cooling. A schematic representation of the molecular lock is shown in Fig. 12.20b. The same principle has been exploited to obtain a thermally switchable self-assembly molecular cage [140].

12.7 Translocation of Metal Ions Several examples of redox- or acid-base-driven reversible translocation of metal ions between two different sites of a supramolecular system have been reported [141, 142]. 12.7.1 Redox-Driven Processes In the redox-driven processes, the movable metal center should have two consecu- tive, stable oxidation states, M "+ and M ("+)+, a quite common property in transi- tion metal chemistry. On this basis a ditopic ligand could be designed in which a compartment, A, has selective affinity for the oxidized form, M ("+)+, whereas the other compartment, B, has higher affinity for the reduced form, M "+. The redox cycle can be performed either chemically or electrochemically. The rate of the pro- cess depends on the extent of reorganization required by the change in the coordi- nation arrangement. Similar problems are encountered in redox-driven mechanical movements in metal-based rotaxanes and catehanes described in Sections 15.3.3 and 16.3. A classical example of redox-driven translocation of a transition metal ion is shown schematically in Fig. 12.21a [143]. The triple-stranded helical ligand con- tains internal, "hard" hydroxamate and external, "soft" bpy binding sites. Fe(III) prefers to reside in the hard coordination environment, [34.Fe], whereas Fe(II) has a large affinity for the bipyridine ligands, [35.Fe] 2+. On chemical reduction of Fe(III) to Fe(II) by ascorbic acid the metal ion therefore translocates to the external soft bipyridine site. The translocation, which occurs with a change in color, can a N ,/N N, O O HN NH + 3H + -3H + [34 � Fe] [35- Fe] 2+ Fig. 12.21. Redox-driven translocation of an iron [143] (a) and a copper [141 b] (b) metal ion within ditopic ligands.] 2+ N N /=N N-- H '---/H' \/"---/X__. [36 � Cu] 2+ -e- +e- "'-'"

be reversed by adding peroxydisulfate. The ion translocation process is rather slow (minutes to hours, depending on the direction) because of the severe steric rearrangements the ditopic system must experience in the course of metal ion movement. Similar systems have since been reported [144], for example with one compartment based on three salicylamide groups and the other on three bpy frag- ments [144b]. Figure 12.21b illustrates the translocation of copper ion between the two coordi- nation sites of the octadentate ligand 36 [141b]. The compartment which consists of four secondary amine groups is suitable for coordination of Cu 2+, whereas that consisting of two bpy moieties is more suitable for coordination of Cu +. The ligand is flexible enough to fulfill the stereochemistry requirements of each metal oxida- tion state (square coordination for Cu 2+, tetrahedral for Cu+). The translocation process is rapid and reversible and occurs on addition of ascorbic acid for the species containing Cu 2+ and on addition of H202 for the species containing Cu +. 12.7.2 (Acid-Base)-Driven Processes An alternative means of causing reversible translocation of a metal ion is based on modification of the coordination properties of one of the two sites of a ditopic receptor. In such circumstances a metal ion can change its location maintaining its oxidation state [141]. This happens, for example, for receptors consisting of a compartment, A, which can exist in the protonated (AH,) or deprotonated (A "-) form, whereas the other compartment, B, is unaffected by acid-base inputs. If the coordination capacity of the sites decreases in the series A "- > B > AH,, the metal ion initially resides in the A compartment and switching from A "- to AH, on addition of acid causes translocation of the metal ion from site A to site B. The translocation can then be reversed on addition of base. An example ofpH-driven translocation is shown in Fig. 12.22a [145]. The ditopic ligands 37 and 38 consist of an A compartment formed by two amide and two amine units, and a compartment B formed by two amine and two quinoline units. Because the amide groups are poor coordinating ligands, in solution at pH 7.5 a metal ion such as Ni 2+ resides in B, with two water molecules completing the octahedral coordination environment. At pH > 9, however, deprotonation of the amide groups concomitant with translocation of the metal ion occurs. The translocation process, which is fully reversible, occurs with a strong color change, because it is accompanied by a change in the spin state of the metal ion (high-spin when coordinated to site B, low-spin when coordinated in the stronger ligand field offered by the deprotonated A "- site). For compound 37 the rate of the B - A translocation (4 s -1) is higher than that of the reverse process (0.45 s-i), as expected, because the initial dissociative reaction of the translocation process is faster for the labile high-spin complex of the weak ligand-field B compartment than for the inert low-spin complex of the strong ligand-field A "- site. Equipping the ditopic ligand with a suitable unit like anthracene (38) enables the transloca- tion process to be signaled by a drastic change in fluorescence intensity. Another

37 12. 7 Translocation of Metal Ions I 313 38 F{= - 2H + + 2H + hv '_ b + H + - H + Fig. 12.22. (a) pH-driven translocation of Ni 2+ within ditopic ligands 37 and 38 containing a pH-dependent (A) and a pH-independent (B)

coordination compartment [145]; (b) reversible acid-base-controlled metal pumping in "molecular syringe" 39 [146]. � k effect of the bulky anthracenyl group is to slow down the reaction rates because it makes the folding process involved in translocation more difficult. An interesting example of metal ion translocation is the ingenuously designed prototype of a so-called "molecular syringe", 39 (Fig. 12.22b) [146], which uses a 1,3-alternate calix[4]arene as a tube that carries a nitrogen-containing crown cap on one side and two ethoxyethoxy groups on the other side. An Ag^+ ion, which is coordinated to the azacrown ether, is pushed through the tube to the side carrying the twin ethoxyethoxy groups when the nitrogen atom in the azacrown ether is protonated. On deprotonation of the nitrogen atom, the Ag^+ ion is sucked back through the middle of the calixarene once again. Examples are also available of pH-driven inside-outside metal ion translocation in suitably designed ditopic ligands [147].

12.8 Ion Channels

12.8.1 Metal-ion Channels in Nature

Membranes, i.e. barriers that define, bound, and protect cells, are essential components of living systems. Although membranes prevent the contents of the cell from being lost and prevent intrusion of inappropriate chemicals into the cell, they must allow the passage of cations such as Na^+, K^+, and Ca^{2+}. Cation transport through a membrane can occur as a result of the action of carriers or through channels [1]. A carrier is a host molecule resident in the bilayer membrane that complexes a cation and "ferries" it across the membrane. The rate of such a transport mechanism is relatively slow because it is limited by diffusion. Ion channels are a widespread class of membrane protein that mediate physiological phenomena so fundamental that they are usually concealed from our awareness - the control of heartbeat, sensory perception (sound, light, odor, and touch), and the generation and processing of all electrical signals in the brain [148]. In the last example ion channels have the same relationship to writer's mental processes as transistors do to the word-processor holding the linear traces of the writer's thoughts [149]. Ion channels accomplish these complex tasks simply by forming aqueous ion-conduction pathways through the center of the protein and hence across the cell membrane it spans. The ensuing movement of ions down to their transmembrane electrochemical gradients delivers net charge to the cell and thereby changes the membrane voltage, which ultimately controls responses specific to cellular context. Typical protein channels can conduct 107-108 ions per second across a phospholipid bilayer, a rate which is several orders of magnitude faster than that of transport by a carrier. Ion channels must be simultaneously very specific and very fast, two properties difficult to reconcile. Specificity alone is not a difficult problem. It is well known that macrocycles (e.g. crown ethers) bind inorganic ions with high specificity [150]. But under such conditions the residence time is long. Many years ago it was suggested that a mechanism capable of reconciling specificity and speed could be multi-ion single-filling [149]. Recent X-ray crystal-structure determination of the K + channel from the microorganism Streptomyces lividaris [151] has shown that this is indeed the operating mechanism [152]. Fig. 12.23 illustrates a simplified view of the structure of the channel, which consists of four s-helical segments of the protein inserted asymmetrically into the bilayer. The overall length is 45 A and the diameter varies with distance. From inside the cell (bottom) the pore begins as a tunnel 18 A long (the internal pore) and then opens into a wide cavity (10 across) near the middle of the membrane. Ion recognition occurs in the narrow "selectivity filter" at the extracellular end of the pore. This region is essentially a "gauntlet" lined by 12-16 oxygen atoms (mostly backbone carbonyls projecting inwards) just wide enough for a naked K + ion to fit and just long enough for two

Cell exterior 12.8 Ion Channels I 315 Cell interior Fi�. 12.:23. Structure of the K + channel from Streptomyces lividans [151]. Two of the four identical subunits have been omitted for clarity. Dark, horizontal lines represent the membrane surfaces and black circles represent carbonyl oxygen used for ion coordination. Positions of K + ions are indicated. Adapted, with permission, from Ref. [149]. such ions to reside there. Two K + ions dwell simultaneously in the selectivity filter, at the "outer" and "inner" sites, separated by enough space for a single water molecule. Each K + ion is octahedrally coordinated, by four equatorial protein oxygen atoms and two axial water molecules. Na + is energetically disfavored by the pore geometry, as happens in suitable macrocycles. Further along the conduction pathway, the pore widens and a third K + ion is present in a hydrated site. This structure, with three ions in line, is a general characteristic of K + channels [149]. Specificity for the first entering ion is ensured by the preassembled coordinating oxygen atoms; entry of a second ion reduces the affinity of the ion which is already coordinated, because of ion-ion electrostatic repulsion allosterically mediated by the protein, the structure of which is also controlled by the outer K + ion. It is likely that other ion-selective channels operate on similar principles; indeed, recent investigations have furnished evidence of significant analogies between the struc- tures of K + and Na + channels [153]. In conclusion, the structure shown in Fig. 12.23 enables understanding, in the language of host-guest chemistry, of the mechanisms by which channels select ions while rapidly transporting them. This finding might help in the design and construction of artificial ion channels.

'12.$.2 A Natural Proton Pump The mechanism of a proton pump, bacteriorhodopsin, has recently been elucidated [154, 155]. Bacteriorhodopsin, a protein from the cell membrane of the salt loving microorganism Halobacterium salinarum, transports hydrogen ions against an electrochemical potential up to 250 mV, which translates into a 104-fold difference in proton concentration on either side of the membrane. Bacteriorhodopsin con- sists of seven membrane-spanning helical structures (A to G in Fig. 12.24) linked by short loops on either side of the cell membrane [156]. Each bacteriorhodopsin contains one molecule of a linear pigment called retinal, one end of which is attached to the nitrogen atom of a lysine residue in helix G. The other end is wedged deep into the protein. Retinal, which is the same chromophore involved in the process of vision, changes its structure from all-trans to 13-cis on excitation with light. Bacteriorhodopsin uses this structural change to push a single proton through the seven-helix bundle, from the cell interior to the outside. This process involves the formation of several intermediates, three of which, L, M, and N, are shown in Fig. 12.24, together with the ground state. The photoinduced isomer- ization of the protonated retinal (1 ps) triggers the transfer of a proton to aspartate 85 (50 ts), aided by a slight movement of this residue in the L intermediate towards the nitrogen atom (b, Fig. 12.24). In the M state (c), the deprotonated ret- inal straightens, pushing against helix F and causing it to tilt. This opens a channel on the inner cytoplasmic side of the membrane through which aspartate 96 is reprotonated (d), having given up its proton to the nitrogen on the retinal. Aspar- tate 85 transfers its proton through a network of hydrogen bonds and water mole- cules to the outside medium, past arginine 82, which has moved slightly. Finally, the retinal relaxes to the all-trans form, helices F and G swing back to their original position, and another proton pumping cycle can begin. The retinal acts as a valve in the middle of the membrane, imparting a unique direction to the pumping process. The movements of the groups of atoms are very small (1A or less), but sufficient to affect the proton affinity. The molecular mechanism of proton pumping by bacteriorhodopsin will hopefully enable understanding of the working mechanism of other more complex membrane transporters, e.g. Ca-ATPase [157], a calcium pump active in muscle contraction, and the channels related to nerve impulses [148, 153, 158]. '12.$.3 Artificial Ion Channels 12.8.3.1 Introduction During the last ten years substantial effort has been devoted [159, 160] to mimicking the action of natural ion channels by the design and synthesis of model systems which could span natural or artificial lipid bilayers. Any model channel must be commensurate with the structure and dimensions of bilayer membranes, which are typically 50-55 A thick. The polar head groups interact with the external aque-

a Ground state all-trans retinal protonated Cell exterior b 12.8 Ion Channels I 317 L intermediate 13-cis retinal protonated Cell G interior B A Asp 96---H r\ c G f d N intermediate C 13-cis retinal protonated Fig. 12.24. Molecular mechanism for proton pumping in bacteriorhodopsin. Helices D and E are omitted in b-d for clarity. The "paddle" attached to helix F represents the bulky side chains, which move to open the cytoplasmic proton channel. Adapted, with permission, from Ref. [155]. Late M intermediate 13-cis retinal neutral ous phase and the internal aqueous compartment of a cell whereas the central part (ca. 30 3. thick), formed by interdigitating fatty acid chains, constitutes the low polarity (insulator) part of the membrane. As we will see below, the artificial channels consist of head groups (e.g. macrocyclic polyethers), for selective capture of

.81 12 Movements Related to Opening, Closing, and Translocation Functions specific cations, connected by long aliphatic chains designed to span the bilayers and often including a "relay unit" which should help ion transport. Alternative head groups include calixarenes [161, 162]. 12.8.3.2 Modification of Natural Channel-formers Naturally occurring low-molecular-weight channel-forming peptides such as gramicidin and alamethicin have provided considerable guidance in the design of non-natural systems [159, 160]. They also serve as starting materials in their own right for "engineered" channels. The best studied among these compounds is probably gramicidin, a peptide thought to function as an end-to-end dimer in which each unit effectively spans one leaflet of the bilayer [163]. Structural alter- ation of this molecule has been performed in an attempt to understand the mech- anism of ion transfer and to alter its properties. For example, gramicidin has been functionalized by adding a trans-azobenzene unit bearing a cationic ammonium group to the carboxy terminus of the peptide, and it has been shown that the isomer results in more effective channel blocking [164]. Alamethicin, a peptide containing aminoisobutyric acid, belongs to the family of voltage-gated channels across membranes. In an attempt to alter its properties, alamethicin was functionalized with a terminal ferrocene unit, providing evidence for formation of redox-sensitive channels [165]. 12.8.3.3 Ion Channels Based on Biopolymers De novo design of peptide ion channels has focused on systems which form amphiphilic. In a membrane environment several helices aggregate to generate ion-conducting channels [166]. Head-group modification in this system results in controlled ion selectivity and in currents which depend on the sign of the applied potential (rectification) [167]. Cyclic peptides that stack upon each other and are organized in nanotubes have been prepared, and it has been shown that they can afford significant ion transport [168]. Functionalization on every fourth residue of the above mentioned amphiphilic helices with benzo[21]crown-7 was conducted to form a poly(crown) channel (see, e.g., 40 in Fig. 12.25) [169]. Modeling studies suggested that the crowns were aligned in a columnar fashion, because the helical peptide backbone oriented them to the same side of the chain. Significant Na + transport was observed from +60 to -60 mV, by use of 0.1 mol L - NaC1. These ion channels have typical single-channel features. Recent studies [170] have shown that such hexacrown peptides maintain their s-helical conformation when incorporated in a lipid bilayer envi- ronment, but are not oriented at a fixed angle in the membrane - they are, rather, in incorporation equilibrium between an active state parallel to the lipid chain and an inactive state adsorbed on the surface of the bilayer. Oligo-THF peptides have also been synthesized and their ion-channel activity has been studied [171]. Natural transporters need not be proteins, because 3-hydroxybutanoic acid oligomers from natural sources, mixed with calcium polyphosphate, form ion channels in vitro [172]. Furthermore, completely synthetic (R)-hydroxybutanoic

12.8 Ion Channels I 319 o ----o_-oR o o=:jo NH ..O __NH /-NH RO , /,, RO-o �,� R, I""O""1 [R= C12H25 J "'O""1 A I""O""1 .N O. .0 Nv v v v v, N 0.

'0 N j L'N o'J L'o NJ L,,,.O,,J '///// LvO-,,J 42 LvOvJ 'R Fig. 12.25. A poly(crown) channel supported on a helical peptide backbone 40 [169], an ion channel based on a central crown ether scaffold 41 [176], and an ion channel consisting of two terminal macrocycles acting as portals and a central macrocycle acting as a relay 4:2 [177].

acid and inorganic polyphosphate form channels that are functionally indistinguishable from naturally derived material of the same composition [173].

12.8.3.4 Synthetic Ion-channel Models

The construction of fully synthetic ion channels, as is found for any artificial system capable of performing a natural function, is an extremely difficult task. Studies in this field are of interest for at least two reasons [160] - to assess specific aspects of the function and, hopefully, to substitute simpler synthetic compounds for the natural products in therapeutic applications. Pioneering work on synthetic ion channel models was performed more than 20 years ago [174, 175], but the field has developed only recently, as a result of following a variety of strategies [159, 160]. In the "central scaffold strategy" the basic notion is that a cyclic structural unit such as a crown ether or a cyclodextrin comprises a building block from which the channel walls or tendrils radiate. An example is shown by the churdle (a contraction from channel and hurdle) compound 41 shown in Fig. 12.25 [176]. These intricate compounds have relatively poor ion transport capability. The basic concept of the "central relay strategy" is that a cation, whether hydrated or not, cannot jump distances as long as 30]k without some polar stabilization. Accordingly, systems containing three macrocycles have been constructed (see, e.g., 42 in Fig. 12.25), two of which act as headgroups and portals and one, in the central hydrophobic region, as a relay [177]. Experimental evidence suggests that the relay macrocycle is actually parallel to the fatty acid chains rather than to the membrane surface. Furthermore, contrary to expectations, hydrophobic channel walls were found to be more effective than polar walls [178, 179]. Attempts have also been made to construct a redox-active channel by inserting a ferrocene unit in the middle of the channel (43, Fig. 12.26) [180]. Apparently, ion transport was promoted by the channel and some rectification was observed. A rigid-rod polyphenylene residue has recently been used as a scaffold for constructing large pore barrels [181]. A novel class of resorcin[4]arenes (see, e.g., 44 in Fig. 12.26) capable of transporting potassium through bulk liquid membranes and across planar lipid bilayers has been synthesized [182] and evidence for a channel or aggregate pore mecha- nism was obtained. Interestingly, the "free" benzo[15]crown-5 compound cannot be used to distinguish between sodium and potassium ions, but incorporated on to a resorcin[4]arene scaffold (44) it is selective for potassium. Subsequent work [183] has shown that cryptand-like structures based on bis-calix[4]arene have strong selectivity for potassium, the complexation of which, according to molecular modeling studies, occurs via the axial route, passing through the calix[4]arene annulus. A molecular recognition membrane has been fabricated which spontaneously opens and closes its pores in response to specific ions and controls its pore size in response to a known concentration of a specific ion [184]. This membrane might be useful not only as a molecular recognition ion gate, but also as a device for spontaneously controlling permeation flux and solute size.

References 1321 R I R, R n R 43 44 Fig. 12.26. An electrochemically-switchable ion-channel model 43 [150], and an ion channel based on a resorcin[4]arene unit with appended crown ethers 44 [152]. '0% Recent studies on the formation of cation-containing polymolecular stacks of helical monomeric components suggest that self-assembly could be used to obtain selective transmembrane ion channels [185].

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329 13 Rotary Movements 13.1 Introduction Living organisms are a synergistic integration of functionally diverse molecular machines. Cells have hundreds of

different types of molecular motor, each spe- cialized for a particular function. Many biological motor-like proteins have been discovered and characterized in recent years [1]. On a molecular-level, however, biological motors are extremely complex arrays the detailed structure and move- ments of which have, with few exceptions (e.g. the natural proton pump described in Section 12.8.2 [2]) not yet been elucidated. Biological motors are fueled by the energy stored in cells. The two most common energy repositories of cells are in the phosphate bonds of nudeotides, generally ATP (adenosine triphosphate) or GTP (guanosine triphosphate) and in transmembrane electrochemical gradients. Molecular motors have evolved to use these energy sources. Rotary motors play a particularly important role in Nature. Their functions span from the synthesis of ATP to bacterial fiagellar movement. Rotary motors, from water mills to turbines, have also played an important role in the development of civilization. Many mechanical devices we use in everyday life are based on rotary motors, since electricity, which is one of the most practical forms of energy available to mankind, is particularly suited to causing rotation of mechanical parts. Design and construction of artificial molecular-level rotary motors has proved very challenging, but interesting results have recently been obtained, particularly by exploiting light energy. 13.2 Natural Rotary Motors The most important and best known natural rotary motor is ATP synthase (Fig. 13.1) [3, 4], the ubiquitous enzyme that manufactures ATP. As mentioned above, in cells energy is stored in the phosphate bonds of nudeotides and in trans- membrane electrochemical gradients. Molecular motors use one or the other of these energy sources, but ATP synthase has the unique property of using both. Molecular Devices and Machines - A Journey into the Nano World. V. Balzani, A. Credi, M. Venturi Copyright � 2003 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim ISBN: 3-527-30506-8

13 Rotary Mouements F 1 F 0 H + b ADP Pi Fig. 13.1. Structure o FoF-ATP synthase [3, transmitted to F via the 7 shaft and the s 4]. The catalytic region consists of the subunits subunit, where it is used to release ATP , fi, 7, 6, and s. The proton channels lie at sequentially from the catalytic sites in Fl. the interface between subunits a and � The � subunit consists of 9-12 twin -helices (dashed lines indicate the putative inlet and arranged in a central membrane-spanning outlet channels). Proton flow through the array. The a subunit consists of 5-7 channels results in the development of torque membrane-spanning -helices and is between the a and � subunits. This torque

is connected to F by the b and 6 subunits. This protein, in fact, consists of two rotary molecular motors attached to a common shaft, each attempting to rotate in the opposite direction. The F motor uses the free energy of ATP hydrolysis to rotate in one direction whereas the F0 motor uses the energy stored in a transmembrane electrochemical gradient to turn in the opposite direction. Which motor "wins" (i.e. develops more torque) depends on cellular conditions. When F0 takes over, which is the normal situation (bacterial photosynthesis, Section 6.2.2), it drives the F motor in reverse whereupon it synthesizes ATP from its constituents, ADP and inorganic phosphate, Pi. When F dominates, it hydrolyzes ATP and drives the F0 motor in reverse, turning it into an ion pump that moves ions across the membrane against the electrochemical gradient. The mechanochemistry of ATP synthase has been studied in great detail [3-7] and new structural information continues to appear [8]. A very short and simplified description is reported below. This enzyme consists of two principal domains (Fig. 13.1). The asymmetric membrane-spanning F0 portion contains a proton channel and the soluble F portion contains three catalytic sites which cooperate in the synthetic reactions. The catalytic region is made up of nine protein subunits with the stoichiometry 3ct:3fi:17:16:le, approximating to a flattened sphere, 10 nm across and 8 nm high. The flow of protons (or of Na + ions) through F0 is thought to generate a torque which is transmitted to F by an asymmetric shaft, the coiled-coil 7-subunit. This subunit acts as a rotating "cam" within F, sequentially releasing ATP from the three active sites. The free energy difference across the inner membrane of mitochondria and bacteria is sufficient to produce three ATP molecules per twelve protons passing through the motor. As mentioned above, the action of FoF-ATP synthase is reversible, i.e. the full enzyme can synthesize or hydrolyze ATP; F in isolation, however, can only hydrolyze it. The spinning of F-ATPase, i.e. the rotary motor nature of this enzyme, was first proposed approximately ten years ago [3]. The rotation of F- ATPase during ATP hydrolysis has since been directly observed [9, 10] by attaching a fluorescent actin filament to the 7 subunit as a marker. It has also been found [11] that an actin filament connected to the c subunit oligomer of F0 can rotate by using ATP hydrolysis, showing that the 7 and c subunits are coupled. In other experiments [10, 12], performed with actin filaments of variable length, discrete 120-degree rotations have been observed, as expected from the threefold rotational symmetry of 7F. More recent investigations [13] have revealed that the 120-degree step consists of roughly 90-degree and 30-degree substeps, each taking only a frac- tion of a millisecond; ATP binding drives the 90-degree substep and the 30-degree substep is probably driven by release of a hydrolysis product. Further performance data on motor rotation have also been obtained by attachment of fluorescent microspheres to the tip of the 7 subunit [14]. 13.3 Hybrid Rotary Motors Recent scientific advances in both molecular biology and supramolecular chemis- try have opened up the possibility of building functional hybrid devices based on natural motors. One long-term objective of this research is to utilize the finest attributes associated with the worlds of both biological and synthetic materials to create nanomechanical systems powered by biological motors. Currently the best characterized biological motor is the above described ATP synthase. Perhaps, the most spectacular molecular-scale machine constructed in recent years is a biomimetic, photon-driven proton pump which is able to power ATP synthase to produce ATP (Section 6.4). In principle, proton-motive force generated by the light-driven process [15] described in Fig. 6.20 can be used to perform work. This result has been achieved [16, 17] by the system illustrated in Fig. 6.21. FoF-ATP Synthase has been incor- porated, with the ATP-synthesizing portion extending into the external aqueous solution, into liposomes containing the components of the proton-pumping photocycle. Irradiation of the membrane with visible light leads to the charge- separation process that causes the previously described (Section 6.4) proton trans-

location, with generation of a proton-motive force. On accumulation of sufficient proton-motive force, protons flow through the FoF1-ATP synthase, with the forma- tion of ATP from ADP and Pi. The system described above is the first complete biomimetic system which effectively couples electrical potential, derived from photoinduced electron transfer, to the chemical potential associated with the ADP-ATP conversion, thereby mimicking the entire process of bacterial photosynthesis. It constitutes a synthetic bio- logical motor that, in principle, can be used to power anything which requires a proton gradient or ATP to work [17], e.g. to pump calcium ions across a lipid bilayer membrane [18], or even future nanomachines. It might also be advanta- geous to use artificial, light-driven systems to produce ATP to perform enzymatic reactions in the absence of interfering biological materials and without a need for living cells [17]. A hybrid nanomechanical device powered by ATP synthase has recently been reported [19]. It consists (Fig.

13.2) of three elements: � nanofabricated substrates of Ni posts, each 50 to 120 nm in diameter and 200 nm high; � F-ATPase molecules, specifically modified for selective interfacing with the nanofabricated structures; � nanofabricated Ni rods (150 nm in diameter and 750 to 1500 nm long). Ni rod ADP + Pt Fig. 13.2. Histidine tag Sketch of a nanomechanical device powered by the F-ATPase molecular rotor [19].

13.4 Rotary Movements in Art�ial S)stems [333 The F-ATPase molecules were attached to the Ni posts by means of histidine tags introduced into the/-subunits [20]. Streptavidin was bound to the biotin resi- due on the 7-subunit tip, and the Ni nanorods, coated with biotinylated histidine- rich peptides, were then attached to the substrate-mounted F-ATPase motors by means of a biotin-streptavidin linkage. Rotation of the nanopropellers, which was observed in a flow cell by means of a CCD camera, was initiated by addition of ATP, and inactivated by addition of NAN3, an F-ATP synthase inhibitor [19]. Although only five of 400 total observed propellers were found to rotate, probably because of incorrect assembly of the components, these experiments demonstrate the possibility of integrating biomolecular motors with nanoengineered systems to produce nano- or micro-mechanical machines. Chemically, however, it should be noted that this device, unlike the ATPase-artificial photosynthetic system described in Section 6.4, does not contain any artificial active component. 13.4 Rotary Movements in Artificial Systems Artificial molecular-level rotary motors are systems capable of undergoing unidi- rectional and repetitive rotation under the action of external energy inputs. The bottom-up construction of molecular-level rotary motors poses several challenges, particularly because it is difficult to satisfy the unidirectional rotation requirement. At present, artificial rotary motors have been obtained only by exploiting light- induced rotation around a carbon-carbon double bond in carefully designed chiral compounds [21]. In this section, we will also include description of the incom- plete unidirectional rotation obtained in suitably designed compounds, and of the rotation-type movements occurring in double-decker compounds [22], and in some rotaxanes and catehanes [23]. Other types of movements in rotaxanes and cate- nanes will be discussed in Chapters 15 and 16. 13.4.1 Chemically Driven Processes An interesting and very clever attempt to construct a molecular rotary motor has been developed [24-27] starting from the previously described molecular ratchet (Section 11.8). Additional functionalities were incorporated in the triptycene-heli- cene system and energy to produce the motion was obtained from a chemical fuel, phosgene [24, 25]. The strategy used to obtain unidirectional rotation is illustrated in Fig. 13.3. The steric hindrance associated with the [4]helicene group of 1 inhibits rotation about the single bond connecting this unit to the 9-triptycyl ring system, as shown (Fig. 13.4) by the calculated energies for rotation around the triptycene bond for the parent compound 15 described in Section 11.8. Treatment of 1 with C12CO and Et3N gives the isocyanate 2, which is chemically "armed" to react with the hydroxy-propyl tether attached to the helicene. At those instants when dockwise rotation

.NHe 1 + Cl2C0 Et3N 2e Urethane cleavage Fig. 13.3. Sequence of events causing unidirectional rotation of 120 � in a triptycene-helicene system powered by phosgene as a chemical fuel [24]. b 10 0 30 60 90 120 Dihedral angle (degrees) Fi�, 13,4, Calculated (AM1) relative ener�ies for rotation around the triptycene-helicene bond [25]: (a) the parent compound 15 discussed in Section 11 ,$; (b) the derived urethane 3 (Fi�, 13,3); (c) the derived urethane of a compound identical with 3 except for a shorter tether,

of the triptycene brings the isocyanate and the hydroxyl group sufficiently close to react intramolecularly (2a), urethane 3 is formed in the shape of a highly strained conformation. The presence of such a strain is shown by the smaller energy for rotation of 3 compared with the parent compound (Fig. 13.4). The strain is released by dockwise rotation of the 9-triptycyl ring system about the single bond connecting it to the [4]helicene, yielding 3a (Fig. 13.3). Cleavage of the urethane linkage regenerates compound 1 in a conformation, la, different from original conforma- tion and that has been obtained as a result of unidirectional 120-degree rotation induced by the formation of a covalent bond. The process can be monitored by H NMR spectroscopy, using the bridgehead proton of the 9-triptycyl ring system as a probe. The rapid transformation of 1 into 3 is accompanied by a downfield shift of the singlet associated with the probe proton and is followed by the unidirectional rotation which causes a decrease in the intensity of this signal with the concomi- tant growth of another singlet. The half-life for rotation of the system is approxi- mately 3 h [24, 25]. To accelerate the speed of rotation a shorter tether attached to helicene was used (two instead of three methylene units), because calculations showed that in the modified compound the energy barrier to rotation is smaller (Fig. 13.4). The speed of rotation for the compound with the 2-carbon tether was indeed much faster (half-life 5 min), and the rate-limiting step became the ure- thane formation [25]. The unidirectional rotation achieved with this system is, indeed, a good result [28]. It should be noted, however, that this rotation is limited to 120 degrees. To achieve full rotation each blade of the triptycene moiety should be selectively armed at the appropriate time, which seems to be a very difficult task. Further- more, repeated rotation in such a chemically powered three-stroke motor would of course produce waste products, the accumulation of which would compromise the operation of the motor (Section 10.3). Nonunidirectional, pirouetting-type movements have been chemically induced in suitably designed rotaxanes. Rotaxane 42+ (Fig. 13.5) [29] comprises a wheel which incorporates a gold(Ill) porphyrin and an axle bearing two zinc(II) porphyr- ins. In the presence of Cu + ions the structure of the rotaxane is such that the gold porphyrin is remote from the two zinc porphyrins, as a consequence of Cu(I) coordination by the two phenanthroline moieties, one of which is contained in the wheel and the other in the axle (left-hand side of Fig. 13.5). After removal of the metal ion weak forces might favor an attractive interaction between the gold porphyrin and the two zinc porphyrins leading to a situation in which the gold porphyrin is pinched by the two zinc porphyrins (right-hand side of Fig. 13.5). The interconversion between the two situations obtained in the presence or absence of Cu + ions implies a 180-degree rotation of the axle within the wheel [29]. By exploiting the cation-binding crown ether contained in the wheel the dynamic behavior of rotaxane 5 (Fig. 13.6) can be strongly influenced in DMSO solution by the presence of K + ions [30]. H NMR Experiments have, indeed, provided evi- dence that the multiple axle-wheel orientations populated by rotaxane 5 are frozen out in a single conformation by addition of K +. The cation acts, therefore, as a brake at the molecular level.

O ioN"cH3 13.4 Rotary Movements in Art�ial S)stems [337 Fig. 13.6. Rotaxane 5 and the braking effect of: K + ions [30]. K + Another example in which K + plays the role o{ a molecular brake is the tetrakis(benzocrown)-appended lanthanum(III) porphyrin double-decker 6 (Fig. 13.7) [31]. Viewed {rom the top o{ a porphyrin ring, 6 can be regarded as two overlapping wheels rotating around the molecular axle perpendicular to the por- phyrin plane and passing through the metal. It has been shown that 6 can bind K + to {orm a 1:4 complex in a cooperative, allosteric {ashion (Section 12.2.2). This means that coordination o{ the first K + ion suppresses rotation o{ the two por- phyrin planes, providing entropically {avorable conditions {or subsequent K + binding [22, 31]. R 6 -o R ,",, R = ' "', -I R Fig. 13.7. The tetrakis(benzocrown)-appended lanthanum(111) porphyrin double-decker compound 6, capable o� a positive allosteric effect [3]].

338 [13 Rotarp Movements Froo rotation Silent in circular dichroism 0 + C OH OH . 0 + 3 C OH OH Cooperative binding 0 Oo x," N---H- 0 Active in circular dichroism 'Hxo o Fig. 13.8. Allosteric effect with suppression of porphyrin ring rotation in the tetrakis(4-pyridyl)-appended Ce(IV) porphyrin double-decker compound 7 on association with (1 R,2R)- cyclohexane-1,2-dicarboxylic acid [32, 33]. A similar positive allosteric effect has been observed for the tetrakis(4-pyridyl)- appended cerium(IV) porphyrin double-decker compound 7 (Fig. 13.8), which has high selectivity for the enantiomers of, e.g. 1,2-cyclohexanedicarboxylic acid [22, 32, 33]. The origin of the cooperative guest binding is again attributable to the succes- sive suppression of the rotation of the porphyrin planes. In this system binding of a chiral guest can be monitored by observing circular dichroism spectral changes arising from the induced chirality in 7. A braking effect on the rotation of the porphyrin rings can also be caused by bulky substituents on the meso phenyl groups. In compound 8 [34] (Fig. 13.9a), for example, the 3,5-dimethoxyphenyl groups make the porphyrin rotation very slow. In this compound the chirality of the guest can again be imprinted, and it can then

13.4 Rotary Movements in Art�ial Systems [339 a b Fi�. 13.9. (a) Brakin� effect oCbulk� substituents in the cerium(IV) porphyrin double-decker compound 8 [4]; (b) metal bisporphyrinate double-decker complexes with redox-controlled rotation [7]. R1 R2 M(DTP)2 H ---CH3 M(MOFPP)2 -OCH3 _F OCH3 F F M = Ce, Zr be erased by heat treatment in the presence of pyridine. After the erasing treat- ment, however, the chiral memory can be stored at low temperature, as estimated by the half-life, 3 days at 0 �C and one year at -37 �C. This concept has also been extended to saccharide recognition in aqueous solution [35, 36], yielding a molec- ular machine for allosteric control (Section 12.2.2) of drug release and information transduction of saccharide-containing guest molecules. The rotary motion of metal bisporphyrinate double-decker complexes 9 can be accelerated or decelerated by redox processes [37] (Fig. 13.9b). Reduction of the chiral bisporphyrinate double-decker complex Ce(MOFPP)2 (MOFPP = 5,15-bis(3,S-dimethoxyphenyl)-10,20-bis(pentafiuorophenyl) porphyrin dianion) by sodium anthracenide in dioxane at 20 �C resulted in acceleration of porphyrin ligand rotation (which leads to racemization) by a factor of more than 300. Photoreduction of Ce(MOFPP)2 in dioxane also resulted in enhanced ligand rotation. In contrast, the monocationic and dicationic forms of the chiral zirconium complex Zr(DTP)2 (DTP = 5,15-ditolylporphyrin dianion), obtained by oxidation with phe- noxathiinylium hexachloroantimonate or FeC13, undergo acid-induced racemiza- tion 21 and 99 times more slowly, respectively, than the neutral complex. 13.4.2 Photochemically Driven Processes trans-cis Photoisomerization around a carbon-carbon double bond is one of the most extensively studied photochemical reactions [38, 39]. In suitably designed alkene-type compounds containing chiral centers (chiroptical switches) the relative direction of the movement leading to geometrical isomerization can be controlled by the wavelength of the light and depends on the chirality of the molecule [40].

13 Rotary Mouements / CH3 > 280 nm (P,P)-trans-10 (M,M)-cis-10 > 380 nm (M, M)-tra ns-10 (P, P)-cis-10 Fig. 13.10. Compound 10 undergoes unidirectional rotation in four steps; each light-driven, energetically uphill process is followed by a thermal, energetically downhill process [41]. The concerted action of two chiral elements in a single chemical (or physical) event, by virtue of their diastereomeric nature, can, furthermore, lead to unique handedness [21]. A light-driven molecular motor has been designed and constructed on the basis of these principles [41]. This project started with the study of the molecular switch discussed in Section 7.5.1 (Fig. 7.8) [42, 43]. The design of this molecular switch was modified (Fig. 13.10) [41] by replacing the thioxanthylidene ring system with another tetrahydrophenanthrene unit. Each of the two helical subunits of the resulting compound 10 can adopt right-handed (P) or left-handed (M) helicity. As a result a total of four stereoisomers (Fig. 13.10) are possible for this compound. The cis-trans isomer- izations are reversible and occur on irradiation at appropriate wavelengths. In contrast, the inversions ofhelicity, while maintaining a cis or a trans configuration, occur irreversibly under the

influence of thermal energy. On irradiation (_>280 nm, 218 K) of a solution of (P,P)-trans-10, a mixture of (P,P)-trans-10 and (M,M)-cis-10 is obtained in a ratio of 5:95. When the solution is warmed to 293 K (M,M)-cis-10 is converted irreversibly to (P,P)-cis-10. Subsequent irradiation (_>280 nm) of the solution produces a mixture of (P,P)-cis-10 and (M,M)-trans-10 in a ratio of 10:90. When the temperature is increased further (333 K), (M,M)-trans-10 is converted irreversibly to the original isomer (P,P)-trans-10. Thus, a sequence of light- and temperature-induced isomerizations can be exploited to move this molecular rotor in one direction only (Fig. 13.10). Indeed, when (P,P)-trans-10 is irradiated (_>280 nm) at 293 K, clockwise 360-degree rotation occurs spontaneously [28, 41]. The overall process can be followed by monitoring the change in the intensity of the absorption band in the 217-nm circular dichroism trace. The unidirectional motion in this system is dictated by the stereogenic centers associated with the two methyl substituents. As a result of trans-els isomerization, the axial methyl substituents of (P,P)-trans-10 are forced to adopt a less favorable equatorial orientation in (M,M)- cis-10. The strain associated with the equatorial methyl substituents is, however, released on thermal conversion of (M,M)-cis-10 to the more stable isomer (P,P)-cis- 10. The subsequent els-trans isomerization forces the methyl groups to adopt, once again, equatorial orientations in the isomer (M,M)-trans-10. Finally, the thermal conversion of (M,M)-trans-10 to the original isomer (P,P)-trans-10 is accompanied by a change from equatorial to the more stable axial orientation for the methyl substituents. The rotary motor was then redesigned so that it had distinct upper and lower parts (Fig. 13.11a) [44]. In such second generation molecular rotors a single stereogenic center is present. Another aim in redesigning the system was to accelerate the rotary motion by reducing the thermal isomerization barriers for helix inversion. The results obtained showed that the presence of a single stereogenic center is, indeed, a sufficient condition for unidirectional rotation and the thermal barrier for helix inversion decreased from 26.2 kcal mol - for compound 10, to 24.7 and 22.7 kcal mol - for compounds 11 and 12, respectively. In perspective, the lower half of these molecular motors could be connected to other molecules or surfaces, thereby playing the role of a stator, while the upper half acts as a rotor. An attempt to control the speed of rotation around a single bond by light excitation has been based on compound 13 (Fig. 13.1lb) [43e], structurally related to compound 11. It was envisaged that photoisomerization of cis-13 to trans-13 would result in a distinct decrease in steric hindrance to biaryl rotation. The results obtained showed, however, that the barrier was slightly higher for the trans isomer than for the cis isomer. Presumably the methyl substituents of the rotor moiety interfere with the methylene groups in the upper part in trans-13, whereas in the cis isomer the naphthalene unit easily bends away to enable passage of the rotor. These resttits are extremely interesting for several reasons: � the occurrence of unidirectional and repetitive rotary motion has been demon- strated to occur in a fully artificial molecular-level machine; � the machine is powered by excitation with light, without production of any waste product; � the rate of rotation can be changed by suitable chemical modification; � because of its chemical structure, the system can be functionalized so it can be connected with other molecules, nanopartides or surfaces [45].

13 Rotary Mouements A very interesting development of this line of research has recently been reported [46]. A host-guest system comprising a nematic liquid crystal film (4- pentyloxy-4'-biphenylcarbonitrile) doped with the chiral light-driven molecular rotor 10, has been assembled. Irradiation of the film results in unidirectional rotary motion of the molecular rotor, which induces motion of the mesogenic molecules leading to molecular reorganization and, as a consequence, a change in the color of the film. In this way, by control of the rotary motion at the molecular level, color tuning over the entire visible spectrum is achieved. These findings demonstrate that a molecular rotary motor can exert a visually observable macroscopic change in a material [46]. In azobenzene-containing catehanes such as 14 4+ (Fig. 13.12) it is possible to control the rate of thermally-activated rotation of the macrocydic components by trans-cis photoisomerization of the azobenzene moiety [47, 48]. Such systems can be viewed as molecular-level brakes operated by light. 13.4.3 Electrochemically Driven Processes In suitably designed rotaxanes the pirouetting-type movements of the wheel around the axle can be electrochemically driven. Rotaxane [15.Cu] + has a structure (Fig. 13.13a) in which Cu(I) is coordinated tetrahedrally by the phenanthroline present in the axle and the phenanthroline contained in the wheel [49]. Electro- chemical oxidation of the Cu(I) center leads to a transient tetracoordinated Cu(II) species (Fig. 13.13b). In response to the preference of Cu(II) for

pentacoordinated geometry and by exploiting the presence in the wheel of a second coordination site, namely the terdendate terpyridine moiety, the transient species rearranges by the pirouetting of the wheel around the axle. This rearrangement leads to a structure in which the Cu(II) center reaches its most stable environment - pentacoordinated by the phenanthroline of the axle and the terpyridine of the wheel ([15.Cu] 2+, Fig. 13.13c). On electrochemical reduction of Cu(I I) a transient pentacoordinated Cu(I) species is obtained (Fig. 13.13d) which rearranges by means of a second pirouet- ting of the wheel to the most stable structure with Cu(I) tetrahedrally coordinated (Fig. 13.13a). The rate constants for each of the sequential steps were determined by use of electrochemical techniques and it was shown that the rate of pirouetting depends greatly on the oxidation state of the copper [50]. The tetracoordinated Cu(II) species rearranges in tens of seconds whereas the pentacoordinated Cu(I) species leads to the tetracoordinated structure on the millisecond time scale [49a]. X-ray absorption spectroscopy study has, furthermore, furnished evidence of mod- ification of the copper coordination sphere on changing its oxidation state [49b]. It should be noted, however, that, as a consequence of the oxidation-reduction cyde, the wheel of this rotaxane does not necessarily perform a 360-degree rotation, but can only oscillate between the two positions on the threaded axle. To make real rotary motors it would be necessary to introduce directionality to the system by using, for example, a wheel containing three different coordination sites and a well defined axle [49a].

References 1345 o o Fig. 13.14. o o 17 Hydrogen-bond assembled rotaxanes 16 and 17 [56]. 13.4.4 Other Effects Alternating-current (ac) electric fields are used to probe electronic structure, to change the orientation of molecules [51-53], e.g. in liquid-crystal displays, and to interact with large-scale molecular motions, e.g. the backbone fluctuations of semi- rigid polymers [54, 55]. It has been shown that modest ac fields can also be used to monitor and affect the pirouetting of the wheel around the axle in the two hydrogen-bond assembled rotaxanes 16 and 17 (Fig. 13.14) [56]. The two rotaxanes contain the same wheel, a benzylic amide macrocycle, but differ in the nature of the axle, which in one compound comprises two nittone hydrogen-bond acceptors and in the other a fumaramide unit. NMR spectroscopic results, simulations, and the absence of the effect when the rotaxane components are not interlocked, indicate that the internal motion can be attributed to wheel pirouetting. In 16 the wheel rotates smoothly around the axle. In 17 the motion of the wheel is more complicated, because the pirouetting is coupled to pivoting of the wheel against the axle with the ideal fulcrum of motion located near the mass center of the molecule. During the NMR experiments it was also possible to observe that in both rotaxanes the wheel rotates faster when the applied field is zero [56]. This result suggests that the electric field acts as a brake on rotation of the wheel. A similar braking effect was observed when the polarity of the solvent was reduced, because of stronger intercomponent hydrogen bonding [56]. References R.D. VArE, R.A. MILLIGAl1, Science, 2000, 288, 88. W. KOHLBRAIIDT, Nature, 2000, 406, 569, and references therein. (a) P.D. BAYER, Blochim. Biophys. Acta, 1993, 1140, 215. (b) P.D. BAYER, Artget. Chem. Int. Ed., 1998, 37, 2296. 4 (a) J.E. WALKER, Artget. Chem. Int. Ed., 1998, 37, 2308. (b) D. STOCK, A.G.W. LESrtE, J.E. WALKER, SCIt.'/'Ce, 1999, 286, 1700. 5 (a) T. ErSTOil, H. WAilG, G. OSTER, Nature, 1998, 391,510. (b) G. OSTER, H. WAilg, Blochim. Biophys. Acta,

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3481 14 Threading-Dethreading Movements 14.1 Introduction As discussed in Section 12.4, supramolecular (host-guest) complexes are appealing systems for construction of simple molecular-level machines, because they can be forced to undergo dissociation into their free molecular components by use of an external stimulus and eventually reassemble on appropriate counter-stimulation (Fig. 12.10). They are an attractive proposition, because they can be prepared under thermodynamic control, simply by mixing the molecular components in solution. The challenge resides in "programming" the system, i.e. in the design and syn- thesis of components which carry, within their structures, the pieces of informa- tion necessary not only for construction of the desired supramolecular architecture, but also for the performance of the required association-dissociation function [1]. For molecular machines the most interesting host-guest systems are certainly the pseudorotaxanes [2-10], structures that can be defined [11] as interwoven inclusion complexes in which a molecular thread is encircled by one or more beads (i.e. macrorings) so that the extremities of the thread are directed away from the center of the bead. At least one of the extremities of the thread does not have a bulky stopper group. Hence, the constituents of the assembly, like any complex, are at liberty to dissociate into separate molecular species (i.e. in contrast with rotaxanes, Chapter 15, there is no attendant mechanical bond to maintain the integrity of the system). A complex made of a thread and a bead should be called a [2]pseudorotaxane. For simplicity, however, we will avoid using the [2] prefix. Some of the molecular motions that can be obtained with pseudorotaxanes are represented pictorially in Fig. 14.1. Dethreading-rethreading of the thread and ring components is reminiscent of the movement of a piston in a cylinder. Starting from this simple motion (Fig. 14.1a), more complex processes can be devised. In a chemical system comprising a macrocycle and two thread-like species one can select, by means of a suitable input, which thread enters the ring's cavity (Fig. 14. lb). Analogously, a suitable stimulus can be used to choose which of the two macrocycles surrounds a partic- ular thread-like species (Fig. 14.1c). Many such systems have been investigated in the last few years [1, 12-26]. It should be pointed out that the processes shown Molecular Devices and Machines - A Journey into the Nano World. V. Balzani, A. Credi, M. Venturi Copyright � 2003 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim ISBN: 3-527-30506-8

.4- 14. I Introduction I 349 b c Fig. 14.1. (a) The dissociation ofa pseudorotaxane and the interchange of (b) a macrocycle between two threads and (c) a thread between two macrocycles. schematically in Fig. 14.1 can also be taken as a basis for binary logic operations and for the design of logic gates (vide infra). The external stimulus used to power such rudimentary molecular machines must be able to weaken the noncovalent bonding forces that stabilize the initial supramolecular complex. The type of stimulus that is used thus depends on the nature of such forces. Most pseudorotaxanes studied so far rely on [N+-H ... O] and [C-H... O] hydrogen bonding or on a combination of [C-H... O] hydro- gen bonding and z-electron donor-acceptor (charge-transfer) interactions [16]. [N+-H ... O] Hydrogen-bonding interactions can easily be destroyed by addition of a base capable of deprotonating an ammonium center, and can be restored by addition of an acid capable of reprotonating an amine function. Thus in pseu- dorotaxanes based on hydrogen-bonding interactions mechanical motions can be driven by chemical (acid-base) stimulation. When the interactions responsible for complexation are donor-acceptor in nature, they can be weakened by oxidation of the electron-donor unit or by reduction of the electron-acceptor one. The reduction of the electron-acceptor unit also weakens the [C-H... O] hydrogen bonds which accompany the donor-acceptor interactions in most of these supramolecular com- plexes. The donor-acceptor interaction can usually be restored by means of the reverse redox process. The oxidation and reduction processes needed to dissociate- associate a pseudorotaxane can be achieved by chemical, photochemical, or elec- trochemical stimulation [16, 18]. If two bulky substituents (stoppers) are placed at the ends of the thread a pseu- dorotaxane is converted into a rotaxane (Section 15.3), a structure that does not

14 Threading-Dethreading Movements a Threading Dethreading 1 Isolated components / Rotaxanes 0 Rotaxane-like character Fig. 14.2. (a) Self-assembly of rotaxane-like entities by slippage of a macrocycle through relatively bulky stoppers [27], (b) Schematic illustration showing that pseudorotaxanes belong to the fuzzy domain between isolated components and rotaxane structures [25], 1 allow dethreading, because of the presence of the two stoppers. If the thread has relatively bulky substituents since the beginning, the ring can slip through them, a process that requires overcoming of a quite high activation barrier (Fig. 14.2a) [27]. For such systems dethreading of the ring is not impossible, but requires over- coming of an even higher activation barrier, so that under appropriate conditions (e.g. low temperature) they behave as rotaxanes. This shows that pseudorotaxanes can have some rotaxane-like character. From another viewpoint we can say that pseudorotaxanes belong to the fuzzy domain between the two extremes (Fig. 14.2b) corresponding to either the two isolated

components or the assembled rotaxane structure [28]. This is indeed a good example of fuzzy logic in chemistry, a concept that is now proving its value in a great variety of industrial chemical processes [29].

Fig. 14.3. The gathering ability of a Cu(I) ion induces the threading of the phenanthroline-based macrocycle 1 on to the phenanthroline-based ligand 2 (CH3CN, ambient temperature) [30]. 14.2 Chemically Driven Movements I 351 + Ou + 14.2 Chemically Driven Movements 14.2.1 Systems Based on MetaI-Ligand Bonds Coordination around a metal center was the first kind of interaction used to orga- nize molecular components in a pseudorotaxane fashion [30]. Suitably designed macrocyclic and thread-like species containing 1,10-phenanthroline (phen) ligands, such as I and 2, self-assemble on addition of Cu(I) ions to yield a pseudorotaxane (Fig. 14.3). Such a complex was used as an intermediate in the template-directed synthesis of metal-containing catenanes [2, 9]. The formation of this complex can be monitored easily both by 1H NMR spectroscopy and visually, because it is accompanied by a change in the color of the solution. Cu(I)-containing pseudo- rotaxanes are very stable and, therefore, difficult to dethread - the copper ion can be removed only by treatment of the complexes with excess of highly nucleophilic ligands, e.g. cyanide ions [31]. For this reason, metal complexation is unsuit- able for development of prototypes of molecular machines based on chemically-stimulated threading-dethreading movements. It is, nonetheless, a very convenient means of promoting threading ofpseudorotaxanes, starting from suitably designed thread-like and macrocyclic ligands. The versatility and the properties of metal complexes have been exploited (vide infra) in the design and construction of ele- gant examples of rotaxane- and catenane-based molecular machines (Chapters 15 and 16). 14.2.2 Systems Based on Hydrogen Bonds and Electrostatic Interactions Pseudorotaxanes which are good candidates for chemical switching include those that rely upon hydrogen-bonding interactions between ammonium ions and crown ethers. It has long been known that organic ammonium ions can form adducts

14 Threading-Dethreading Movements with crown ethers [4, 5]. More recently, it has been forrod [32, 33] that, in nonpolar solvents, suitable thread-like dialkylammonium ions (e.g. the dibenzylammonium cation) can interpenetrate suitably-sized crown ethers (e.g. dibenzo[24]crown-8) to form pseudorotaxanes [34, 35]. These complexes, the formation of which can be

shown by H NMR spectroscopy in solution and by X-ray crystallography in the solid state, are stabilized by [N+-H ... O] and, to a lesser extent, by [C-H... O] hydrogen bonds, and sometimes also by [z... z] stacking interactions. When the pseudorotaxane has been obtained, it can easily be dethreaded by adding a base able to destroy the hydrogen bonds by deprotonation of the -NH2 +- center. Suit- able bases are bulky, nonnudeophilic amines such as i-Pr2NEt and n-Bu3N. The pseudorotaxanes can also be prepared, starting from a mixture of the crown ether and a thread-like dialkylamine by addition of an acid (typically, CF3SO3H or CF3CO2H) which protonates the amine function. The threading process can again be reversed by addition of a base. The acid must be selected so that it does not give insoluble ammonium salts and such that its anion does not promote ion-pairing. Chromophoric and/or luminescent units such as dioxybenzene [36], dioxynaph- thalene [36bc], binaphthyl [37], anthracene [36ab], and fullerenes [38] have been incorporated into crown ethers or ammonium ions to study the processes that occur within pseudorotaxanes. In all these studies the goal is to design chemically (acid-base) controllable molecular machines which give a light signal as a readout. Plug-socket [37a, 39a] and extension-cable [39b] devices based on pseudorotaxane formation and operating by acid-base stimulation have been described in Chapter 4. Here we illustrate in more detail the plug-socket system for energy transfer [37a] that was briefly mentioned in Section 4.2.3. The absorption and fluorescence spectra of a CH2C12 solution containing equal amounts of crown ether 3 and amine 4 indicate the absence of any interaction between the two compounds (Fig. 14.4). Addition of a stoichiometric amount of acid causes profound changes in the fluorescence spectrum of the solution - quenching of the luminescence of 3 and sensitization of the luminescence of [4H] + on excitation with light absorbed ex- clusively by the crown ether. These observations are consistent with the formation of a pseudorotaxane-type adduct wherein very efficient energy transfer occurs from the binaphthyl unit of the crown ether to the anthracenyl group incorporated within the dialkylammonium ion. Such a pseudorotaxane can be disassembled by subsequent addition of a stoichiometric amount of base, thereby interrupting the photoinduced energy flow; evidence of this is that the initial absorption and fluo- rescence spectra are restored. Besides the machine aspect, such systems can be viewed as molecular-level plug-socket devices (Fig. 4.12), because they are charac- terized by chemically controlled, reversible plug in-plug out behavior, and photo- induced energy-transfer in the plug-in state. Interestingly, the plug-in process does not occur when a plug component incompatible with the size of the socket, e.g. the benzyl-substituted amine 5, is employed. A similar system, in which the chemical stimuli provided by counterions are used to achieve switching, has been reported [40]. The (9-anthrylmethyl) methylammonium cation [4H] + dissolves in CH2C12 as its hexafluorophosphate salt and threads through the cavity of dibenzo[24]crown-8 to form a pseudo-

H3C-... 3 Fi 8, 14,4, A molecular-level plu-socket system For energy transfer based on reversible add-base driven threadins-dethreadin8 motions in the hydrosen-bonded pseudo- -t- CF3SO3H Plug in + n-Bu3N Plug out 14.2 Chemically Ddven Movements [353 +N [3'4H] + -t- CF3SO3H -- NO complexation rotaxane [3.4H] + (CH2CI2, 298 K). Acid-driven threading oFcompound 5, incorporating a bulky benzyl group, through the macrocyclic cavity oF3 does not occur [37a]. rotaxane. Such a pseudorotaxane can be dethreaded by addition of one equivalent of n-Bu4NC1 as a result of the formation of an ion pair between chloride ions and the -NH2 +- center incorporated in [4H] +. Rethreading of the molecular compo- nents can be performed by the further addition of one equivalent of n-Bu3NH + ions (as hexafiuorophosphate salt) which compete with [4H] + to bind chloride ions. All processes can be followed by changes in the luminescence properties of the solution and the cyde can be repeated several times on the same system, be- cause tertiary and quaternary ammonium ions do not compete with [4H] + in its association with dibenzo[24]crown-8. Such a chemical system can also be viewed as a fluorescent chemosensor for species as different as protons, amines, and chloride ions. These kinds of multi-mode molecular device, that can be operated by either acid-base or anionic stimuli, are expected to prove useful for information processing, e.g. for the construction of molecular-level logic gates (Chapter 9). Thread-like dimeric pyridylpyridinium dications, in which the aromatic units are linked by a long alkyl chain, have been used as guests for -cydodextrin [15, 41]. In this system the formation of a pseudorotaxane in aqueous solution is driven by hydrophobic interaction between the aliphatic chain and the lipophilic cavity of -cyclodextrin. It has been shown that the pseudorotaxane can be partially dethreaded by protonating the two basic nitrogen atoms of the terminal pyridyl units of the thread. This response can be explained by the decrease of the hydro- phobic character associated with the alkyl chain in the protonated guest.

14 Threading-Dethreading Movements Thread-like species containing both z-electron acceptor and hydrogen-bonding recognition sites have been prepared and used to generate multicomponent pseu- dorotaxanes of different stoichiometry that, in their turn, can be used to construct acid-base-controlled molecular machines with a complex pattern of dethreading- rethreading motions [36c]. Acid-base-controlled assembly and disassembly of a triply threaded two- component superbundle has recently been reported [42]. The system (Fig. 14.5) consists of the tritopic receptor 6 in which three benzo[24]crown-8 macrorings are fused on to a triphenylene core and the trifurcated trication [7H3] 3+ wherein three dibenzylammonium ions are linked to a central benzenoid core. The intense fluo- rescence emissions of the two recognition components are quenched on associa- tion, with the concomitant appearance of a lower energy, broad fluorescence band originating from [z. � � z] stacking in the 1:1 adduct of the aromatic cores in the two matching components. Titration experiments, including Job plots, establish the 1:1 stoichiometry of the adduct, an observation which is also confirmed by electro- chemical experiments. In acetonitrile solution dethreading-rethreading of the 1:1 adduct can be controlled quantitatively by addition of base and acid. This system is an outstanding example of a supramolecular entity based on a triple cooperative binding motif that can be switched on and off by chemical stimulation [42, 43]. As we will see in Section 15.3.2, the system shown in Fig. 14.5 can be used as the starting point in the construction of a molecular lift. Cucurbit[6]uril is a hexameric macrocyclic compound self-assembled from an acid-catalyzed condensation reaction of glycouril and formaldehyde [10, 44]. It has a cavity of 5.7 A diameter, accessible from the exterior through two carbonyl laced portals of 4A diameter. Cucurbit[6]uril forms very stable 1:1 host-guest com- plexes with protonated diaminoalkanes [10, 44, 45], because of charge-dipole and hydrogen-bonding interactions between the protonated amino group and the portal carbonyl groups, and hydrophobic interactions between the internal methylene units and the inside wall of the cavity. When appropriate triamine compounds are used as molecular threads, the position occupied by the cucurbituril macro- cycle along the thread can be controlled by changing the pH of the solution [46]. Pseudorotaxanes of this type, which behave as pH-driven molecular shuttles, will be described in Section 15.3.2.3. Cucurbituril-based pseudorotaxanes with terminal 3-pyridyl moieties coordinate Cu 2+ ions, giving rise to 2D polyrotaxanes (molecular necklaces) which, in the presence of oxalate ions, connect to form large 2D

hexagonal arrays [47]. Interestingly, cucurbituril has also been used to cap poly(propyleneamine) dendrimers decorated with protonated diaminobutane units in the periphery. The generation-five dendrimer contains 64 beads threaded at the periphery, which form a rigid shell [48]. All or a part of the beads can be deth- readed by addition of a base, which provides the possibility of opening-dosing the dendrimer shell. The interaction of cucurbituril pseudorotaxanes with bio- molecules such as DNA has been investigated [49] and new cucurbituril homologs which contain 5, 7, 8, and 10 glycoluryl units have been reported [50]. The proper- ties of the heptameric and octameric homologs, which are equivalent to fi- and 7-

14.2 Chemically Driven Movements [355 =:z+ + ,.t-

356 14 Threading-Dethreading Movements cyclodextrins, respectively, in terms of the cavity size, are being explored (Section 14.3) [51]. 14.2.3 Systems Based on Donor-Acceptor Interactions As an alternative to metal coordination and [N+-H ... O] hydrogen-bonding inter- actions, the stabilization that occurs between z-electron donor and z-electron acceptor species, often aided and abetted by [C-H... O] hydrogen-bonding in- teractions, is a means of template direction which has been used extensively to produce threaded superstructures. In the last few years several complexes with pseudorotaxane geometry have been prepared by self-assembly of a z-electron-rich thread-like component such as 9 and a z-electron deficient macrocyde [1, 4, 6, 12, 14-16, 22-25, 52] such as the tetracationic cyclophane cydobis(paraquat-p- phenylene) 84+ (Fig. 14.6a). Similarly, pseudorotaxanes in which a linear melectron deficient species, e.g. the 1,1'-dibenzyl-4,4'-bipyridinium dication 112+, threads through the cavity of a z-electron-rich macrocyde such as 1,5-dinaphtho[38]crown- 10 (10) (Fig. 14.6b), have been characterized [1, 4, 6, 12, 14-16, 22-25]. Computa- tional modeling of complexes of the tetracationic cydophane 84+ has also been performed [53, 54]. a + N.II,N+ 9 [8'9] 4+ b h 9 + - 10 112+ [10'11] 2+ Fig. 14.6. Formation of the pseudorotaxanes [8.9] 4+ and [10.11] 2+ incorporating 2z-electron rich and 2z-electron deficient components [4].

+ 2H + 3 JU 12 2+ 14.2 Chemically Driven Movements [357 [10.12] 2+ +2 Il12 Fi�. 14.7. Schematic representation oCthe amine-acid- controlled dethreadin�-rethreadin� cycle of the pseudorotaxane [10.12] 2+ (CH3CN, 298 K) [55]. The 2,7-dibenzyldiazapyrenium dication 122+ sdf-assembles in solution with crown ethers, e.g. 10, to give pseudorotaxanes (Fig. 14.7, process 1), as shown by a variety of techniques, including absorption, luminescence, and H NMR spec- troscopy [55]. The dication 12 2+ can also form adducts with aliphatic amines, pre- sumably as a result of charge-transfer interactions and, possibly, also because of hydrogen-bonding to the acidic s-protons of the dication. This affinity has been exploited chemically to drive the dethreading of its pseudorotaxane with 10. In fact, on addition of a 20-molar excess of n-hexylamine to a CH3CN solution of the pseudorotaxane, profound absorption and luminescence spectral changes are observed, which indicates that the free crown ether and the adduct between 12 2+ and the amine are formed (process 2). The dethreading can be reversed quantita- tively (process 3) by addition of a stoichiometric amount (with regard to the added amine) of CF3CO2H to the solution. Despite its structural similarity to 12 2+ the 1,1'-dibenzyl-4,4'-bipyridinium dica- tion, 112+, does not interact with amines. This observation has led to extension of the above system to one in which the amine-acid chemical inputs select which of two thread-like species enters the cavity of the macrocyde and can cause reversible interchange to occur between the threads (Fig. 14.8) [56]. The disassembly of pseudorotaxanes composed of 122+ and aromatic crown ethers by aliphatic amines has been coupled with the possibility of dethreading the same systems by protonation of the crown ether in nonpolar solvents. It has been shown [57] that the pseudorotaxane formed by 122+ and 2,3-dinaphtho[30]crown- 10 in CH2C12 can be dethreaded by addition of r-Bu3N and reassembled by addi-

10 112+ 12 2+ [10-12] 2+ + 2H + + 2 IH 2 [10.11] 2+ Fig. 14.8. Reversible amine-add-controlled interchange of the two threads '112+ and 12 2+ into the cavity of macrocycle 10 [56]. tion of protons. The same result can be obtained by reversing the order of the two chemical inputs, i.e. dethreading can be achieved by protonation of the crown ether cavity and rethreading can be achieved by addition of n-Bu3N. All these processes are accompanied by on/off switching of easily monitorable changes in the absorp- tion and luminescence spectra, in particular of an intense fluorescence band, characteristic of the aromatic crown ether, with a maximum at 343 nm. It is worth emphasizing that these results contrast with the usual behavior of chemical sys- tems that either remain unchanged or undergo very different changes on addition of reactants of opposite chemical types, e.g.

amines and acids. An important consequence of this behavior is that the input-output relationships of the system correspond to those of the XOR (eXclusive OR) logic operation (Fig. 9.12, Chapter 9). This development shows that carefully designed dual-mode chemically-driven molecular machines are potentially useful for information processing. The assembly of complexes based on electron-donor-acceptor interactions can be controlled by means of redox stimuli which can be provided by addition of oxidants and reductants. The inclusion complex formed between the electron-acceptor cydophane 84+ and the wall-known electron-donor tetrathiafulvalene (TTF), and pseudorotaxanes composed of 84+ and thread-like species containing a tetrathiafulvalene unit, can be disassembled [58] into their free components by oxidation of the tetrathiafulvalene unit to its radical cation with one equivalent of Fe(C104)3 in acetonitrile or aqueous solution. The one-electron oxidized form of the TTF unit is stable under such conditions and can be reduced back to its neutral form by adding a stoichiometric amount of ascorbic acid. This reduction results in the insertion of the tetrathiafulvalene unit into the tetracationic cydophane. Dethreading can also be achieved by adding o-chloroanil, which forms an adduct with the TTF unit; on addition of Na252Os in the presence of water o-chloroanil is reduced, affording the original pseudorotaxane [58c]. Such dethreading-rethreading processes can be easily monitored by UV-visible absorption spectroscopy, because: � the complex has a broad absorption band with a maximum at 850 nm, ascribed to the charge-transfer interaction between the electron-rich tetrathiafulvalene unit and the electron-poor bipyridinium units of 84+, � the neutral and cationic forms of the tetrathiafulvalene unit have very different absorption features. A system of this kind can, moreover, serve as a basis for the construction of a supramolecular device in which it is possible, by means of chemical stimuli, to select which of two guests enters the cavity of a macrocycle, and to interchange the two guests reversibly (Fig. 14.9) [56]. Addition of the thread-like compound 9, which contains a z-electron-rich dioxynaphthalene unit, to an aqueous solution of the [8.TTF] 4+ complex affects neither the charge-transfer absorption band characteristic of the complex nor the strong fluorescence band of the dioxynaphthalene-based thread 9, indicating that this thread does not displace TTF from inside the macrocydic host. On addition of a stoichiometric (with regard to TTF) amount of Fe(C104)3 the absorption bands of the radical cation TTF + are formed, the charge-transfer band of [8.TTF] 4+ disappears, and the fluorescence band of the dioxynaphthalene-based species 9 is substantially quenched. These results show that oxidation causes expulsion of TTF + from 84+ and its replacement by the dioxynaphthalene-based thread. On subsequent addition of ascorbic acid the sys- tem returns to its initial state. 359 Fig. 14.9. The chemically redox-induced interchange of guests 'l-rF and 9 into the cavity of cyclophane 84+ [56].

36o I 8 4+ 14 Threading-Dethreading Movements Another way of controlling association between the cyclophane 84+ and thread- like guests containing electron-donor units takes advantage of the electrostatic repulsion that arises when a positive charge is created in the vicinity of the tetra- cationic cydophane. For example, the pseudorotaxane composed of 84+ and a molecular thread, incorporating in its middle a dioxybenzene unit and terminated at each end by [12]crown-4 rings, is dethreaded readily in acetonitrile solution on addition of excess alkali metal salts such as NaPF6 or LiPF6 [59]. These changes are a response to the electrostatic repulsion between the alkali metal cation within the [12]crown-4 macrocycles and the tetracationic cydophane. The dethreading of the pseudorotaxane can be followed visually by monitoring the decrease in the inten- sity of the charge-transfer absorption band characteristic of the pseudorotaxane. The same strategy can be employed to design a device where not only the de- threading of the system but also the replacement of a thread with another can be controlled by chemical stimuli provided in the form of alkali metal cations (Fig. 14.10). The [18]crown-6 derivative 13, carrying a 1,5-dioxynaphthalene moiety, is a ditopic compotmd that can act as a host for alkali metal cations and as a _Or-XOH 13 14 [8 � 13] 4 + + K + Repulsion [8.14] 4+ Fig. 14.10. The metal ion-controlled competition in acetonitrile at 298 K between the two thread-like species 13 and 14 for the cavity oftetracationic cyclophane 84+ [60].

14.2 Chemically Driven Movements guest for 8 4+, in this latter circumstance with the formation of a pseudorotaxane [60]. In CH3CN the [8.13] 4+ species is not affected by the presence of the 1,4- dioxybenzene-containing thread 14, whereas it dethreads on addition of K + ions, because of electrostatic repulsion between the bound potassium cation and the 84+ tetracation, which is then free to host within its cavity the neutral thread 14, thus forming the pseudorotaxane [8'14] 4+. Because the exchange of guests causes the color of the solution to change from purple to red-orange, this molecular machine can also be regarded as a metal-controlled chromophoric molecular switch. The exchange processes occurring in these supramolecular systems can also be moni- tored by H NMR spectroscopy. Although exploitation of the electrostatic repulsion exerted by positive charges to dethread pseudorotaxanes is a promising strategy, if metal cations are used to provide such positive charges problems with the reversibility of the system (Sec- tion 10.4.3) can be expected, because of the difficulty of removing the bound metal cations to achieve rethreading. For this reason acid-base reactions are preferred, owing to their reversibility and simplicity. The pseudorotaxane [8.15] 4+, which comprises a dioxybenzene-containing thread 15 terminated by t-butylaniline groups, has been self-assembled in acetonitrile solution (Fig. 14.11). In this supra- molecular system, protonation of the nitrogen atoms of the thread with CF3 CO2H results in the complete dethreading of the pseudorotaxane [61]. Addition of i-Pr2NEt, which acts as a base, brings back to the original equilibrium, restoring the pseudorotaxane. Other very interesting systems are those in which the bead- and wire-type com- ponents are covalently linked to form a scorpion-like structure. An example is given by compound [16H] 2+ (Fig. 14.12a) [62] which is sdf-complexed in CH2C12 solution because of: � the donor-acceptor interaction between the 1,5-dioxynaphthalene electron donor and the bipyridinium electron-acceptor moiety, � the more favorable environment offered to the dication by the macrocycle oxygen atoms compared with the non-polar solvent molecules. / 'L .,-J O- + CF3C022 [8 � 15] 4+ FiB. 14.11. The add-base controlled dethreadin-rethreadin motions oCthe pseudorotaxane [8.15] 4+ in acetonitrile at 298 K 84+ H q' 361 [15H2] 2+

14 Threading-Dethreading Movements in-[16H] 2+ out-[16H] 2+ b + n-Bu3N + CF3CO2H in-[16H] 2+ out_16 + Fi�. 14.12. (a) The scorpion-like compound [16H] 2+ is threaded in CH2CI2 solution and alethreaded in CH3CN solution, (b) The base-acid driven dethreadin�-rethreadin� process of [16H] 2+ in dichloromethane solution [62], In the more polar solvent CH3CN , however, dethreading occurs, as indicated by the disappearance of the charge-transfer band at 510 nm and the partial restoration of 1,5-dioxynaphthalene fluorescence. In dichloromethane solution, furthermore, dethreading can be achieved by addition of tributylamine, and the process can be reversed quantitatively by adding trifluoroacetic acid, as shown

schematically in Fig. 14.12b. The base-acid driven dethreading-rethreading cycle has been used to trigger the complexation of an external electron-acceptor guest, 172+, into the macrocyclic cavity of 16 +, as shown schematically in Fig. 14.13 [62]. A pseudorotaxane structure is also formed by macrocycle 18, which con- tains bis(2,5-dimethylpyrrolo[3,4-d])tetrathiafulvalene (BPTTF) and 1,4-dimethoxy- benzene electron-donor units, and the electron acceptor 2,7-dimethyldiaza- pyrenium 192+ (Fig. 14.14) [63]. In acetonitrile solution addition of Fe(C104)3 causes oxidation of the BPTTF unit of the macrocycle; this process is followed by dethreading because: � the electron donor properties of BPTTF (and the consequent charge-transfer stabilization of the pseudorotaxane structure) are cancelled on oxidation,

l?a+ /-[15H] 2+ 14.2 Chemically Driven Movements [363 + n-Bu3N out-16 + Fig. 14.13. + CF3CO2H [out-16.17] 3+ Base-add control of the complexation of 172+ by compound 16 + [62], � strong Coulombic repulsion arises between the two positively charged compo- nents of the structure. The changes in the absorption spectra show that BPTTF is first monooxidized and then dioxidized. Dethreading can be easily followed by monitoring the com- plete recovery of the intense fluorescence of 19 2+. After dethreading, addition of Ag powder causes reduction of the oxidized BPTTF unit and rethreading. It is worth noting that the changes in fluorescence properties that occur on for- mation of pseudorotaxanes based on donor-acceptor interactions can be exploited for sensory purposes [15, 64]. + Fe(C104)3 + Ag [18.19] 2+ 18 + 192+ Fig. 14.14. Chemically redox-induced dethreading-rethreading of pseudorotaxane [18.19] 2+ [63].

3641 14 Threading-Dethreading Movements 14.3 Electrochemically Driven Movements Electrochemical methods have been used extensively to control molecular recogni- tion [1, 12, 15, 16, 22, 65-69]. As discussed in Section 10.3.3, electrochemical techniques can be used not only to induce chemical or conformational changes in supramolecular systems but also to probe their superstructures and organization. In other words, electrochemistry gives us a handle on both the input stimuli and the readout signals that are necessary for monitoring the operation of molecular machines. Key features of the systems that can be electrochemically controlled are: � the presence in one component of an electroactive unit characterized by revers- ible redox processes; � the effect of the other component on the electrochemical behavior of the component containing the electroactive unit. This second property enables investigation of the complexation-decomplexation process by, for example, voltammetric techniques. Cydodextrins [70] are a dass of hosts that are inactive electrochemically yet can form stable pseudorotaxanes with a variety of electroactive guests [15, 17, 67, 69, 71]. It has been found, for example, that whereas bipyridinium-containing compounds in the dicationic forms (e.g. 202+, Fig. 14.15) are not bound by fi- cyclodextrin (fi-CD), when reduced to their monocationic forms they interact weakly with the cavity of this host and give fairly stable pseudorotaxane complexes with fi-CD when they are finally reduced to their uncharged forms [72]. Similar results have been found for cobaltocenium derivatives, which do not interact with cyclodextrins yet become good guests for inclusion in fi-CD upon one-electron reduction to yield the neutral cobaltocene [73]. Ferrocene and its derivatives [74] and tetrathiafulvalene (TTF) [75] behave in the opposite manner, i.e. they are strongly bound in their most stable oxidation states, which correspond to uncharged species, but when they are oxidized they are not bound. These features have been exploited to construct dendrimers with redox-controllable multisite fi-CD +e- _ + HQ 02 202+ Fig. 14.15. The electrochemically-induced threading- alethreading processes oFthe thread 202+ into the cavity o�fi- CD [721. +e- L6'-CD - 20]

14.3 Electrochemically Ddven Movements complexation offi-cydodextrin, because the dendrimers contain up to 16 ferrocene units [76] or up to 32 cobaltocenium units [77] on their peripheries. Such den- drimers form very large supramolecular architectures that can be either broken apart, or assembled, on oxidation of the ferrocene units or on reduction of the cobaltocenium units, respectively. Very recently ferrocene has been used as the core of water-soluble dendrimers containing glucopyranosyl residues in the branches. In these compounds the ferrocene unit is indeed complexed by fi-CD, but only if only one of its two cyclopentadienyl rings bears a dendritic substituent [78]. The cyclodextrin-ferrocene binding motif has also been exploited to achieve recognition on surfaces [79] and, more recently, on nanopartides [80]. Similar investigations have been performed on calixarenes, another impor- tant dass of electroinactive receptor [81]. In CH2CI2 solution the tris(N- phenylureido)calix[6]arene 21 can complex the molecular thread 1,1'-dioctyl-4,4'- bipyridinium dication 222+ in a pseudorotaxane-type fashion

(Fig. 14.16) [82] with an association constant exceeding 106 L tool -. The pseudorotaxane species are stabilized by [...] stacking, [C-H... �] hydrogen bonding, [C-H...] interac- 365 Dethreading -I- (Re)threading [21-22] 2+ Fig. 14.16. The electrochemically-induced dethreading- rethreading processes associated with the pseudorotaxane [21.22] 2+ [83]. 222+

14 Threading-Dethreading Movements tions, and, interestingly, by hydrogen-bonding interactions between the counter- anions of the dicationic guest and the N-H ureido groups of the host. Inclusion of 222+ within 21 causes a large shift of the first reduction potential of 222+ towards more negative values; the second reduction process, however, occurs at the same potential as for the free thread, indicating that one-electron reduction of the thread promotes dethreading (Fig. 14.16) [83]. Oxidation of the radical cation 22 + back to the dication leads to rethreading. Cyclic voltammetric studies and stopped-flow absorption experiments suggest that for this species the (re)threading process is relatively slow (kth 3 x 105 L mol - s - at 298 K). H NMR studies [84] indicate, moreover, that in nonpolar solvents the insertion of 222+ into the cavity of 21 occurs exclusively through the rim bearing the ureido groups; this observa- tion suggests the possibility of designing pseudorotaxanes with unidirectional threading-dethreading motions [83]. Another family of redox-inactive receptors are the cucurbit[n]urils. Cucurbit[7]uril forms a pseudorotaxane-type complex with the 1,1'-dimethyl-4,4'- bipyridinium dication (methylviologen, MV 2+) in aqueous solution (Koss = 2.0 x 105 L mol -) [85]. This complex can be progressively destabilized by electro- chemical reduction of the bipyridinium guest to the radical cation (Koss 8.5 X 10 4 L mol -) and to the neutral form (Koss = 2.5 x 102 L mol-). Whereas dimerization of the methylviologen radical cation in water is prevented by its indusion in cucurbit[7]uril, it has been reported very recently that this process is greatly enhanced in the presence of the larger cucurbit[8]uril, which forms pseudorotaxane-type complexes of 1:1 and 1:2 stoichiometry with the methylviol- ogen dication and radical cation, respectively [86]. Thus, this system affords the interesting possibility of triggering the stoichiometry of a host-guest complex by redox control of the guest. One of the most extensively studied receptors in recent years has been the cyclophane 84+ (Fig. 14.6), which is a very efficient host for a wide variety of electron donating guests [4]. Because it is redox-active [87, 88], its binding capacity can be subjected to electrochemical control. Two bielectronic reduction processes are observed

for the tetracationic cyclophane 84+, the first corresponding to the uptake of the first electron by each of the equivalent bipyridinium units and the second to the subsequent reduction of radical cations to neutral units. When an electron-donor unit is located inside the cavity of the cyclophane the potential associated with the first reduction process is shifted to more negative values, as a consequence of the charge-transfer interactions with the two bipyridinium groups of 84+ which stabilize the complex [68, 87-90]. The second reduction process at more negative potentials observed for this cydophane is very important because it can be used to monitor the occurrence of decomplexation induced by the first two- electron reduction [15, 68]. For example, in the presence of excess of a thread-like compound composed of a polyether chain which bears a 1,4-dioxybenzene unit in the middle, the potential value for the first bielectronic reduction of 84+ is shifted cathodically, whereas the second reduction process is almost unaffected [87]. This observation is consistent with formation of a pseudorotaxane between the cyclo- phane and the thread, and dethreading of the pseudorotaxane upon two-electron reduction of the 84+ host, so that the second two-electron reduction process reflects that of the free host. The occurrence of the dethreading reaction is not surprising, because reduction of the electron-acceptor component weakens the charge-transfer interaction that helps to hold together the components of the supramolecular architecture. Because a]] these processes are reversible, oxidation of 8 back to the tetracationic form affords the original pseudorotaxane. It should, in principle, also be possible to obtain useful information about the occurrence of dethreading-rethreading pro- cesses from the electrochemical behavior of the guest; the poor reversibility of the oxidation process associated with a 1,4-dioxybenzene unit, however, prevents the use of this type of control. More interesting are pseudorotaxanes wherein both the cyclophane and thread components are characterized by chemically reversible redox processes; one example is the complex of tetrathiafulvalene (TTF) with 84+ [58a, 90] and related pseudorotaxanes [58]. This improvement in design not only enables monitoring the formation of the supramolecular species by studying both the reduction of the electron-acceptor component and the oxidation of the electron-donor species, but also provides a dual mode (reductive and oxidative) of control on the dethreading-rethreading process. The molecular thread 23, obtained by attaching two polyether chains to a TTF unit (Fig. 14.17), forms a very stable (Kass = 5 x 105 L mol - in CH3CN) pseudo- rotaxane with 84+ [58a]. Although the TTF unit in 23 retains the same electron- donor power of unmodified tetrathiafulvalene, as revealed by comparing their voltammograms, the Kass value for the complex [8.23] 4+ is 50 times higher than that for the complex [8.TTF] 4+, indicating that the presence of the polyether chains strengthens the association, because of hydrogen bonding between the oxygen atoms in the chain and the hydrogen atoms in positions to the nitrogen atoms of the bipyridinium units. This cooperative interaction is extremely important in improving the on/off switching. Reversible dethreading-rethreading cycles of the pseudorotaxane [8.23] 4+ (and of [8.TTF] 4+) can be performed either by oxida- tion and successive reduction of the electron-donating thread or by reduction and successive oxidation of the electron-accepting cydophane [58a]. Such processes are accompanied by pronounced spectral differences that can be followed easily with the naked eye, because the solution changes color from the emerald green typical of the pseudorotaxane to either brown or deep blue on oxidative or reduc- rive dethreading, respectively. This unique behavior makes this system appeal- ing for the construction of electrochromic display devices and, because its input (electrochemical)-output (color) characteristics correspond to those of the XNOR (eXclusive NOR) logic operation, for the design of molecular-level logic gates (Sec- tion 9.4.8). The cyclic voltammetric behavior on oxidation of this system is, more- over, scan-rate dependent, which indicates that the dethreading-rethreading pro- cesses (Fig. 14.17) associated with the redox steps occur on the timescale of the electrochemical experiment. It is therefore possible to obtain the rate constants for the processes involved by digital simulation of the experimental voltammetric pat- terns [69]. In suitably designed compounds charge-transfer interactions can give rise to

368 I 14 Threading-Dethreading Movements Dethreading +2e- I [8 � 23] 4+ (Re)threading + N.IC.N + 84 +)r'OH 'O.. S 23 - 2- Dethreading -t- Fig. 14.17. The electrochemically-induced dethreading- rethreading processes associated with the pseudorotaxane [8.23] 4+ [55a]. intramolecular pseudorotaxane structures. An example is compound in-244+ (Fig. 14.18), which incorporates a z-electron-deficient head and a z-electron-rich tail [91, 92]. In solution, the tail threads through the cavity of its own head, positioning the 1,5-dioxynaphthalene moiety between the two bipyridinium units [91]. This conformation is stabilized by [z...z] stacking interactions between the comple-

menta W z-electron-rich and z-electron-deficient aromatic units, and by [C-H � .. O] hydrogen bonding between the ct-bipyridinium hydrogen atoms and the polyether oxygen atoms. Consistently, the absorption spectrum recorded in acetonitrile at 298 K of in-244+ contains a band at 515 nm, which arises from charge-transfer interactions between the 1,5-dioxynaphthalene moiety and the sandwiching bi- pyridinium units. The absorbance of the charge-transfer band increases linearly

14.3 Electrochemically Driven Movements [369 ._O/--__Ri/ Rethreading in_244+ + 2e- Dethreading Fig. 14,18, The dethreading-rethreading of the electron-donor tail of the self-complexing compound 244+ can be induced electrochemically in acetonitrile solution by reducing-oxidizing the bipyridinium units of the electron-deficient head [91]. with concentration. This behavior is remarkably similar to that of a model self- complexed system bearing a bulky stopper at the end of the tail; the stopper prevents dethreading of the tail and so this model compound can exist only in a self-complexed conformation. The similarities between the absorption spectra of irt-244+ and this model compound indicate that the former also exists completely in its self-complexed conformation in solution. The cydic voltammogram of in- 244+ contains two reversible two-electron reduction waves at -0.35 and -0.71 V, respectively, relative to the SCE. A model tetracationic cydophane that does not incorporate the 1,5-dioxynaphthalene tail undergoes two consecutive two-electron reduction processes at -0.29 and -0.70 V, respectively. Thus the first reduction process occurs at a more negative potential for irt-244+ whereas the second reduc- tion process occurs at the same potential for both compounds. These observations indicate that the 1,5-dioxynaphthalene unit of irt-244+ is initially sandwiched (Fig. 14.18) between the two bipyridinium units, making their first reduction more dif- ficult. After addition of one electron to each of the two bipyridinium units, how- ever, the 1,5-dioxynaphthalene unit is expelled from the cavity of the tetracationic cydophane and the second reduction process is not affected by the presence of the z-electron-rich unit. Subsequent removal of the electrons previously injected in the bipyridinium units leads back to insertion of the tail into the cyclophane. This is an example of an artificial molecular machine in which both the input and the output are electrochemical [91].

3,o[14 Threading-Dethreading Movements Electrochemically controlled threading-dethreading of a ring-in-ring sdf- complexed system has also been reported [62]. A three-component supramolecular system composed of tetrathiafulvalene (TTF), which can exist in three stable forms, namely, TTF, TTF +, and TTF 2+, and two hosts, specifically the z-electron-accepting cydophane 84+ and the z-dectron- donating crown ether 10, can be switched reversibly between three distinct states by exercising dectrochemical control of the guest behavior of TTF, as described in detail in Section 12.4 [93]. The electrochemically induced molecular motion in pseudorotaxanes based on Cu(I) complexes [94] is quite similar to that occurring in rotaxanes and catenanes of the same family (discussed in Chapters 15 and 16). 14.4 Photochemically Driven Movements Stimulation by light is the most interesting way to power molecular-level machines (Section 10.3.2). Photons, like electrons, can be exploited both to causing changes ("writing") in chemical systems and to monitor ("reading") their states [1, 12, 14, 16, 18-20, 22-25, 95]. In general, systems of this type that have been reported so far can be subdivided into those relying on photoinduced electron-transfer pro- cesses, and those based on photoisomerization. Complexes such as [8.9] 4+ (Fig. 14.19) are primarily stabilized by z-electron Dethreading I ! Back hv electron transfer [8.9] 4+ Threading 8 4+ Fig. 14.19. Photochemical processes associated with pseudorotaxane [8.9] 4+ on excitation of its charge-transfer absorption band. The processes indicated by dashed arrows are unlikely to occur (see text).

14.4 Photochemically Driven Movements [371 donor-acceptor interactions. These interactions usually introduce new energy levels that cause the appearance of charge-transfer absorption bands, often in the visible region of the spectrum [57, 58, 87, 91]. Excitation in these bands leads for- mally to the transfer of an electron from the donor to the acceptor component and is, therefore, expected to destabilize the charge-transfer interaction responsible for self-assembly. Occasionally, furthermore, photoinduced electron transfer leads to the formation of charges of the same sign that repel each other and so contribute to forcing the molecular components apart. This simple approach to dethreading is, however, precluded, because back-electron-transfer, i.e. the deactivation of the charge-transfer excited state to the ground state, is much faster than the separation of the molecular components, a process which requires extended nuclear motions and solvation processes [96]. In some particular instances [97], laser flash photol- ysis experiments have been interpreted as indicating dissociation of a small fraction of the irradiated complex. To achieve light-induced dethreading of the [8.9] 4+ complex, a different approach was devised [91, 96a] which was based on the use of an external electron- transfer photosensitizer (P) and a reductant scavenger (Red) species (Fig. 14.20). The photosensitizer must be able to absorb light efficiently and have a sufficiently long-lived and reductant excited state, so that its light irradiation (process 1) in the presence of the pseudorotaxane will lead (process 2) to the transfer of an electron to a bipyridinium unit of the cydophane. The relatively fast back-electron- transfer from the reduced cyclophane component to the oxidized photosensitizer is prevented by the reductant which, if present in a sufficient amount (10 -3 mol L-i), intercepts the oxidized photosensitizer and regenerates (process 3) the original photosensitizer. Good candidates for the role of photosensitizer are 9-anthracenecarboxylic acid [98] and metal complexes [99] such as [Ru(bpy)3] 2+ whereas efficient reductant scavengers are triethanolamine and polycarboxylate anions, e.g. oxalate anions [100]. Under these conditions the persistent reduction of a bipyridinium unit of 84+ is achieved and the pseudorotaxane dethreads (process 4), as evidenced by absorption spectral changes and, more importantly, by the increase in the intensity of the 1,5-dioxynaphthalene fluorescence, which can only originate from free 9. Oxygenation of the solution, from which 02 was initially removed, reoxidizes the cyclophane back (process 5) to the tetracationic form, thereby promoting rethreading (process 6) with 9 as shown by the absorption and luminescence spectra. This system has been recently incorporated and operated in solid supports and surfaces (Section 14.5). Such a strategy has then been extended to second-generation pseudorotaxanes in which the metal-complex photosensitizer ("light-fueled" motor [101]) has been incorporated (Fig. 14.21) either into the thread [102, 103] or into the macrocycle [104] component. The construction of these "integrated" pseudorotaxanes is not an easy task and so careful design is of paramount importance before embarking on time-consuming and demanding synthetic work. The successful operation of such a molecular machine is the result of the appropriate choice of the functional units and their covalent linking into the thread and ring components to achieve the correct integration of functions and sequence of processes, and lack of interference

14 Threading-Dethreading Movements between the units. As in the molecular machine shown in Fig. 14.20 the deth- reading and rethreading motions of the pseudorotaxanes represented in Fig. 14.21 can be triggered by irradiation with visible light and by oxygenation of the solution, respectively; the motions can also be easily monitored by means of UV-visible absorption and luminescence spectroscopy. Once again the most important read- out signal is the intensity of the 1,5-dioxynaphthalene fluorescence associated with the free macrocycle 10 (Fig. 14.21a) or free thread 9 (Fig. 14.21b) components. It is worth noting that by means of a repeated sequence of deoxygenation and irradi- ation followed by oxygenation many dethreading-rethreading cydes can be per- formed on the same solution without any appreciable loss of signal until most of the reductant scavenger is consumed. It should also be remarked that systems which rely on this photosensitizer-scavenger strategy produce "waste" species resulting from the decomposition of the chemical reductant and oxidant. In this regard, the search for efficient molecular machines exploiting "deaff', reversible photochemical reactions (in other words, machines which use only light as an en- ergy supply) is of fundamental importance [18, 95, 105]. The well-known reversible trans-cis photoisomerization of the azobenzene group [106] has long been used to exert photocontrol on chemical systems, as is also discussed in other chapters of this book. Thread-like species containing a z-electron-rich azobiphenoxy unit such as trans-28 (Fig. 14.22) have been used in conjunction with electron-accepting hosts to obtain charge-transfer complexes with pseudorotaxane geometries. Compound trans-28 self-assembles with 84+ (Fig. 14.6) to give a pseudorotaxane (Koss = 470 L mol - in CH3CN at 298 K), as shown by H NMR spectroscopy in solution and X-ray crystallography in the solid state [107]. On irradiation at 360 nm of an equimolar acetonitrile solution of 84+ and trans-28, which are in part associated to give a pseudorotaxane superstructure, the -N=N- double bond isomerizes to the cis form and the pseudorotaxane dethreads. The trans isomer of the guest can be reformed and, as a result, rethreads inside the cyclophane, either on irradiation at 440 nm or by warming the solution in the dark. These photoinduced dethreading-rethreading motions have been monitored by H NMR spectroscopy and by careful photochemical studies, which have also shown that the photoisomerization efficiency of trans-28 is reduced considerably when it is encircled by the tetracationic cydophane. It is not clear whether such

reduced photoreactivity, and the lower affinity of cis-28 for 84+, are consequences of steric or electronic effects. Because of its excellent reversibility, a system of this type is of considerable potential interest for the development of molecular machines featur- ing photoinduced dethreading-rethreading motions. The efficiency of the self-as- sembly of the molecular components trans-28 with 84+ is, however, very low (vide supra). To improve the system the cydophane 274+, in which the bipyridinium units have been replaced (Fig. 14.22) by the more effective z-electron accepting 2,7-diazapyrenium units [56, 57, 108], has been used instead of 84+ as a host for trans-28. Also, because the 2,7-diazapyrenium unit has highly characteristic ab- sorption and luminescence bands, 274+ provides additional readout signals for the system. In fact, 274+ self-assembles very efficiently (Koss = 1.5 x 10 s L mol - in CH3CN at 298 K) with the trans isomer of 28, but it also interacts with the cis form

274+ HO,,_ trans-28 14.4 Photochemically Driven Movements [375 [27-trans-28] 4+ 440nm I I 360nm cis-28 [27. cis-28] 4+ Fig. 14.22. Controllable dethreading-rethreading processes, based on a trans-els photoisomerization reaction, of pseudorotaxane formed by self-assembly ofcyclophane 274+ and thread 28 in acetonitrile at room temperature [109]. (Ka** = 1 x 104 L tool - under the same conditions) [109]. The photochemical and chemical processes occurring in this system are shown schematically in Fig. 14.22. Although irradiation with light does not lead to 100 % dethreading, these photocontrolled dethreading-rethreading motions can be followed easily by ob- serving the change in fluorescence intensity characteristic of the uncomplexed macrocycle 274+. This system is fully reversible and powered only by light without production of any waste product. The trans-cis photoisomerization of the azobenzene group has also been used to achieve photoswitching of the association of a Janus pseudorotaxane dyad [110] and to design heterogeneous switchable systems (Section 14.5). An attempt to construct a photocontrollable pseudorotaxane-type system based on metal-ligand bonds [111] has recently been reported [112]. As illustrated in Fig. 14.23, the system consists of a [Ru(phen)2] 2+ fragment coordinated to a bipyridine ligand incorporated in a macrocycle. On excitation with light in acetonitrile solu- tion the macrocycle is released from the [Ru(phen)2] 2+ fragment. The reaction can

376 I 14 Threading-Dethreading Movements f,,...O-O.,... --2+ h ...'""0/'-0'"0..,,,.i Fig. 14.23. Photochemically-driven detachment of the [Ru(phen)2] 2+ fragment from a bipyridine-containing macrocycle and thermal back reaction [112]. , ' 2+ .-N=C-CH3 f.N" 'N_=C-CH3 be reversed by replacing CH3CN with ethylene glycol as a solvent and boiling the mixture for 2 h. Extension of this work includes replacement of the [Ru(phen)2] 2+ fragment with metal complexes with a well defined axis [113], which would enable the assembly of real pseudorotaxane structures. Photochemical chelate exchange, instead of simple chelate expulsion, is also under investigation [114], with the purpose of designing light-driven molecular machines. 14.5 Heterogeneous Systems The compounds discussed above have been studied in solution, in which each molecule behaves independently. Incoherence therefore remains a major impedi- ment to the design and realization of systems capable of performing useful func- tions. Despite this limitation the systems described illustrate a number of very interesting concepts concerning molecular-level movements controlled by external inputs. The problem of obtaining ordered arrays of molecular devices [115, 116] can be addressed by a variety of techniques. One can, for example, design systems like those illustrated in Fig. 14.24 in which either the thread or the macrocycle is immobilized on an appropriate solid surface. Interesting systems have been reported in which a fi-cydodextrin monolayer has been immobilized on gold electrodes to act as an active interface for the electro- chemical and microgravimetric transduction of an optical signals recorded by a bipyridinium-azobenzene guest [115b, c, 117]. If the surface is an electrode [118], it might be possible to induce a coherent dethreading-threading movement under electrochemical control. By using a semiconductor surface, it might be possible to sensitize light-induced processes. A general approach is provided by the emerging field of heterosupramolecular chemistry, in which molecular or supramolecular species are linked to nano- partides [119]. Confinement of molecular-level devices and machines in restricted environments such as those offered by porous materials [120] (e.g. zeolites [121]) can also be investigated. The ability to attach chemically driven molecular

Adsorption 14.5 Heterogeneous Systems I 377 Self assembly Solid surface / So' / p Adsorption 9 Solid surface / Fi�. 14.24. Serf-assembly o� pseudorotaxanes on solid supports by �raCtin� (a) a thread or (b) a macrocycle on a surface. Self assembly machines to solid supports would also facilitate supply of the chemical "fuel" and removal of the "exhaust" products. By following the strategy described in Fig. 14.24a, a pseudorotaxane-type com- plex has been assembled at a solid-liquid interface by use of an immobilized TTF derivative bearing a disulfide tail and the tetracationic cyclophane 84+ [122]. Cydic voltammetric studies showed that, similarly to the solution behavior of related systems (Section 14.3 [58, 90]), one-electron oxidation of the TTF unit leads to dethreading of the pseudorotaxane. It has recently been shown that the photochemically driven molecular machine illustrated in Fig. 14.20 can indeed operate on a solid support [123]. In a first instance, a sol-gel silica framework [120a] was condensed around the pseudo-rotaxane composed of cyclophane 84+ and a z-electron donor thread identical to 9 but lacking one -CH2CH20- unit on each arm, the photosensitizer (9-anthracenecarboxylic acid, ACA), and a sacrificial reagent (ethylenediaminetetra- acetate, EDTA). Irradiation of the resulting solid sample, under a N2 atmosphere, with 365-nm light led to spectral absorption changes indicative of reduction of 84+ and an increase in the fluorescence characteristic of the free dioxynaphthalene- containing thread. The latter signal indicates clearly that the pseudorotaxane has dethreaded [123]. After exposure to air for 12 h the emission intensity decreased to its initial level as a consequence of rethreading of the pseudorotaxane. Unfortu- nately, prolonged and localized irradiation led to decomposition of the molecular species. An alternative possibility is the assembly of this molecular machine on the sur- face of a solid support according to the approach illustrated in Fig. 14.24a. A modified dioxynaphthalene-containing molecular thread has been chemically linked on one side to the silanol groups on the surface of a silica sol-gel film [123]. Such a chemically modified film has an intense emission band with ;max = 344 nm, arising from the fluorescence of the dioxynaphthalene unit. On immersion of the film in an aqueous solution of 84+ for two days the emission intensity diminished to 4 % of its initial value. This is consistent with the formation of a pseudorotaxane structure on the film surface. The film was then soaked in an aqueous solution containing the photosensitizer (ACA) and the chemical "fuel" (EDTA), and subsequently irradiated at 365 nm for several hours. This procedure led to a slight increase in the luminescence intensity at 344 nm (up to 14 % of its initial value), as a result of both pseudorotaxane re-equilibration and photochemically induced dethreading [123]. The same results were obtained by chemical reduction of the 84+ component with NaBH4. Threading-dethreading cycles could be per- formed on the same film, but with progressive loss of reversibility. The threading of the dibenzylammonium cation into dibenzo[24]crown-8 (Sec- tion 14.2) has been exploited to assemble pseudorotaxanes at the surface of a nanocrystal [124] and to induce and control formation of aggregates of nanopar- tides (Fig. 14.25) [125]. It was shown that in chloroform-acetonitrile solution at room temperature aggregation of near size-monodisperse Ag nanocrystals stabi- lized by chemisorption of a mixture of thioIs 29 and 30 is initiated by addition of the bis-dibenzylammonium species [31H2] 2+. This behavior was attributed to the formation of pseudorotaxanes in which each ditopic thread [31H2] 2+ associates with two nanopartide-bound 30 species, thereby "gluing" them together. Subse- quent addition of excess dibenzylammonium cation, which occupies and inacti- vates the binding sites on the nanopartide surface, results in inhibition of aggre- gation. The same effect is obtained by adding excess dibenzo[24]crown-8, which competes with the nanopartides for binding of [31H2] 2+. The possibility of pH- triggering of aggregation, related to the acid-base controlled dethreading of hydrogen-bonded pseudorotaxanes (Section 14.2) was not explored. Other stimulating experiments arise from the possibility of investigating supra- molecular host-guest interactions by force spectroscopy on single molecules [126- 129]. As shown in Fig. 14.26, the tip of an atomic force microscope (AFM) could be chemically modified with a thread-like guest, and moved towards a surface bearing suitable macrocydic hosts, therefore acting as a nanoscopic "fishing rod". As the surface is approached (Fig. 14.26a) recognition between the host and the guest would lead, ideally, to formation of a single pseudorotaxane structure (Fig. 14.26b). At this point, retraction of the tip is expected to stretch the supramolecular sys-tem and eventually produce dethreading of the pseudorotaxane (Fig. 14.26c). For instance, the decomplexation between ferrocene moieties immobilized on atomic

29 .. SH O O O [o o IoSH 30 14.5 Heterogeneous Systems I 379 Ag + Ag Aggregate Fig. 14.25. A��re�ation of silver nanoparticles induced by pseudorotaxane formation [125]. force microscopy tips and fi-cyclodextrin receptors in highly ordered self-assembled monolayers on Au(111) has been studied [130]. The rupture force of individual ferrocene-cydodextrin complexes has been estimated as 56 q- 10 pN. Among the many factors that

must be taken into account in the design of such experiments, the molecular connection of the guest to the tip and of the host to the surface are of great importance in the production of ordered monolayers and to avoid direct interactions between the tip and the surface. To increase the chances of having a very small number of molecular contacts, or even a single contact, between the tip and the substrate, the chemical functionalities on the two approaching surfaces should, moreover, be appropriately diluted by careful engineering of the mono- layers.

380 I 14 Threading-Dethreading Movements b Fig. 14.26. Schematic representation of a "fishing rod" experiment on single pseudo- rotaxane species: (a) approach of an AFM tip to the substrate, (b) formation and stretching References I V. BALZANI, A. CREDI, M. VENTURI, Proc. NatL Acad. Sci. USA, 2002, 99, 4814. 2 J.-C. CHAMBRON, C.O. DIETRICH-BUCHECKER, J.-P. SAUVAGE, Top. Cttrr. Chem., 1993, 165, 131. 3 H.W. GtBSON, H. MARAND, Adv. Mater., 1993, 5, 11. 4 D.B. AMABtrtNO, J.F. STODDART, Chem. Rev., 1995, 95, 2725. 5 R. J;(GER, F. V6GTrE, Angew. Chem. Int. Ed. Engt., 1997, 36, 930. 6 M.C.T. FYFE, J.F. STODDART, gcc. Chem. Res., 1997, 30, 393. 7 F.M. RAYMO, J.F. STODDART, Chem. Rev., 1999, 99, 1643. 8 G.A. BREAULT, C.A. HUNTER, P.C. MAYERS, Tetrahedron, 1999, 55, 5265. 9 Molecular Catehanes, Rotaxanes and Knots (Eds.: J.-P. SAUVAGE, C.O. DIETRICH-BUCHECKER), Wi]ey-VCH, Weirrheim, 1999. 10 K. KtM, Chem. Soc. Rev., 2002, 31, 96. of a single pseudorotaxane supermolecule between them, and (c) dethreading of the molecular components during retraction of the tip. 11 P.R. ASHTON, D. PHILP, N. SPENCER, j.p. STODDART, J. Chem. Soc. Chem. Commun., 1991, 1677. 12 V. BALZANI, M. Gb)Ez-LbPEz, J.F. STODDART, gcc. Chem. Res., 1998, 31, 405. 1:) J.-P. SAUVAGE, Act. Chem. Res., 1998, 31,611. 14 V. BALZANI, A. CREDI, M. VENTURI, itl Supramolecular Science: Where It Is and Where It Is Going (Eds.: R. UNGARO, E. DALCANALE), Kluwer Academic Publishers, Dordrecht, 1999, p. 1. 15 A.E. KAIFER, ACt;. Chem. Res., 1999, 32, 62. 16 V. BALZANI, A. CREDI, F.M. RAYMO, j.p. STODDART, Angew. Chem. Int. Ed., 2000, 39, 3348. 17 A. HARADA, ACt;. Chem. Res., 2001, 34, 456. 18 R. BALLARDINI, V. BALZANI, A. CREDI, M.T. GANDOLFt, M. VENTURt, ACt. Chem. Res., 2001, 34, 445.

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387 15 Linear Movements 15.1 Introduction Linear-like movements are essential both in Nature and in technology. In Nature, movements related to intracellular trafficking, cell division, and muscle contraction are produced by protein linear motors [1-5]. In the artificial macroscopic world, most machines are powered by internal combustion engines working on the prin- ciple of linear alternating motion of a piston in a cylinder. Simple, artificial molecular-level systems capable of performing linear move- ments are not difficult to construct since the development of rotaxane chemistry [6-13]. Such artificial systems are completely different from natural linear motors not only structurally and functionally, but also because most of them can be pow- ered by photochemical or electrochemical inputs (vide infra). In this chapter we briefly illustrate the working principles of natural linear motors, and then we discuss artificial molecular-level machines based on rotax- anes. Both topics are currently the object of extensive investigations. 15.2 Natural Linear Motors Enzymes such as myosin, kinesin, dynein and their relatives are linear motors that move along polymer substrates converting the energy of ATP hydrolysis into mechanical work; myosin moves along actin filaments in muscle and other

cells, and kinesin and dynein along microtubules [1-4]. Motion is derived from a mechano-chemical cycle during which the motor protein binds to successive sites along the substrate in such a way as to move forward on average. In the last few years much progress has been made in elucidation of the moving mechanisms of natural linear motors, particularly of myosin [2, 14-19] and kine- sin [2, 20-26]. This progress has been made because, in addition to established physiological and biochemical methods, novel in vitro techniques have been devel- oped which combine optical and mechanical methods to observe the behavior of a single protein. The term myosin refers to at least 14 dasses of proteins, each containing actin-

Molecular Devices and Machines - AJourne,/into the Nano World. V. Ba]zani, A. Credi, M. Venturi Copyright � 2003 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim ISBN: 3-527-30506-8

based motors. Myosin is composed of two large heads, containing a catalytic unit for ATP hydrolysis, connected to quite a long tail. Myosin-II provides the power for all our voluntary motion (running, walking, lifting, etc.) and for involuntary mus- cles (e.g. beating heart). In muscle cells many myosin-II molecules combine by aligning their tails, each staggered relative to the next. Muscle cells are also filled with filaments of actin, which are used as a ladder on which myosin climbs (Fig. 15.1a). The head groups of myosin extend from the surface of the resulting fila- ment like bristles in a bottle brush. The bristling head groups act independently a Samomem "Thick" myosin filament ..... "Thin" actin filament b Optical trap Actin filament Optical trap Fig. 15.1. (a) Schematic representation of muscle protein fibers (feather shapes) with myosin molecules bound to the actin filament (shaded) or free (white). (b) Experimental geometry used to observe single myosin molecules binding and pulling an actin filament [14a]. The filament was attached at both ends to a trapped bead. These beads were used to stretch the filament taut and move it near surface-bound silica beads that were decorated sparsely with myosin molecules.

and provide the power to contract muscles. They reach from the myosin filament to a neighboring actin filament and become attached to it. Breakage of an ATP molecule then forces the myosin head into a radically different shape. It bends near the center and drags the myosin filament along the actin filament. This is the power stroke of muscle contraction. In a rapidly contracting muscle, each myosin head may stroke five times a second, each stroke moving the filament approxi- mately 10 nm. The working stroke of myosin-II has been observed [14a] by optical methods (Fig. 15.1b). An actin filament was bound at both end to a polystyrene bead, to form a dumbbell structure. Both beads were then optically trapped and the fila- ment was pulled taut and moved near surface-bound silica spheres that were coated sparsely with myosin molecules. Transient bead deflections parallel to the long filament axis were observed and interpreted as reflecting myosin binding and pulling the filament. These experiments could not resolve, however, some issues, e.g. the motor mechanism, which are still the subject of extensive investigation. Detailed studies have enabled the proposal of a model (Fig. 15.2) for the stepping kinetics of myosin-V which, unlike myosin-II, is a motor that moves progressively along its actin track transporting organelles [19]. Myosin-V dwells with both heads attached to the actin filament, the leading head with ADP and the trailing head in rigor (top left). ATP binding to the trailing head (step 1) promotes its dissociation from actin and forward movement (step 2) of the released head discharges intra- molecular strain; the previous leading head then becomes the trailing head. Note that the trailing head moves 72 nm to reach its new site of attachment, but this movement results in a 36-nm step only of the body of myosin-V or of any cargo attached to the cargo attachment domain. The new, detached leading head quickly hydrolyzes ATP (step 3) and then binds actin (step 4). Force generation follows either actin binding or phosphate release (step 5). At this point (bottom left) one finds the molecule in its kinetically dominant state, because subsequent ADP release (step 6) is slow. In this state both heads are bound to actin and ADP, the leading head in a prestroke-like configuration and the trailing head in a poststroke- like configuration. The leading head is stressed along this direction, an asymmetry that should promote subsequent ADP release to occur at the trailing head and not the leading head. Models of the motility cycles of kinesin have also been elaborated [2, 21, 22, 26, 27] and the movement of single kinesin molecules on microtubule tracks under different ATP concentrations and loads has been studied (Fig. 15.3). It has been found [20b] that: � a single ATP hydrolysis causes a mechanical advance of 8 nm; � the stall force depends on ATP concentration; � the maximum velocity decreases with increasing load. A puzzling problem is the mechanism of motion along tracks that do not have any chemical or electrical gradient. According to recent studies, kinesin moves by an "inchworm" mechanism, which implies that the two heads of kinesin remain

390 I 15 Linear Movements 1 ADP 2 ADP ADP I ~ 36 nm ADP ADP ADP ADP ADP Pi ADP 4 Fig. 15.2. Model for myosin-V stepping [19] (for details, see text). Optical tweezer Kinesin ATP,,,, ADP + Pi ?.,.. :, ...-, 8nm Fig. 15.3. A molecule okinesin modified with a microbead wanders along a microtube; shining the microbead by use o optical tweezers enables the orce to be measured [20b].

15.3 Linear Movements in Rotaxanes I 391 in a different environment (one always leading, the other always trailing) during continuous progressive movement [28]. Such a mechanism requires that only one of the two heads ofkinesin is an active ATPase during progressive movement. This unorthodox conclusion would call for re-evaluation of the mechanisms proposed for other motor enzymes. Even if the precise mechanism of movement is not yet known, the fact remains that motor proteins generate force and transport cargo unidirectionally. Recon- stituting motor proteins in their active state ex-vivo was initially pursued to study the mechanism by which they generate force. More recently molecular shuttles based on kinesin and microtubules have been constructed by use of two different approaches - either the microtubules are fixed to a surface and kinesin is moving similar to cars driving on a highway and transporting kinesin-coated objects, or the kinesin is bound to the surface and the microtubules are propelled by the kinesin in a manner analogous to a linear motor [29, 30]. An interesting application of the second technique is a statistical approach to surface imaging using fluorescent microtubules moving as probe robots across a surface coated with kinesin [31]. 15.3 Linear Movements in Rotaxanes 15.3.1 Introduction A [2]rotaxane [6-13] (hereafter, simply called rotaxane) is a supramolecular species composed of a macrocyclic and a dumbbell-shaped component. The macrocycle encircles the linear rod-like portion of the dumbbell-shaped component and is trapped mechanically around it by two bulky stoppers. The two components cannot, therefore, dissociate from one another, even though they are not linked covalently. In a rotaxane the wheel component can rotate around or shuttle along the axis component (Fig. 15.4). Rotation of the wheel component is usually a spontaneous process; rotary motors based on rotaxanes are discussed in Section 13.4. If, during b Fig. 15.4. Schematic representation of the simple movements that can occur in a rotaxane.

39,[the template-directed synthesis of a rotaxane, location of two identical recognition sites within its dumbbell component can be arranged, the result is a degenerate, conformational equilibrium state in which the macrocyclic component sponta- neously shuttles back and forth along the linear portion of the dumbbell [32]. Compounds 14+ and 24+ are examples of rotaxanes that behave as degenerate molecular shuttles (Fig. 15.5) [32]. Several structural and kinetic studies have been devoted to examination of the slipping process (see also Section 14.1) [33]. A theoretical description of the shuttling process of the macrocycle in pep- tide rotaxanes has been reported [34]. The complicated classical motion has been reduced to a one-dimensional quantum-mechanically based motion. Starting from a simple model (double minimum potential), the average kinetic energies and rate constants have been obtained and, by use of the partition function, the free energies of activation have been calculated. The picture that emerges has many Fig. 15.5. Examples of rotaxanes that behave as degenerate molecular shuttles [32].

similarities with that of a cart rolling along a roller coaster shaped like a double minimum potential. At energies below the transition state the cart/macrocyde sits around one of the two minima. When its energy is barely sufficient to overcome the barrier it spends the longest time passing over it and the greatest probability is that of finding it at or near the top of the barrier. When the energy is much higher, the turning points, where the classical particle must slow down, are where it is preferentially located. The mechanical analogy cannot, however, be carried too far because the barrier heights (10 kcal mol -) indicate that kinetics is not only a matter of diffusion [34]. When the two recognition sites ("stations") in the dumbbell component differ in their constitution, a rotaxane can exist as two different equilibrating conformations the populations of which reflect their relative free energies as determined primarily by the strengths of the two different sets of noncovalent bonding interactions. In the schematic representation shown in Fig. 15.6 it has been assumed that the molecular shuttle resides preferentially in "state 0" until a stimulus is applied that switches off the stronger of the two recognition sites, thus inducing the macrocyde to move to the second weaker recognition site, "state 1". In appropriately designed rotaxanes this nondegenerate process can be controlled reversibly by use of chemical, electrochemical, or photochemical stimuli [9-

13, 35-51]. Protonation- deprotonation, oxidation-reduction, and other reversible processes can be ex- ploited to alter reversibly the stereoelectronic properties of one of the two recogni- tion sites, thus affecting their relative capacities to sustain noncovalent bonds. By switching off and on again the recognition properties of one of the two recognition sites, the relative proportions of the two species can be controlled reversibly. These kinds of controllable molecular shuttle can be self-assembled by use of one of a number of different template-directed synthetic strategies which indude thread- ing-capping, slipping, and dipping procedures [6-13]. The controlled shuttling movement is interesting not only mechanically, but also for information-process- ing (binary logic). 15.3.2 Chemically Driven Systems 15.3.2.1 Rotaxanes Based on Metal Complexes Metal complexes have been extensively used as templates to obtain rotaxanes [6, 13]. A unique feature of this approach is that the template can easily be removed at the end of the synthesis whereas, in other strategies based on organic fragments, interaction between the template and the components of the final rotaxane struc- ture is usually maintained. The presence of the metal ion, however, is essential for obtaining controlled movements. An exciting development in the field of linear artificial molecular machines has been the construction of a rudimentary molecular-scale muscle [42, 52, 53]. The idea [52] starts from the topology of a pseudorotaxane dimer which, when suitably designed, can undergo contraction and stretching movements, as shown schemat- ically in Fig. 15.7. The synthesized system ([3.3.Cu2] 2+, Fig. 15.8) is a rotaxane

a 15.3 Linear Movements in Rotaxanes I 395 b Expanded Contracted Fig. 15.7. Expansion-contraction of (a) a natural muscle, and (b) a pseudorotaxane dimer [52]. dimer [54] that contains two Cu(I) metal ions and two identical ring-and-string components 3 [52]. Each component 3 consists of a ring containing a bidentate phenanthroline-type unit, and a string containing a bidentate phenanthroline, a terdentade terpyridine and a bulky stopper unit. Each of the two Cu(I) metal ions present in the rotaxane dimer is coordinated to two bidentate chelates, because Cu(I) prefers a four-coordination arrangement. Under these conditions, the system is "extended" (length 8.3 nm, estimated from a CPK model). On electrochemical oxidation of Cu(I) it was expected that the system would contract, because Cu(II) prefers a five-coordination arrangement and should, therefore, be surrounded by a bidentate and a terdentate ligand. This change in the coordination environment had, in fact, been previously observed for rotaxanes and catehanes of the same family (vide infra) [36, 42, 43, 45]. In [3.3.Cu2] 2+, however, electrochemical oxidation has apparently no effect; contraction can be obtained (Fig. 15.8) by extraction of Cu(I) with a large excess of KCN (CH2C12-H20, room temperature) and successive remetalation of the [3.3] free ligand with Zn(NO3)2 (CH2C12-CH3OH). Both demetalation of [3.3.Cu2] 2+ and remetalation of [3.3] to obtain [3.3.Zn2] 4+, the length of which is estimated to be 6.5 nm, were quantitative. The transformation of the contracted [3.3.Zn2] 4+ species to the extended [3.3.Cu2] 2+ species could be achieved by addition of [Cu(CH3CN)4][PF6] in CH2C12-CH3CN [52]. We would like to recall here two artificial systems completely different, but functionally related to the one described above. Controlled and reversible telescopic extension of multiwall carbon nanotubes [55, 56] has been investigated. Repeated extension and retraction of telescoping nanotube segments, observed by high resolution transmission electron microscopy, revealed no wear or fatigue on the atomic scale, showing that nanotubes might constitute near perfect, wear-free surfaces [56]. Individual polymers containing photosensitive azobenzene units have been investigated by single-molecule force spectroscopy. On photoexcitation, lengthening and contraction of the individual polymers were observed, demonstrating optomechanical energy conversion in a single-molecule device [57].

[3- 3- Cu2] 2+ +CN- [3'3] + Zn(11) [3 � 3. Zn2] 4+ Fig. 15.8. The component 3 of the rotaxane dimer [3.3.Cu2] 2+ and the contraction of [3.3.Cu2] 2+ on demetalation and remetalation with Zn 2+ [52].

15.3.2.2 Rotaxanes Based on Hydrogen Bonds and Donor-Acceptor Interactions Rotaxane 4 4+ incorporates (Fig. 15.9) a z-electron-deficient cyclophane and a electron-rich dumbbell [58]. In solution the macrocycde resides around the benzidine or the biphenol recognition site. The two conformations are stabilized by [z... z] stacking interactions between the bipyridinium units of the macrocycde and the sandwiched z-electron rich recognition site of the dumbbell, and by [C-H... O] interactions between the ct-bipyridinium hydrogen atoms and the polyether oxygen atoms. The H NMR spectrum (CD3CN, 229 K) of this rotaxane has distinct signals for the two conformations. The ratio between them is 84:16 in favor of the isomer with the benzidine unit inside the cavity of the cyclophane. This selectivity is a result of the relative binding affinity [59] of the tetracationic cydo- phane for the two z-electron rich recognition sites. The association constant for a complex formed between the tetracationic cyclophane and a model benzidine guest is one order of magnitude higher than that for an equivalent complex incorporat- ing a biphenol guest. After the addition (Fig. 15.9) of CF3CO2D to a CD3CN solu- tion of the rotaxane, protonation of the benzidine unit occurs [58]. As a result the tetracationic cyclophane shuttles away from the newly formed dicationic unit to encirde exclusively the biphenol recognition site in [4D2] 6+. Consistently, the H NMR spectrum shows only signals of the isomer with the biphenol recognition site inside the cavity of the tetracationic cyclophane. On addition of CsDsN, the benzidine recognition site is deprotonated and the original equilibrium between the two conformations is restored. Rotaxane [SH] 3+ incorporates a dialkylammonium and a bipyridinium recogni- tion site in its dumbbell-shaped component (Fig. 15.10) [60]. Gradient-enhanced nudear Overhauser effect spectroscopy demonstrated that the macrocyde, namely a dibenzo[24]crown-8, resides exclusively around the ammonium recognition site in (CD3)2CO at 298 K. The preference of the macrocycle for the ammonium rec- ognition site is a result of a combination of [+N-H... O] and [C-H... O] interac- tions between the [CH2NH2 +] hydrogen atoms of the dumbbell and the oxygen atoms of the macrocycle. On addition of excess i-Pr2NEt to a (CD3)2CO solution of [SH] 3+, deprotonation of the ammonium recognition site occurs. As a result the intercomponent hydrogen bonds are destroyed and the macrocyde shuttles to the bipyridinium recognition site. The original conformation is restored by addition of CF3CO2H, because protonation of the ammonium recognition site is followed by the shuttling of the macrocyde back to encircle the [NH2 +] center. The shuttling process in this rotaxane is quantitative and can be followed by H NMR spectros- copy and electrochemical techniques. Combining the ideas of a trifurcated trication shown in Fig. 14.5 of Section 14.2.2 [61] with that of a two station dumbbell (vide supra) enabled the prepara- tion of the trifurcated compound [6aH3] 9+, which contains two stations in each of its three arms (Fig. 15.11a) [62]. Threading of [6all3] 9+ into the tritopic receptor 7, in which three benzo[24]crown-8 macrorings are fused on to a triphenylene p- [SH] 3+ + i-Pr2NEt 15.3 Linear Movements in Rotaxanes I 399 H + I +H + Fig. 15.10. The acid/base-controllable molecular shuttle [5H] 3+ [60]. 5 2+ core, yielded pseudorotaxane [7.6aH3] 9+ which was then converted into rotaxane [8H3] 9+ by functionalization with bulky groups. On the basis of the results obtained with the one-station trifurcated pseudorotaxane (Fig. 14.5 of Section 14.2.2) and rotaxane [SH] 3+ (Fig. 15.10), [8H3] 9+ is expected to perform as a molecular l on acid-base stimulation. Even more exciting is compound [9H3] 9+ which, in principle, could be mounted on a surface, as shown schematically in Fig. 15.1lb. In molecular shuttles containing in the dumbbell two equivalent peptide stations separated by a lipophilic methylene chain the position and the shuttling rate of the macrocyclic ring are affected by the nature of the solvent [63]. In CDC13, the ring shuttles between the two peptide stations on which it is stabilized by hydrogen- bonding interactions. On addition of 5 % CD3OD, however, the strength of hydro- gen bonding decreases and the shuttling rate increases from 8 s - to 2300 s -. In polar solvents the ring is positioned primarily at the lipophilic region. Solvent-induced localization of macrocycles in rotaxanes consisting of a polyurethane thread and a [30]crown-10 macrocycle has also been reported [64] and rotaxanes incorporating the potentially photoreactive cycloheptatrienyl station have recently been synthesized [65]. Finally, we would like to recall the interesting "rivetting" of two pseudorotaxanes containing semi-dumbbell-shaped components [66]. 15.3.2.3 Rotaxanes Based on Cucurbituril As discussed in Section 14.2.2, cucurbit[6]uril (usually called cucurbituril) forms very stable 1:1 host-guest complexes with protonated diaminoalkanes [67], because of charge-dipole and hydrogen-bonding interactions between the proto- hated amino group and the portal carbonyl groups, and hydrophobic interactions between the internal methylene units and the inside wall of the cavity. When appropriate triamine compounds are employed as molecular threads the posi- tion occupied by the cucurbituril macrocycle along the thread can be controlled by

400 I 15 Linear Movements N + O /) O O) Pseudorotaxane [7 -6all3] 9+ Rotaxane [8H3] 9+ Surface-mounted device [9H3] 9+ b H + H + [9H3] 9+ H + _ 3H + + 3H + 9 6+ Fi�. 15.11. (a) Molecular components of pseudorotaxane [7.6aH3] 9+ and rotaxanes [8H3] 9+ and [9H319+; (b)

schematic representation o� a molecular lift [62].

15.3 Linear Movements in Rotaxanes I 401 [10H3] 3+ Fig. 15.12. H2 _ H + + H + [1 OH2] 2+ Yellow, fluorescent Violet, non-fluorescent The cucurbituril-based rotaxane [10H3] 3+ and its switching scheme [69]. IH 3 changing the pH of the solution. Pseudorotaxanes of this type behave as pH-driven molecular shuttles [68, 69] and can thus be induded among rotaxanes as far as molecular movements are concerned. In rotaxane [10H3] 3+ formed by cucurbituril with a tris-ammonium ion (Fig. 15.12), the bead resides predominantly on the diprotonated diaminohexane site at pH < 5.7, but translocates to the diprotonated diaminobutane site at higher pH, when the [10H2] 2+ form is obtained [69]. An acid solution of the pseudorotaxane is yellow and fluorescent, whereas at pH 7 the solution is violet and non-fluorescent. Rotaxane [11H2] 8+ (Fig. 15.13) consists of a cucurbituril bead and a thread-like component which contains a central protonated diaminobutane unit (station A), two pyridinium groups as linkers, two hexamethylene units (stations B), and two terminal viologen groups which prevent dethreading [50, 70]. The bead resides exclusively on station A at neutral pH, because of charge-dipole and hydrogen- bonding interactions between the protonated amino groups and the portal carbonyl groups. On addition of a base (Fig. 15.13), deprotonation of the protonated dia- minobutane unit promotes movement of the bead from station A (state I) to one of the stations B (state III) of compound 116+. On addition of acid, reprotonation of the diaminobutane unit occurs (state IV), but translocation of the bead back to station A is slow at room temperature (AG = 26 kcal mol-). At 80 �C, however, the bead shuttles rapidly and completely to station A. This bistable rotaxane thus behaves as a kinetically controlled machine in which the state reached on stimula- tion is maintained after removal of the applied stimulus [70]. 15.3.2.4 Rotaxanes Based on �yclodextrins Polyrotaxanes in which many cyclodextrins (CD) are threaded on to a poly-mer chain (molecular necklaces, Fig. 15.14) have been prepared starting from poly(ethylene glycol), PEG, and c-CD by capping the end chains with bulky stop- pers (dinitrophenyl groups) [40, 71]. These polyrotaxanes are insoluble in water.

402 I 15 Linear Movements +Z '1- '1-Z+

15.3 Linear Movements in Rotaxanes I 403 + H + I' + OH- Fig. 15.14. (a) A molecular necklace formed by poly(ethylene glycol) and c-CD. (b) The position of the CD beads can be manipulated along a polymer chain by means of chemical (acid-base) stimulation [71]. In basic solution (0.1 mol L - NaOH), however, these systems are soluble, because the OH groups of the CD are deprotonated and the hydrogen bonds between the CD are destroyed. Under such conditions, the CD rings move away from each other along a polymer chain because of the repulsive interactions between ionized hydroxyl groups (Fig. 15.14b) and move back to each other on neutralization to form a hydrogen-bond network (Fig. 15.14a). It has recently been shown that in these kinds of polyrotaxane one or two rings can be displaced along the polymer chain by using the tip of a scanning tunneling microscope (STM) [72]. Fig. 15.15 shows, for example, an STM image of a poly- rotaxane composed of -CD beads threaded in poly(ethylene glycol). One CD in the polyrotaxane was mechanically pushed by the STM tip along the main chain of PEG. On moving the tip in the reverse direction the -CD went back to its original position. Solvent- and temperature-sensitive molecular shuttling has been observed in the polyrotaxane shown in Fig. 15.16, which consists of an -CD as a bead, three bipyridinium units, which repel the bead, and two dodecamethylene hydrophobic stations [73, 74]. 15.3.3 Electrochemically Driven Systems Rotaxane [12.Cu] + (Fig. 15.17) has a phenanthroline and a terpyridine unit in its dumbbell-shaped component [75]. It also incorporates a Cu(I) center coordinated

4041 15 Linear Movements 2nm 2nm Fig. 15.15. STM image of a polyrotaxane composed ofc-CD beads threaded in poly(ethylene glycol). One CD in the polyrotaxane was mechanically pushed by the STM tip along the main chain of the polymer [72]. Adapted, with permission, from Ref. [72]. tetrahedrally by the phenanthroline ligand of the dumbbell together with the phe- nanthroline ligand of the macrocycle. Oxidation of the tetracoordinated Cu(I) cen- ter of [12.Cu] + to a tetracoordinated Cu(II) ion occurs on electrolysis (+1.0 V rela- tive to the SCE) of a CH3CN solution of the rotaxane [75, 76]. In response to the NO2 O2 N O2N -(CH2)2- --(CH2)12-- -(CH2)12- -(CH2)2- NO2 G = 20 kcal mol '1 k= 0.015 s '1 at T= 30 �C k= 80 s '1 at T= 130 �C Fig. 15.16. Temperature-controlled molecular shuttling in a polyrotaxane (DMSO-d6) [73].

preference of Cu(II) for a pentacoordination geometry, the macrocycle shuttles away from the bidentate phenanthroline ligand of the dumbbell and encircles the terdentate terpyridine ligand instead. In this conformation, the Cu(II) center adopts pentacoordinated geometry that is significantly more stable than the tetracoordination one associated with the original conformation. Consistently the cyclic voltammogram shows the disappearance of the reversible wave (+0.68 V) associated with the tetracoordinated Cu(II)/Cu(I) redox couple and the concomitant appearance of a reversible wave (-0.03 V) corresponding to the pentacoordinated Cu(II)/Cu(I) redox couple. A second electrolysis (-0.03 V) of the CH_3CN solution of the rotaxane reduces the pentacoordinated Cu(II) center back to a pentacoordinated Cu(I) ion. In response to the preference of Cu(I) for tetracoordination geometry the macrocycle moves away from the terdentate terpyridine ligand and encircles the bidentate phenanthroline ligand. The cyclic voltammogram recorded after the second electrolysis shows the original redox wave (+0.68 V) corresponding to the tetracoordinated Cu(II)/Cu(I) redox couple. The shuttling of the macrocyclic component of rotaxane 4^{4+} along the linear portion of its dumbbell-shaped component (Fig. 15.9) can also be controlled electrochemically [59]. The benzidine recognition site undergoes two consecutive one-electron oxidations. Comparison of the potentials of 4^{4+} with those of a model compound incorporating a benzidine unit not encircled by the tetracationic cyclophane shows that the potential for the first oxidation is more positive in the rotaxane whereas that for the second oxidation is the same in both compounds. These observations indicate that the tetracationic cyclophane makes the first one-electron oxidation of the encircled benzidine unit more difficult. Once this unit is oxidized to the corresponding radical cation, however, the tetracationic cyclophane moves away from it to encircle the biphenol unit and so does not affect the second one-electron oxidation. On reduction of the benzidine unit back to its neutral state, the original equilibrium between the two conformations associated with the rotaxane is restored. As we have seen in the previous section, rotaxane $[5H]^{3+}$ undergoes acid/base-controllable molecular shuttling (Fig. 15.10) [60]. After deprotonation, the ring resides around the electron-acceptor bipyridinium station, as shown by the fact that its first reduction potential is more negative than that found for the dumbbell component. The second reduction potential, however, is not affected. This observation shows that after one-electron reduction of the bipyridinium station, the macrocycle moves away from it. Rotaxane 13^{4+} (Fig. 15.18) incorporates a z-electron-deficient macrocyde and a z-electron rich dumbbell [77]. In solution the macrocyde resides around the 2,6- dioxyanthracene recognition site. This conformation is stabilized by CT and [z... z] stacking interactions between the bipyridinium units of the macrocycle and the sandwiched 2,6-dioxyanthracene recognition site of the dumbbell, and by [C-H... O] interactions between the -bipyridinium hydrogen atoms and the poly-ether oxygen atoms. The H NMR spectrum (in (CD3)2CO , 298 K) of 134+ shows a singlet at 4 = 4.30 for the protons in positions 9 and 10 of the 2,6-dioxyan- thracene moiety. In contrast, these protons resonate at 4 = 8.16 in the H NMR

4o81 15 Linear Movements spectrum of the "free" dumbbell. The dramatic chemical shift change (&$ = -3.86 ppm) experienced by the resonances associated with these protons is a result of shielding effects exerted on them by the sandwiching bipyridinium units. The cy- dic voltammogram of a CH3CN solution of this rotaxane has a first oxidation wave (+1.03 V relative to the SCE) that corresponds to the oxidation of the 2,6-dioxyan- thracene recognition site. This oxidation occurs at a potential that is more positive than that of a model compound incorporating this unit. As far as the oxidation of the two 1,4-dioxybenzene moieties is concerned, two distinct processes (+1.29 and +1.59 V) are observed. The oxidation of the first 1,4-dioxybenzene unit of the ro- taxane occurs at a potential that is almost identical with that of a model compound incorporating this unit. The oxidation of the second 1,4-dioxybenzene unit of the rotaxane occurs at a potential that is almost identical with that of a model rotaxane incorporating this unit encirded by the tetracationic cyclophane. These observa- tions suggest that the tetracationic cydophane resides (Fig. 15.18) initially around the 2,6-dioxyanthracene recognition site, making its oxidation more difficult. Once this recognition site is oxidized, however, the tetracationic cydophane moves away from it and encirdes one of the two 1,4-dioxybenzene rings [77]. The electrochemical and photophysical properties of a series of rotaxanes (e.g. 14 4+, Fig. 15.19) consisting of an electron-accepting cyclophane and a dumb- bell containing monopyrroletetrathiafulvalene (PTTF) and 1,5-dimetoxynaphthalene (1,5-DMN) units have recently been investigated in acetonitrile solution [78]. Both PTTF and 1,5-DMN are potential stations for the tetracationic cydophane, because they can establish charge-transfer interactions with its electron-accepting bipyr- idinium units. On the basis of the redox properties one might expect a strong preference of the tetracationic cyclophane for the PTTF station compared with the 1,5-DMN station. The interaction of the cydophane with electron-donating units also depends on other factors, however, induding the extension of the [z... stacking and the formation of hydrogen bonds. Comparison with the behavior of suitable model compounds and of the free dumbbell components has provided evidence that two station rotaxanes of this kind have unexpectedly complex elec- trochemical and spectral features that cannot simply be related to the presence of the two expected translational isomers. It seems that, owing to their length (50- Fig. 15.19. In rotaxanes such as 144+ there is an equilibrium between the two translational isomers [79]. In the isomer represented in the figure, the tetracationic cyclophane moves away from the PTTF unit upon one-electron oxidation of this station [78].

15.3 Linear Movements in Rotaxanes 1409 60 nm) and flexibility, such compounds can fold up in the solvent used to max- imize the charge-transfer interactions. It seems also that the two stoppers (in par- ticular, the dendritic one) play a much more active role than that of simple bulky groups. Because of their not negligible electron-donating power, they presumably fold around the tetracationic cydophane, thereby contributing to establishing its localization along the thread. The electrochemical results indicate that, in the iso- met in which the cyclophane surrounds the PTTF unit first oxidation of this unit induces the displacement of the cyclophane. H NMR studies have also furnished evidence that the presence of a bulky thiomethyl substituent on the PTTF unit, when situated in between the two stations as in 14 4+ , slows down the shuttling movement [79]. As we will see below (Section 15.4), rotaxanes of this type have been used to construct two-dimensional molecular electronic circuits. 15.3.4 Photochemically Driven Systems The shuttling (Fig. 15.17) of the macrocydic component of rotaxane [12.Cu] + along the linear portion of its dumbbell-shaped component can be also induced photochemically [75b]. Irradiation (464 nm) of a CH3CN solution of the rotaxane, in the presence of p-nitrobenzylbromide, leads the Cu(I)-based chromophoric unit to its metal-to-ligand charge-transfer excited state. Electron transfer from the pho- toexcited rotaxane to p-nitrobenzylbromide follows, generating a tetracoordinated Cu(II) center. In response to the preference of the Cu(II) ion for a pentacoordina- tion geometry the macrocycle shuttles away from the bidentate phenanthroline ligand of the dumbbell and encircles the terdentate terpyridine ligand instead. On addition of ascorbic acid the pentacoordinated Cu(II) center is reduced to a penta- coordinated Cu(I) ion. In response to the preference of Cu(I) for tetracoordination geometry the macrocycle moves away from the terdentate terpyridine ligand and encircles the bidentate phenanthroline ligand to restore the original conformation. Rotaxane trans-154+ (Fig. 15.20) incorporates an -cyclodextrin torus and a trans- azobiphenoxy-containing dumbbell [80]. Comparison of the H NMR spectra (D20, 303 K) of the rotaxane and of its "free" dumbbell-shaped component indicates that the cydodextrin resides exclusively around the trans-azobiphenoxy recognition site. Whereas only two sets of signals are observed for the trans- azobiphenoxy protons of the "free" dumbbell, four sets of resonances are asso- ciated with the same protons in the rotaxane. The local C2 symmetry of the trans- azobiphenoxy unit is lost in the rotaxane as a result of the toroidal shape of the -cydodextrin component, and the two p-phenylene rings are no longer equivalent. The circular dichroism spectrum (H20, 278 K) of the rotaxane also contains a positive band (360 nm) corresponding to z - z* transitions of the azobiphenoxy unit. This observation indicates that this unit is encircled by the -cydodextrin component, because long-axis polarized transitions of aromatic guests inserted through the cavity of -cyclodextrin hosts produce positive bands. On irradia- tion (360 nm) the azobiphenoxy unit isomerizes from trans to cis "pushing" the a-

NaO \ x /Na .ao- 8 -�"a trans- 16 Fig. 15.21. 340 nm 265 nm 15.3 Linear Movements in Rotaxanes I 411 Na Na NaO ONa cis-16 Photoinduced process in a stilbene-based -CD rotaxane [$1]. cydodextrin component away to encirde one of the CH2CH20 chains (Fig. 15.20). As a result, the intensity of the positive circular dichroism band decreases. On ir- radiation at 430 nm, the azobiphenoxy unit isomerizes from cis back to trans. This process is accompanied by the shuttling of the -cyclodextrin component back to encirde the trans-azobiphenoxy recognition site and, consequently, by an increase in the intensity of the positive band at 360 nm [80]. In the stilbene-based CD rotaxane trans-16, the translational motion of the CD bead occurs in one direction only (from left to right, Fig. 15.21), presumably for steric reasons [81]. It might be that for both trans-15 4+, and trans-16, shuttling is caused only by the photo- isomerization of units not surrounded by CD. The interesting possibility of exploiting the trans-cis photoisomerization of an azobenzene unit located in the middle of the dumbbell component to generate a stopper-like barrier for the ring component in a rotaxane has been proposed [82]. This would correspond to a "mechanical frequency doubling" of the shuttling process because, at a given temperature, the effective length for this motion would be cut in half. The photochemical behavior of rotaxanes based on charge-transfer interac- tions, e.g. those shown in Fig. 15.22, has been investigated [83]. In compound 17 4+ 0 � ** 18 + X._ + Fig. 15.22. Rotaxanes investigated by direct excitation which are characterized by fast photoinduced and back-electron- transfer processes [83].

15 Linear Movements excitation of the anthracene stoppers is followed by rapid (picosecond time-scale) and reversible electron transfer to the electron-acceptor cydophane. Direct excita- tion on to the charge-transfer absorption band results in formation of an intimate radical ion pair which undergoes rapid charge recombination. In compound 18 4+ , oxidation of the terminal ferrocene unit competes (25 %) with charge recombina- tion. To achieve photoinduced ring-switching in rotaxanes containing two different recognition sites in the dumbbell-shaped component, the carefully designed com- pound 196+ shown in Fig. 15.23 was synthesized [84]. This compound consists of the electron-donor macrocyde R and a dumbbell-shaped component which contains: � [Ru(bpy)3] 2+ (P) as one of its stoppers; � a p-terphenyl-type ring system as a rigid spacer (S); � a 4,4'-bipyridinium unit (A) and a 3,Y-dimethyl-4,4'-bipyridinium unit (A2) as electron-accepting stations; � a tetraarylmethane group as the second stopper (T). The structure of rotaxane 196+ was characterized by mass spectrometry and NMR spectroscopy which, with cyclic voltammetry, also established that the stable translational isomer is the one in which the R component encirdes the A unit, in keeping with the fact that this station is a better electron acceptor than the other. The electrochemical, photophysical, and photochemical (under continuous and pulsed excitation) properties of the rotaxane, its dumbbell-shaped component (Fig. 3.5, Section 3.4), and some model compounds were then investigated and two strategies were devised to obtain the photoinduced abacus-like movement of the R macrocyde between the two stations A and A2 - one was fully based on processes involving only the rotaxane components (intramolecular mechanism), whereas the other required the help of external reactants (sacrificial mechanism). The intramolecular mechanism, illustrated on the left

of Fig. 15.23, is based on four operations [84]: (a) Destabilization of the stable translational isomer. Light excitation of the photo- active unit P (step 1) is followed by transfer of an electron from the excited state to the A station, which is encircled by the ring R (step 2), with the con- sequent "deactivatioff' of this station; such a photoinduced electron-transfer process must compete with the intrinsic decay of the excited state of P (step 3). (b) Ring displacement. The ring moves from the reduced station A- to A2 (step 4), a step that must compete with the back-electron-transfer process from A- (still encircled by R) to the oxidized photoactive unit P+ (step 5). This is the most difficult requirement to meet in the intramolecular mechanism. (c) Electronic reset. A back-electron-transfer process from the "free" reduced station A- to P+ (step 6) restores the electron-acceptor power to the A station. (d) Nuclear reset. As a consequence of the electronic reset, back movement of the ring from A2 to A occurs (step 7).

The results obtained seem to indicate that electronic reset of the system after light excitation (step 5; k = 2.4 x 105 s -1) is faster than the ring displacement (step 4). It is worth noticing that in a system which behaves according to the intra- molecular mechanism shown in the left-hand side of Fig. 15.23 each light input causes the occurrence of a forward and back ring movement (i.e. a full cycle) without generation of any waste product. This system can thus be regarded as a "four-stroke" cyclic linear motor powered by light. The alternative, less demanding sacrificial mechanism is based on the use of external redox reactants (a reductant such as triethanolamine, and an oxidant such as dioxygen) that operate as illustrated on the right of Fig. 15.23: (a) Destabilization of the stable translational isomer. As in the previous mechanism; (b') Ring displacement after scavenging of the oxidized photoactive unit. Because the solution contains a suitable reductant, a rapid reaction of this species with P+ (step 8) competes successfully with the back electron-transfer reaction (step 5); the originally occupied station thus remains in its reduced state A-, and the displacement of ring R to A2 (step 4), although slow, does occur; (c') Electronic reset. After an appropriate time, restoration of the electron-acceptor power of the A station is achieved by oxidizing A- with a suitable oxidant such as dioxygen (step 9); (d) Nuclear reset. As in the previous mechanism (step 7). The results obtained show that such a sacrificial mechanism is fully successful. This mechanism is, of course, less appealing than the intramolecular mechanism, because it leads to the formation of waste products. Instead, however, of using a sacrificial reductant and a sacrificial oxidant, it should be possible to use a re- versible redox couple as an electron relay; this strategy was successfully employed for rotexane 20 described below. It should also be stressed that the mechanical movement of the cyclic compo- nent between the two stations and the related changes in the spectroscopic and electrochemical properties obey binary logic and can, therefore, be taken as a basis for information processing [85]. A light-driven molecular shuttle which relies on an external electron relay has been reported [86]. Rotaxane 20 (Fig. 15.24) consists of a benzylic amide macrocycle that surrounds an axle containing two hydrogen-bonding stations - succinamide and naphthalimide units - separated by a long alkyl chain. Initially the macrocycle resides on the succinamide station, because the naphthalimide unit is a much poorer hydrogen-bonding recognition site. Excitation with light at 355 nm (step 1) in acetonitrile at 298 K generates the singlet excited state of the naphthalimide unit, which then undergoes high-yield intersystem crossing to the triplet excited state. Such a triplet state can be reduced in bimolecular encounters by an electron donor (1,4-diazabicydo[2.2.2]octane, DABCO) added to the solution in a sufficiently large amount (step 2). Because the back-electron-transfer process (step 3) is spin-forbidden, and thus slow, the photogenerated ion pair can dissoci-

oJo 20 !'-. DABCO + ... [" [["r "' N "HN' u OO Fi 8. 15.24. Light-induced reversible shuttlin of the macrocyclic component of the hydrogen-bonded rotaxane 20 [86]. The operation oFthis system relies on the use oF DABCO as an eleron relay. 15.3 Linear Movements in Rotaxanes 1415 o NH-.' II I o H 0 ate efficiently - as a matter of fact the naphthalimide radical anion survives for hundreds of microseconds before it decays by bimolecular charge recombination with a DABCO radical cation. Because the naphthalimide anion is a much stronger hydrogen-bonding station compared with the succinamide, on reduction of the naphthalimide unit the macrocycle is expected to shuttle from the latter to the for- mer station (step 4); this has been demonstrated by cyclic voltammetric experi- ments and confirmed by laser flash photolysis. The time required for ring shut- tling (1 its) is much shorter than the lifetime of the naphthalimide radical anion (100 its). After charge recombination (step 5) the macrocycle moves back to its original position (step 6). This rotaxane is an outstanding example of a linear molecular motor driven exclusively by light, although its operation still relies on the presence of an external reactant which, however, is not consumed. The device can be cycled at a frequency depending on the charge recombination rate of the rotaxane radical anion. It can be estimated that if the shuttle is pumped by a laser at the frequency of its "recovery stroke" (step 5), i.e. 10 4 S -1, this molecular-level machine generates 10 -5 W of mechanical power per molecule [86]. In a very recent work [87] the complex fluorescence behavior of a similar peptide-based rotaxane bearing an anthracene unit as one of the stoppers has been

15 Linear Movements interpreted in terms of very fast (subnanosecond), short-amplitude translation of the macrocyde on light excitation of the anthracene unit. It seems, however, that alternative explanations, such as the formation of intercomponent exciplexes [88], cannot be discounted. 15.3.5 Perspectives There is no doubt that the functioning mechanisms of several natural linear motors at molecular-level resolution will be fully elucidated in the next few years. The detailed knowledge obtained will greatly help in the design of novel artificial linear machines. Even the artificial machines constructed so far can, however, be taken as a basis for the design of very interesting systems. A few examples are outlined below. 15.3.5.1 Three-station Rotaxanes It is possible to design rotaxanes in which the dumbbell-shaped component contains three different stations, e.g. a stronger (A) and a weaker (A2) electron- acceptor, and an appropriate amine/ammonium moiety (Fig. 15.25). The A and A2 stations can be 4,4-bipyridinium and 3,3-dimethyl-4,4-bipyridinium units, re- spectively [41]. Depending on the sequence in which the three stations are as- sembled, a suitable macrocyclic polyether component can be moved along the thread according to predetermined patterns. For example, with dibenzo[24]crown-8 as a macrocycle and the three stations assembled as in Fig. 15.25, the macrocycle which is originally located on the central station A can be displaced either towards the left-hand side by reduction of A or to the right-hand site by protonation of the amine. By using the photoactive [Ru(bpy)3] 2+ unit as a stopper, it should be pos- sible to perform the reduction of A by excitation with light [89]. The possibility of determining the direction along which the macrocycle can be moved by selecting the nature of the input opens the way to a variety of switching functions. 15.3.5.2 Rotaxanes as Carriers The controlled movement of the ring component along the dumbbell in rotaxanes could be exploited to transport

chemical species. Such a carrier function could be performed by appending to the shuttling macrocycle a host (or guest) unit capable of recognizing and linking an external species [41]. In the example shown sche- +e- +H + Fig. 15.25. A three-station rotaxane in which the direction of ring displacement is determined by the selected input [41].

15.3 Linear Movements in Rotaxanes I 417 a Fig. 15.26. A rotaxane carrier powered by electrochemical inputs designed to perform (a) transport of an amine, (b) approach of two appended units, and (c) stretching of a molecular spring [41]. c matically in Fig. 15.26a the dumbbell-shaped component of the rotaxane contains two different electron-donors (e.g., a tetrathiafulvalene and a 1,5-dioxynaphthalene unit) and the shuttling electron-acceptor ring (which could be the previously seen bipyridinium-based tetracationic cydophane) is functionalized with a crown ether (e.g. [24]crown-8) capable of linking an ammonium species (e.g. anthracenyl ammonium). Shuttling of the cyclophane could be controlled by electrochemical input whereas loading and unloading of the transported amine could be controlled by acid-base input. As a further elaboration of this concept, systems can be designed in which the transported species is driven to interact with another, appropriate unit. The

4,8[15 Linear Movements system shown schematically in Fig. 15.26b depicts an example of redox-controlled approach of two appended traits via the rotaxane "rail". Several other functions based on rotaxanes as carriers can be devised, for example stretching of a molecular spring (Fig. 15.26c), a movement that could be used as the basis of artificial molecular-level musdes. Further schemes can be designed by using the photoactive [Ru(bpy)3] 2+ unit as a stopper, to take advantage of photoexcitation [89]. 15.4 Interfacing Rotaxanes with Surfaces and Solid Supports Investigation of supramolecular systems in solution is of fundamental importance to understanding their complex behavior. Solutions, however, contain very many molecules which behave incoherently, because they cannot be addressed individually and hence controlled. It seems reasonable, therefore, that, in several instances, for real device applications, rotaxanes must be interfaced with the macroscopic world by ordering them in some way at interfaces or on surfaces [39]. In such ordered arrays, rotaxanes can behave coherently, either in parallel or in series, and can also be manipulated on the nanometer scale. These problems have been recently addressed by several research groups. We will briefly describe a few typical examples. The interested readers can consult the original papers and the review artides mentioned below. 15.4.1 A Surface-bound Photoswitchable Rotaxane A surface-bound photoswitchable rotaxane (Fig. 15.27) has recently been reported [90-92]. Rotaxane 21, which consists of a ferrocene-functionalized fi-cydodextrin molecule threaded on a "string" containing a photoisomerizable azobenzene unity and a long alkyl chain, was assembled on a gold electrode. The fi-CD component of the rotaxane is prevented from dethreading by a bulky anthracene stopper group. When the azobenzene unit is in the trans configuration (trans-21), it is complexed by fi-CD, but photoisomerization to cis-21 makes complexation sterically impossible, so the fi-CD is translocated to the alkyl component. Back-photoisomerization restores the original state trans-21. The position of the fi-CD-tethered ferrocene unit was determined by chronoamperometry. A rapid current decay (k = 65 s -) was observed for the trans isomer, implying that the fi-CD is dose to the electrode sur- face. Photoisomerization of the monolayer to the cis state resulted in a chronoam- perometric transient characterized by a substantially lower electron-transfer rate constant (k = 15 s-l). This result indicates that in cis-21 the fi-CD is more distant from the electrode surface. Because the azobenzene isomerization is reversible, a cyclic pattern for the rate constant of the heterogeneous electron-transfer process was observed. In this peculiar optoelectronic system, optical information is trans- duced by a mechanical shuttling to an electronic signal.

15.4.2 Rotaxane-based Electronic Devices Rotaxanes have been used [93-98] to construct switchable electronic junctions in solid-state devices that will be illustrated in Section 16.6 and Fig. 16.26. In a first attempt [93, 94], the V-shaped rotaxanes 224+ and 234+ (Fig. 15.28) 3C0 0 O.& Fig. 15.28. Rotaxanes 224+, 234+, 244+, and 254+ have been used to construct switchable electronic junctions for memo and logic function purposes [94, 95, 98].

were used in the form of molecular monolayers sandwiched between lithographi- cally fabricated metal wires. The switches were read by monitoring current flow at reducing voltages. In the "dosed" state current flow was dominated by resonant tunneling through the electronic states of the system. The switches were irre- versibly opened by applying an oxidizing voltage across the device. The V-shaped dumbbell component of the rotaxanes has similar properties. The results obtained showed that these systems behave as singly configurable logic gates. In more recent work [95-98], Langmuir-Blodgett monolayers of rotaxanes 244+ and 254+ (Fig. 15.28) were used, because of their amphiphilic properties. Compound 244+, and the catenane shown in Fig. 16.28, have a (noncapacitative) hysteretic current- voltage response that switches the device between high- and low-conductivity states. Correlations between the structure and solution-phase dynamics were investigated. It should be recalled (Section 15.3.3) that in solution 244+ is present as two translational isomers and has rather complex electrochemical behavior [78]. Rotaxane 254+, which is initially present only as the translational isomer shown in Fig. 15.28, was then used. This rotaxane does not have phenolic residues, which are thought to compromise the oxidative stability of the switch, although the readily oxidizable dioxynaphthalene unit is still present. It has been shown that the device can be scaled-down from micrometer (107 molecules) to nanometer (a few thousand molecules) dimensions without changing its behavior.

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4,61 16 Motions in Catenanes 16.1 Introduction 16.1.1 Synthesis A catenane is a supramolecular species composed of two or more interlocked macrocyclic components [1-3]. The macrocycles are not linked covalently to each other, instead a mechanical bond holds them together, preventing their dissociation.

The most frequent example is that of catenanes made of two rings, [2]catenanes. In the following text the prefix [n], where n is the number of interlocked rings, will not be used unless it is strictly necessary. Early attempts at the synthesis of catehanes were based on the so-called statisti- cal approach. In this approach a molecular thread X-Y, functionalized on both ends, can enter a macrocycle of appropriate size; subsequent cyclization of X-Y leads to two interlocked rings [4]. Because the probability that cydization occurs while X-Y is threaded through the macrocyde is very small, only poor yields, at most, can be expected from use of this procedure. The first evidence for formation ofa catenane by use of this approach was reported in 1960 [5]. In 1967 it was discovered that catehanes are also formed in Nature by DNA [6]. With the development of the host-guest chemistry in the late nineteen-seventies [7-10], several research groups began developing new methods for synthesizing catehanes. As for rotaxanes, the general strategy for preparing catehanes in high yields is based on the template effect [11], which relies on the presence of molecular rec- ognition sites between the components to be assembled. The most common tern- plated syntheses involve the use of metal ions [3a, b], donor-acceptor components [3d-f], and formation of hydrogen bonds [3d-g], although other properties, e.g. hydrophobic-hydrophylic character, [...] stacking, ion-ion, ion-dipole, and dipole-dipole forces can also play a role. In several instances, in fact, more than one type of interaction is operative. It should also be noted that occasionally the strongest interaction, as far as association is concerned, is not that causing the most relevant changes (compared with the separated components) in properties such as electrochemical behavior and absorption, fluorescence, and NMR spectra.

Molecular Devices and Machines -A Journey into the Nano World. V. Ba]zani, Ai Credi, Mi Venturi Copyright � 2003 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim ISBN: 3-527-30506-8

Fig. 16.1. Clipping routes for the synthesis ofcatenanes. clipping double clipping The most rational preparation strategy is clipping of a preformed macrocyde with a suitable U-type component that is subsequently cydized. A double clipping procedure can also be used (Fig. 16.1). Fig. 16.2 shows the synthesis, templated by donor-acceptor and hydrogen- bonding interactions, of catenane 14+ [12]. Reaction of the dication 22+ with the dibromide 3 gives a tricationic intermediate which interacts with bis-p- phenylene[34]crown-10 (4) to afford a pseudorotaxane-like, or

precatenane, structure. The subsequent macrocyclization, as a result of nucleophilic displacement of bromide ion, gives the corresponding catenane 14+. Occasionally catenanes are formed from relatively small molecules by one-pot synthesis [13-15]. Fig. 16.3 shows the one-pot synthesis of the amide-based catenane 5 from very simple compounds [15]. This synthesis is thought to involve the perpendicular preorganization of the components caused by three templating effects - steric complementarity, hydrogen bonding between carbonyl oxygen atoms and amide protons, and [z... z] interactions between the benzene rings of host and guest units. Besides simple [2]catenanes, a great variety of more complex systems has been synthesized, including catenanes comprising three, five (olympiadane, Fig. 1.8), or seven interlocked macrocycles [16], polycatenanes [3c, f], catenanes with very special shapes [17], and rotacatenanes [18] (Fig. 16.4).

16. I Introduction 1 429 r..O--S S/-'O- o-/ OOO g O O O-i O OOOO - Fi 8, 6,4, (a) A catenane with three rins [17d] and (b) a rotacatenane [18], 16,1,2 Circumrotational Processes If during the template-directed synthesis it is arranged for two identical recognition sites to be located within two different macrocycles (as, e.g., in the compound 14+ shown in Fig. 16.2), the resulting catenane undergoes degenerate conformational change when one of the macrocycles spontaneously circumrotates through the cavity of the other and vice versa, as illustrated in Fig. 16.5. Computational analyses of the circumrotational processes associated with some catenanes have been performed [19]. For benzylic amide catenanes the results show, as expected, that the interlocked macrocycle dynamics is governed by a delicate combination of steric effects, intricate inter-macrocyclic arrays of hydrogen bonds, [z... z] stacking, and T-type interactions. The precise structure of diacylaromatic units was found to have tremendous effects on the frequency of macrocyclic ring rotation. The polarity of the solvent also plays a crucial role in the inter-ring dynamics, because it affects the strength of the hydrogen-bonding network. When one of the two macrocyclic rings carries two different recognition sites, the opportunity exists to control the dynamic processes (Fig. 16.6) in a manner reminiscent of controllable molecular shuttles (Fig. 15.6, Section 15.3). The two conformations can be interchanged by use of appropriate stimuli. In a diagram of potential energy against angle of rotation

of the asymmetric macrocycle, the two conformations correspond to energy minima provided by the intercomponent noncovalent bonding interactions. The initially populated conformation is that associated with the most favorable energetic state (state 0). Stimulus S has the effect of destabilizing this conformation and leads to the other conformation (state

4301 16 Motions in Catenanes Fig. 16.5. Dynamic processes associated with circumrotation of one ring in a catenane made of two different macrocycles each incorporating two identical recognition sites {see, e.g., compound]4+ in Fig. 16.2). Asterisks are used to highlight the exchange of position of identical units. 1), a change that can simply be viewed as a circumrotation of the asymmetric macrocyde. An opposite stimulus S2 restores the original situation. By switching off and on again the recognition properties of one of the two recognition sites of the asymmetric macrocycle, the relative populations of the two species can be con- trolled reversibly. It should be remarked, however, that repeated switching between the two states does not need to occur through a full rotation. In fact, because of the intrinsic symmetry of the system, both movement from state 0 to state 1 and that from state 1 to state 0 can occur with equal probability along a dockwise or anti- + s1 + S 2 State 0 State 1 Fig. 16.6. The two conformations associated with a catenane incorporating two different recognition sites within one of its two macrocyclic components can be interchanged by use of appropriate stimuli (S and S2).

16. I Introduction 1 431 b Fig. 16.7. Some dynamic processes associated with catenanes [21]. clockwise direction. A full (360 �) rotation movement can occur only in ratchet-type systems, i.e., in the presence of asymmetry elements which can be structural or ftmctional in nature (Sections 13.4 and 16.5). Mechanical movements in suitably designed catenanes can be induced by chemical, electrochemical and photochemical stimulation [20-34]. From a macro- scopic mechanical viewpoint the movement of one ring relative to the other in a catenane is reminiscent of a "ball and socket joint", as illustrated in Fig. 16.7a. Similarly, twisting of one ring around the main axis of the catenane forces the other ring to rotate in the same direction in a manner reminiscent of a "universal joint" (Fig. 16.7b)[21]. 16.1.3 Functional Catenanes Because the synthetic methods used to obtain catenanes are well established, increasing attention is currently being devoted to incorporation of novel func- tions into these structures. Particularly interesting, for example, are catenanes in which

either the electron-acceptor cyclophane ring or the electron-donor macrocycle contain a 2,2'-bipyridine (bpy) ligand. The mononuclear complexes [Re(CO)3(C1)(6)] 4+, [Ru(bpy)2(6)] 6+, [Ag(6)2] 9+, and [Cu(6)2] 9+ have been prepared starting from the cydophane ligand 64+ (Fig. 16.8), and the dinuclear com- plexes [{Re(CO)3C1}2(7)] 4+ and [{Ru(bpy)2}2(7)] 8+ have been obtained from the bis-chelating cyclophane ligand 74+ (Fig. 16.9) [35]. It was not possible to synthe- size catenanes from 74+, because the cavity of this cyclophane is too large to give stable complexes with aromatic crown ethers in the templated synthetic approach. Starting from 64+, however, it was possible to prepare the catenane ligands 84+ and 94+ which were then used to prepare several mononudear catenane complexes

+ [Re(CO)5CI] oc :co -14+ OC- -,ReJ--Cl 16 Motions in Catenanes 64+ [Re(CO)3(CI)(6)] 4+ lag(6)2] 9+ [Ru(bpy)2(6)] 6+ [0U(6)2] 9+ Preparation o� mononuclear complexes oFthe c�clophane ligand Fig. 16.8. Oq ..CO l 4+ oc- :.ReJ--cl od bo [{Re(CO)3CI}2(7)] 4+ Fig. 16.9. [{Ru(bpy)2}2(7)] 8+ Preparation of binuclear complexes of the c�clophane ligand 74+ [35].

9 4+ I 1[+ [Re(CO)sOl] oq ;co -I t+ oc- :.Re,'--Cl � j_ . 'Ol,O+O9 %o%oo [Re(CO)3(Cl)(9)] 4+ Fig. 16.10. + [Ru(bpy)2C12] N + +) O]? O O [Ru(bpy)2(8)] 6+ [Ru(bpy)2(9)] s* Introduction 1 433 + Ag(CF3SO3) +1 [Cu(CH3CN)4](PF6) +1 lAg(S)2] [Ag(9)2] 9+ [Cu(9)2] 9+ Preparation oF mononuclear complexes oFthe catenane li�ands 8 4+ and 9 (Fig. 16.10; see also Section 6.3.3). These compounds were characterized by NMR spectroscopy, mass spectrometry, and, occasionally, X-ray crystallography. The absorption spectra, luminescence properties, and electrochemical behavior of the ligands 64+, 74+ and 94+, and the complexes [Re(CO)3(C1)(6)] 4+, [Re(CO)3(C1)(9)] 4+, [{Re(CO)3C1)2(7)] 4+, [Ru(bpy)2(6)] 6+, [Ru(bpy)2(9)] 6+, and [(Ru(bpy)2)2(7)] 8+ have been investigated [35]. Besides the ligand-centered bands, the Re(I) and Ru(II) complexes give metal-to-ligand charge-transfer (MLCT) bands in the visible region; these are similar to those of the [Re(CO)3(C1)(bpy)] and [Ru(bpy)3] 2+ model compounds. None of the complexes examined emits at room temperature, because the potentially luminescent MLCT excited state undergoes electron-transfer quenching by the bipyridinium-type units contained in the 64+, 74+, and 94+ ligands. In a rigid matrix at 77 K, under which conditions electron transfer cannot occur, emission can be observed from the complexes containing the

tetracationic cyclophane ligands 6 4+ and 7 4+, brtt not from those containing the catenane ligand 94+, in which quenching can still occur by energy transfer to a low-energy charge-transfer excited state of the catenane moiety [35]. In the po-

16 Motions in Catenanes tential window examined (from -2.2 to +2.1 V relative to the SCE), 64+ and 74+ can reversibly accept five and six electrons, respectively, as a result of processes localized on their bipyridinium- and bpy-type units. The catenane ligand 9 4+, besides reduction processes involving the 6 4+ cyclophane, undergoes two oxidation processes involving the dioxynaphthalene moieties of the 1,5-dinaphtho[38]crown- 10 (1/5DN38C10) component. The [Re(CO)3(C1)(6)] 4+, [Re(CO)3(C1)(9)] 4+, [{Re(CO)3C1}2(7)] 4+, [Ru(bpy)2(6)] 6+, [Ru(bpy)2(9)] 6+, and [{Ru(bpy)2}2(7)] 8+ complexes participate in several redox processes (up to a total of ten exchanged electrons for [Ru(bpy)2(6)] 6+ and [{Ru(bpy)2}2(?)] 8+) as a result of: � reduction of the bipyridinium- and bpy-type moieties of the catenane ligands; � reduction of the bpy ligands (in the Ru complexes); � oxidation of the metals; � oxidation of the dioxynaphthalene moieties of the 1/5DN38C10 crown ether (in the complexes containing the 9 4+ catenane ligand) [35]. An interesting aspect of the metal catenanes described above is the topologically different ("alongside" and "inside") positions of the two bipyridinium units with regard to the crown ether (Fig. 16.10) and, as a consequence, their redox asymme- try [36], as discussed in Section 6.3.3. A coordinating bipyridine unit can also be incorporated in the electron-donor macrocycle of a catenane. This strategy has been followed to prepare a catenane ligand and, by reaction with [Ru(Me2bpy)2C12] (Me2bpy=4,4'-dimethyl-2,2'- bipyridine), its Ru(II) complex (Section 6.3.3, Fig. 6.11) [37]. Such a catenane complex has also been used as a component of a triad and incorporated into a protein scaffold [38]. Several catenanes incorporating a calix[4]arene unit in their electron-acceptor cyclophane components have also been prepared (see, e.g., Fig. 16.11) [39]. In these compounds the characteristic charge-transfer bands arising from the donor- acceptor interaction are present, and no luminescence can be observed. Fig. 16.11. Catehanes incorporating a calix[4]arene unit in their electron-acceptor cyclophane components [39].

+ CN- + [Cu(CH3CN)4] + 16.2 Chemically Driven Motions I 435 ".",O v.O

10 Fig. 16.12. Demetalation-metalation oFthe catenate [10.Cu] +- catenand 10 is accompanied by conformational changes involving the circumrotation oCthe macrocyclic components through each other's cavity [40]. 16.2 Chemically Driven Motions Metal complexes have been extensivdy used as templates to obtain catenanes [3a, b]. As mentioned for rotaxanes, a unique feature of this approach is that the tem- plate can be removed at the end of the synthesis whereas when other strategies based on organic fragments are used the interaction between the template and the components of the final structure is usually maintained. Catenanes containing a metal ion surrounded by macrocycles which play the role of ligands are often called catenates, and the catenanes obtained from their demetalation are called catenands [3a, b]. Catenate [10.Cu] + (Fig. 16.12) incorporates two identical macrocyclic compo- nents [40] which have a phenanthroline unit and a polyether chain connected by two p-phenylene rings. X-ray crystallographic analysis of [10.Cu] + reveals [41] that the two phenanthroline ligands embrace the "central" Cu(I) ion whereas the two polyether chains are located away from each other. A conformational change involving the circumrotation of both macrocycles through the cavity of each other occurs upon demetalation (Fig. 16.12). Catenand 10 is thus obtained quantita- tively by treating a solution of catenate [10.Cu] + with KCN [40, 42]. X-ray analysis of catenand 10 shows [41] that the conformation is markedly different from that adopted by [10.Cu] +. In catenand 10 the phenanthroline ligands are positioned away from each other whereas the entangled polyether chains are located at the "center" of the structure. Complete rearrangement of 10 occurs [43] on addition of [Cu(CH3CN)4]BF4 - the two macrocyclic components circumrotate through the cavity of each other to enable coordination of the Cu(I) ion by the two phenan- throline ligands and yield back the catenate [10.Cu] +. A similar conformational change was observed [44] on metalation of the catenand with a variety of metal ions or on protonation. Similar behavior is observed for other phenanthroline-con- taining catenates on demetalation-metalation or demetalation-protonation [45].

4361 16 Motions in Catenanes + 2H + 114+ 124+ Fig. 16.13. Porphyrin catenanes 114+ and 124+ and possible structural changes accompanying protonation of the porphyrin unit [48]. Chemical control of the conformation behavior of a catenane as a result of anion chelation has also been reported [46]. Catenanes 114+ and 12 4+ (Fig. 16.13) incorporate a bipyridinium-based tetraca- tionic cydophane and a z-electron-rich macrocydic polyether comprising a por- phyrin and either a 1,4-dioxybenzene or a 1,S-dioxynaphthalene unit [47]. The tetracationic cydophane encircles the dioxyarene unit only, as a result of stacking interactions between this recognition site and the sandwiching bipyr- idinium units. The protons of the 1,4-dioxybenzene unit of 114+ resonate at = 2.62 in the H NMR spectrum (CD3CN , 343 K). Similarly, the protons in positions 4 and 8 of the 1,5-dioxynaphthalene unit in catenane 124+ resonate at = 1.47 in the H NMR spectrum in (CD3)280 at 378 K. These "unusual" chem- ical shifts for the dioxyarene protons are a result of shielding effects exerted upon them by the sandwiching bipyridinium groups. The porphyrin unit is also engaged in [z. � � z] stacking interactions with the bipyridinium unit located inside the cavity of the macrocyclic polyether. The tetracationic cydophane, however, circumrotates through the cavity of the macrocyclic polyether exchanging the inside and along-

16.2 Chemically Driven Motions side bipyridinium units; for 114+, the rate of circumrotation is 1500 s - (CD3CN, 298 K). At 238 K in (CD3)2CO this dynamic process is slow on the H NMR time scale and signals for the inside and alongside bipyridinium groups can be dis- tinguished. On addition of CF3CO2H, the porphyrin unit is protonated (Fig. 16.13) [48]. As a result of electrostatic repulsion the inside dicationic bipyridinium group of the tetracationic cyclophane moves away from the now dicationic porphyrin unit. As a consequence the H NMR spectra in (CD3)CO at 238 K of the protonated catenanes [11H] 6+ and [12H] 6+ reveal two distinct environments for the two p-phenylene rings of the tetracationic cydophane. In the conformation obtained after protonation one of the p-phenylene rings is located inside the cavity of the macrocydic polyether whereas the other is positioned alongside. Chemical shift differences of A6 = -0.39 and -0.50 are observed between the resonances for the protons of the inside and alongside p-phenylene rings of [11H2] 6+ and [12H2] 6+, respectively. Catenanes 134+ and 144+ (Fig. 16.14) incorporate a bipyridinium-based tetraca- tionic cydophane and a z-electron-rich macrocyclic polyether comprising a tetra- thiafulvalene (TTF) group and either a 1,4-dioxybenzene or a 1,5-dioxynaphthalene unit [49, 50]. X-ray crystallographic analysis of catenane 14 4+ revealed that the tetracationic cydophane encirdes exclusively the TTF unit in the solid state. Also, the H NMR spectra (CD3CN, 298 K) of 134+ and 144+ indicate that the tetrathia- fulvalene unit resides preferentially inside the cavity of the tetracationic cydophane in solution, and the dioxyarene unit is positioned alongside. The 1,4-dioxybenzene protons of 134+ and the 1,5-dioxynaphthalene protons of 144+ resonate at chemical 13 4+ 14 4 + -o 15 + S2052- Fig. 16.14. The circumrotation of the macrocyclic polyether component of catenanes 1:t 4+ and 14 4+ can be controlled reversibly by adding or removing o-chloroanil (15), which forms a charge-transfer adduct with the tetrathiafulvalene unit of these catenanes [49, 50]. The adduct can be disrupted by reducing o-chloroanil with Na2S2Os. 437 Cl 15

16 Motions in Catenanes shifts downfield from cs = 6.4. Thus, if the conformation with a dioxyarene unit inside the cavity of the tetracationic cydophane is present at all in solution, its concentration must be below the limit of detection by H NMR spectroscopy. Nonetheless, the tendency of o-chloroanil (1S) to stack against TTF can be exploited [49, 50] to "lock" this unit alongside the cavity of the tetracationic cyclophane (Fig. 16.14). Indeed, comparison of the H NMR spectra recorded at 298 K before and after addition of 1S to a CD3CN solution of either 134+ or 144+ reveals signifi- cant upfield chemical shift changes for the resonances associated with the 1,4-dioxybenzene protons of 134+ (ACS --3 ppm) and the protons in positions 4 and 8 of the 1,5-dioxynaphthalene group of 144+ (ACS --5 ppm). These observations indicate that after addition of 1S the dioxyarene rings become encircled by the tetracationic cyclophane and their protons experience pronounced shielding effects exerted by the sandwiching bipyridinium units. On addition of a mixture of Na25205 and NH4PF 6 in H20 the adduct formed between the TTF unit and o- chloroanil is destroyed, and the original conformation with tetrathiafulvalene inside the cavity of the tetracationic cyclophane is restored. The original resonances of the protons of the alongside dioxyarene rings are, again, consistently observed in the H NMR spectra of both catenanes. Catenane 164+ (Fig. 16.15) incorporates a 1,4-dioxybenzene-based macrocyclic polyether and a tetracationic cyclophane comprising a bipyridinium and a diaza- pyrenium unit. X-ray crystallographic analysis revealed that the macrocyclic poly- ether encircles exclusively the diazapyrenium unit in the solid state. The H NMR 17 + H + T + i H2 17 Fig. 16.15. The circumrotation of the tetracationic cyclophane component ofcatenane 16 4+ can be controlled reversibly by adding or removing (by protonation) n-hexylamine (17), which forms a charge-transfer adduct with the

diazapyrenium unit of the catenane [54].

16.3 Electrochemicall) Driven Motions I 439 spectrum of 164+ in (CD3)2CO at 193 K contains signals from two distinct con- formations in the ratio 96:4. In the major isomer the diazapyrenium unit is located inside the cavity of the macrocyclic polyether and the bipyridinium unit is posi- tioned alongside. In the minor isomer the bipyridinium unit is located inside the cavity of the macrocydic polyether and the diazapyrenium unit is positioned alongside. The tendency of -hexylamine (17) to form adducts with diazapyrenium [S1-S3] can be exploited [S4] to displace the equilibrium between the two con- formations in favor of the isomer with the diazapyrenium unit alongside the cavity of the macrocydic polyether. The differential pulse voltammogram (CH3CN, 298 K) of 16 4+ contains two peaks at Ep = -0.31 and -0.S7 V relative to the SCE aris- ing from the monoelectronic reduction of the alongside bipyridinium unit and of the inside diazapyrenium group, respectively. On addition of -hexylamine the first peak shifts by -60 mV to a potential that corresponds to the monoelectronic reduction of a bipyridinium unit encircled by the 1,4-dioxybenzene macrocyclic polyether. Similarly, the second peak shifts by -20 mV to a potential that is asso- ciated with the monoelectronic reduction of a diazapyrenium unit interacting with -hexylamine. On addition of CF3SO2H, protonation of -hexylamine occurs and, as a result, the adduct formed between -hexylamine and the diazapyrenium unit of the catenane is destroyed and the original equilibrium between the two conformations associated with 16 4+ is restored. The differential pulse voltammo- gram recorded after addition of CFSO2H is identical with that recorded before addition of -hexylamine. Acid-base switching after electrochemical reduction in a family of [2]- and [3]catenanes containing both bipyridinium and amine units in one macrocyclic ring [SS] will be discussed in the next section. Interesting examples of solvent-dependent translational isomerism in catenated structures have been reported [24, S6, S7]. 16.3 Electrochemically Driven Motions Catenate [18.Cu] + (Fig. 16.16) incorporates a terpyridine ligand in one of its two macrocyclic components and a phenanthroline ligand in both [S8]. Oxidation of the tetracoordinated Cu(I) center of [18.Cu] + to a tetracoordinated Cu(II) ion occurs on electrolysis (+0.8 V relative to the SCE) of an acetonitrile solution of the catenate [S8, S9]. In response to the preference of Cu(II) for pentacoordinated geometry the terpyridine-containing macrocycle circumrotates through the cavity of the other macrocyde. In the resulting conformation the Cu(II) center adopts pentacoordinated geometry, which is significantly more stable than the original tetracoordination. The cyclic voltammogram reveals the disappearance of the reversible wave (+0.63 V) associated with the tetracoordinated Cu(II)/Cu(I) redox couple and the concomitant appearance of a reversible wave (-0.07 V) corresponding to the pentacoordinated Cu(II)/Cu(I) redox couple. A second electrolysis (-0.40 V) of the CHCN solution of the catenate reduces the pentacoordinated

[18'0u]+ +e- [18.Cu]2+

Fig. 16.16. The circumrotation of the terpyridine-containing macrocyclic component ofcatenate [18.Cu] + can be controlled reversibly by oxidizing or reducing the metal center [55, 59]. Dark and light circles represent Cu(I) and Cu(11), respectively.

Cu(II) center back to a pentacoordinated Cu(I) ion. In response to the preference of Cu(I) for a tetracoordination the terpyridine-containing macrocycle circumrotates through the cavity of the other macrocycle, restoring the original conformation. The cyclic voltammogram recorded after the second electrolysis contains the original redox wave (+0.63 V) corresponding to the tetracoordinated Cu(II)/ Cu(I) redox couple. Carenate [19.Cu] + (Fig. 16.17) incorporates two identical macrocyclic components comprising terpyridine and phenanthroline ligands [60]. The Cu(I) ion is coordinated tetrahedrally by the two phenanthroline ligands whereas the two terpyridine ligands are located well away from each other. The cyclic voltammogram obtained for [19.Cu] + contains a reversible wave (+0.63 V relative to the SCE) associated with the tetracoordinated Cu(II)/Cu(I) redox couple. The visible absorption spectrum of the carenate contains a metal-to-ligand charge-transfer band at 439 nm for the tetracoordinated Cu(I) chromophore. On electrochemical oxidation of [19.Cu] + or on treatment with NOBF4 the tetracoordinated Cu(I) center is converted into a tetracoordinated Cu(II) ion. As a result, the visible absorption spectrum contains a band at 670 nm for the tetracoordinated Cu(II) chromophore. The intensity of this band decreases with time, however. Indeed, in response to the

preference of the Cu(II) ion for a coordination number higher than four, one of the two macrocycles circumrotates through the cavity of the other, affording a pentacoordinated Cu(II) ion. Subsequently the other macrocycle undergoes a sim- ilar circumrotational process, yielding a hexacoordinated Cu(II) ion which gives, instead, a weak absorption band at 687 nm. Electrolysis (-1.0 V) of the acetonitrile solution of the carenate reduces the hexacoordinated Cu(II) center to a hexaco- ordinated Cu(I) ion. In response to the preference of Cu(I) for tetracoordinated geometry the two macrocycles circumrotate through the cavity of each other in turn, affording the original conformation quantitatively. The conformational motion associated with catenanes 134+ and 144+ (Fig. 16.14) can also be controlled electrochemically by reversible oxidation-reduction of the tetrathiafulvalene unit [49, 50]. The cyclic voltammogram of the free macrocyclic polyether contains a reversible wave (+0.3 V relative to the SCE) for mono- electronic oxidation of the TTF unit. In the catenanes, this unit is located inside the cavity of the tetracationic cydophane and its monoelectronic oxidation occurs at more positive potentials. Large separation between the anodic and cathodic peaks associated with this process is observed. This separation varies as the scan rate is changed. On increasing the scan rate the anodic peak moves to more positive potentials whereas the cathodic peak shifts to less positive values. These observa- tions indicate that the oxidation-reduction of the TTF unit is accompanied by cir- cumrotation of the macrocyclic polyether through the cavity of the tetracationic cyclophane and that this conformational change is occurring on the time scale of the electrochemical experiment. Indeed, after oxidation the newly formed mono- cationic tetrathiafulvalene unit is expelled from the cavity of the tetracationic cyclophane and is replaced by the neutral dioxyarene unit. After reduction the original conformation is restored as the neutral TTF unit replaces the dioxyarene unit inside the cavity of the tetracationic cydophane. Catenane 204+ (Fig. 16.18) incorporates a 1,4-dioxybenzene-based macrocyclic polyether and a tetracationic cyclophane comprising one bipyridinium and one trans-l,2-bis(4-pyridinium)ethylene unit [61]. The H NMR spectrum of 204+ in (CD3)2CO at 243 K contains the signals for two distinct conformations in the ratio 92:8. In the major isomer, the bipyridinium unit is located inside the cavity of the macrocyclic polyether and the trans-bis(4-pyridinium)ethylene unit is posi- tioned alongside. The first two reduction waves in the cyclic voltammogram of the free tetracationic cyclophane occur at -0.31 and -0.43 V relative to the SCE. They correspond to the first monoelectronic reductions of the bipyridinium and the trans-bis(4-pyridinium)ethylene units, respectively. In the catenane these two waves are shifted to more negative potentials and occur at -0.39 and -0.49 V. These observations indicate that the bipyridinium unit is preferentially located inside the cavity of the macrocyclic polyether (Fig. 16.18) and its reduction is more difficult than for the free tetracationic cydophane. When this unit is reduced, however, the tetracationic cydophane circumrotates through the cavity of the macrocydic poly- ether moving the trans-bis(4-pyridinium)ethylene unit inside, as shown by com- parison of its reduction potential with that of a catenane model compound [61b].

Fig. 16.18. The circumrotation oFthe tetracationic cyclophane component oFthe catenane :204+ can be controlled reversibly by reducing or oxidizing its bipyridinium unit electrochemically [61]. The original equilibrium between the two conformations associated with catenane 204+ is restored on oxidation of both units back to their dicationic states. The behavior of catenane [21H] s+, shown in Fig. 16.19, has recently been examined [55]. The absorption spectra and electrochemical properties show that the macrocyclic polyether surrounds a bipyridinium unit both in [21H] s+ and in its deprotonated form, 214+, indicating that protonation-deprotonation does not cause displacement of the macrocycle. Electrochemical measurements show that after one-electron reduction of both the bipyridinium units of [21H] s+ the macro- cycle is displaced on the ammonium function, which means that electrochemically induced conformational switching does occur. Furthermore, upon deprotonation of the two-electron reduced form [21H] 3+, the macrocyclic polyether moves to one of the monoreduced bipyridinium units. Therefore 214+ behaves according to AND logic, a function associated with two energy inputs of different nature. Similarly, in [3]catenane [22H2] 6+ the two macrocyclic polyethers surround the two bipyr- idinium units (Fig. 16.20); on one-electron reduction of both these units, however, the two macrocydes move on the ammonium stations and remain there even after deprotonation [55]. In catenane 234+, the tetracationic cydophane surrounds the p-phenylene unit of the macrocyclic polyether (Fig. 16.21). Variable temperature NMR has furnished evidence of two spontaneous dynamic processes [62]:

+ 2e- _ H + +h H + 214+ I _ H + + H + 0 [21 H] 5+ Fig. 16.19. Switching processes of catenane [21 H] s+ [55]. Starting from catenane 214+, the position othe macrocyclic po17ether switches under acid-base and redox inputs according to AND logic. 0 [21 H] 3+ - 2e- . + 2e-

+ 2e- - 2e- H + H + [22H2] 6+ [22H2] 4+ Fig. 16.20. Switching processes associated with redox stimulation of the [3]catenane [22H2] 6+ [55]. - 2H + + 2H + 222+

234+ +-+ S S N I ' I*' s. s 'Lo oY 16.4 Photochemically Driven Motions I 445 o o +(-+ S S N N -(I*' I ' S- S I .o Fig. 16.21. The dynamic processes associated with catenane 234+ [62]. Asterisks are used to highlight the exchange of position of identical units. � circumrotation of the tetracationic cyclophane through the cavity of the macro- cyclic polyether; � rocking of the -CH2-C6H4-CH2- axis of the encirded p-phenylene unit relative to the mean plane of the tetracationic cydophane as defined by the four methyl- ene carbon atoms. Although this catenane undergoes both oxidation and reduction, no dear evi- dence of a conformational change induced by such stimuli has been obtained. The electrochemically controlled suppression of circumrotation in a catenane caused by the formation of a covalent C-C bond between the two macrocyclic components has been reported [63]. A sequence of reduction and translational events has also been proposed to explain the intriguing electrochemical behavior of a catenane that contains a pyromellitic and a naphthalene diimide units [64]. 16.4 Photochemically Driven Motions The conformational motion associated with the catenate [18.Cu] + (Fig. 16.16) can be also induced photochemically [58b]. On irradiation (464 nm) of a CH3CN solution of the catenate in the presence of p-nitrobenzylbromide the Cu(I)-based chromophoric unit is excited to a metal-to-ligand charge-transfer excited state.

16 Motions in Catenanes Electron transfer from the photoexcited catenate to p-nitrobenzylbromide follows, generating a tetracoordinated Cu(II) center. In response to the preference of the Cu(II) ion for pentacoordinated geometry the terpyridine-containing macrocycle circumrotates through the cavity of the other affording a pentacoordinated Cu(II) center. On addition of ascorbic acid the pentacoordinated Cu(II) center is reduced to a pentacoordinated Cu(I) ion. In response to the preference of Cu(I) for tetra- coordinated geometry the terpyridine-containing macrocycle circumrotates through the cavity of the other, restoring the original conformation. As we have seen in Section 16.1.3, it is possible to construct catenates incor- porating a [Ru(bpy)3] 2+-type photosensitizer (see, e.g., [Ru(bpy)2(9)] 6+, Fig. 16.10). In suitably designed catenanes of this type it should be possible to cause photo- chemical switching

between two different conformations [65]. For example, in a catenane like that shown in Fig. 16.22a excitation of the Ru-based complex should be followed by electron transfer to the bipyridinium unit. In the presence of a sacrificial electron donor the oxidized Ru-based complex would be immediately a Products + Ox P b Xv Q Products P Red Fig. 16.22. Suggested systems for achieving light-driven switching in catehanes [65].

16.5 Perspectiues 1447 reduced and circumrotation of the cydophane would occur to enable formation of a more stable configuration in which the trans-bis(4-pyridinium)ethylene unit occupies the inside position. Oxidation of the reduced bipyridinium unit would then lead back to the original configuration. Similarly, in the system shown in Fig. 16.22b switching could be caused by a reductive photoinduced process with the assistance of a sacrificial oxidant, and back switching could be achieved by means of a reductant. Catenanes containing photoactive azobenzene moleties have been synthesized [66, 67]. As mentioned in Section 13.4.2, it is sometimes possible to control the rate of thermally-activated rotation of the macrocyclic components by photoisomerization of the azobenzene moiety [66]. 16.5 Perspectives 16.5.1 Unidirectional Ring Rotation in Catenanes In catenanes such as those shown in Fig. 16.14, it is possible to induce reversible switching between two different conformations but there is no reason why this movement should happen by unidirectional rotation of a ring around the other ring. To obtain a molecular-level rotary motor the direction of each switching movement should be controllable. This requires introduction of anisotropy fea- tures into the system (Section 10.3). It has been suggested [25] that the goal of unidirectional rotation could be reached by using catenane [24H] 5+ shown in Fig. 16.23. Such a catenane is derived from 144+ displayed in Fig. 16.14 by introducing an ammonium function and a bulky group (B) in appropriate positions on the electron-donor macrocycle. In the starting conformation /, the better electron-donor TTF unit is inside the tetracationic cydophane. When the TTF unit is oxi- dized, it has to escape from the cavity of the tetracationic cydophane. The presence of the ammonium group is expected to favor dockwise rotation of the macrocycle against anticlockwise rotation, because the latter would imply threading of the +1 charged ammonium unit through the +4 charged cydophane. The dockwise rota- tion leads, through intermediate II, to conformation III in which the dioxynaph- thalene unit is inside the cyclophane. At this stage, if deprotonation of the ammo- nium function is performed before back reduction of the oxidized TTF trait, the preferred rotation direction, restoring TTF inside the cydophane (conformation V) should again occur by dockwise rotation (through intermediate IV), because threading of the small amine unit into the cyclophane should compete favorably with that of the bulky group B. Protonation of conformation V regenerates the starting compound L Such a catenane can be viewed as a four-stroke rotary motor working on alternate red-ox and base-acid energy inputs. It is also worth noticing that, because all the processes are reversible, one can obtain anticlockwise rotation by reversing the order of the inputs.

448 I 16 Motions in Catenanes H H + Clockwise 1. - H + - e- rotation 2. + e- Clockwise rotation - 90 H + 0 90 180 H + 270 360 Rotation angle (degrees) [24H] s+ Fig. 16.23. Catenane [24H] s+ designed to perform as a molecular-level rotary motor powered by red-ox and acid-base stimuli [25]. lhe working scheme is based on the potential energy changes expected for conformational rearrangements associated with oxidation- reduction and deprotonation-protonation of the catenane. 16.5.2 Rotacatenane Molecular Gears Combination of a rotaxane and a catenane in a supramolecular structure would lead to second-generation molecular machines capable of coupling different mechanical movements. Examples of rotacatenanes are already available (Fig. 16.4b, [18]), and by suitable design it should be possible to construct a molecular machine in which a "linear" shuttling motion is coupled with a "rotary" ring motion [25]. In principle, this goal could be reached by use of the rotacatenane shown schematically in Fig. 16.24a, which is made of a macrocyclic crown ether C containing an electron-donor unit, interlocked with a dumbbell-shaped component

H + C2 16. 6 Interfacing Catehanes with Surfaces and Solid Supports [449 02 _ H + + H + Cl b H + P H + + Ox f/""x Re d Products Fig. 16.24. Rotacatenanes designed to couple linear and rotary motions under (a) acid-base [25] and (b) light-chemical [65] stimulation. D, containing an electron donor and an ammonium-amine function, and a macrocycle C2 containing an electron-acceptor unit. The working scheme of this machine should be as follows. In the protonated form of the rotacatenane the dumbbell-shaped component D occupies the cavity of macrocycle C1 with the ammonium function, whereas the acceptor unit of macrocycle C2 prefers an alongside interaction with the donor unit of C1, for steric and electrostatic reasons. On deprotonation, the amine function of D escapes from macrocycle C1 and the electron-acceptor moiety of C2 is expected to go into C1, together with the electron- donor unit of D, to give a structure stabilized by donor-acceptor-donor stacking interactions. Reprotonation of the amine function of D reverses the movements and leads back to the original conformation. An alternative project for a switching rotacatenane, based on photochemical stimulation, is shown in Fig. 16.24b [65]. 16.6 Interfacing Catenanes with Surfaces and Solid Supports 16.6.1 Aligning Catenanes in Two Dimensions One of the most important problems in the construction of practical devices is that of preparing organized arrays of molecules to obtain coherent movement. One route toward this objective is to iramobilize the pertinent molecules on a solid support and then to build a framework around which the molecules can be addressed [31, 68, 69].

4s01 16 Motions in Catenanes Catenates in which one of the macrocyclic rings contains a disulfide bridge that enables adsorption of the carenate on the gold surface of, e.g., an electrode, have been prepared [70]. The adsorbed species can be viewed as catenates in which the gold atoms of the surface constitute an integral part of one of the two rings. Such systems yield dear electrochemical responses, but no motion is observed for a cat- enate similar to [18.Cu] + (Fig. 16.16), irrespective of the oxidation state of the metal [70b]. These experiments seem to indicate that intramolecular motion in the surface-confined carenate is severely slowed down, if not totally frozen, in compar- ison with the species in solution. Ordering suitably tailored molecules in two dimensions at interfaces and then transferring them to surfaces is a widely used technique. A series of investigations [71-73] has shown that catenanes 14+ (Fig. 16.2) and 144+ (Fig. 16.14) can be self- organized at the air-water interface when the PF6- counterions are replaced by amphiphilic counterions such as the dimyristoylphosphatidyl anion (DMPA-) (Fig. 16.25). When these counterions are aligned parallel to each other at a surface the phosphonate portion is aligned pointing toward the aqueous substrate. To balance this high negative charge density a layer of tetracationic catenanes associates near the surface as a highly ordered, reproducible monolayer, stabilized by [z... stacking interactions between adjacent catenane molecules. Monolayers of cate- nane 14+ (Fig. 16.2) can be transferred to hydrophobized quartz by use of the Langmuir-Blodgett technique. Stable multilayers up to 30 bilayers thick could be obtained. The redox-active catenane 144+ (Fig. 16.14) was also found to form stable monolayers. The area per catenane tetracation is approximately 1.2 nm 2, with the four DMPA- counterions believed to be clustered in a layer above the tetracations (Fig. 16.25). When catenane 144+ was oxidized to its hexacationic state, 146+, before Langmuir film deposition, and then deposited as its hexakis DMPA- salt, different behavior was observed. Two stable films were obtained, with areas per catenane of 2.7 and 1.5 nm 2, respectively. These areas were interpreted in terms of the anions dictating the area occupied when the surface pressure was below 20 mN m -1, whereas at higher surface pressures the area occupied was determined by the [z... z] stacking interactions. Both states of the catenane were transferred (below 20 mN m -1) on to freshly cleaved mica and on to the (111 face of gold. When the mica-bound monolayers were examined by tapping-mode atomic force microscopy (AFM) it was observed that whereas the monolayer containing the cat- enane 144+ was extremely flat, that ofcatenane 146+ was very bumpy, with roughly 25 nm wide and 2 nm high "hills". When the corresponding gold-supported monolayers were examined by scanning tunneling spectroscopy (STS), important differences were noted. The monolayer containing 144+ only conducted current above +0.3 V whereas that containing 146+ afforded a linear I-Vcurve reminiscent of that of a metal [73]. 16.6.2 A Catenane-based Solid-state Device The results reported above encouraged an attempt to incorporate catenane 144+ into a solid-state device [74, 75]. A monolayer of the catenane was transferred on to

a photolithographically patterned polysilicon electrode. The patterning was such that the Langmuir film was deposited along several parallel lines of polysilicon on the electrode. A second set of wires was then deposited on top of the first set, ori- ented in the orthogonal direction. This second set of electrodes consisted of a 5-nm thick layer of Ti, followed by a 100-nm thick layer of A1. The bottom polysilicon electrode of the molecular sandwich was 7 [tm wide and the top Ti/A1 electrode was 10 [tm wide. This approach was used to construct an array of junctions, each a 1.2 E(V) 0.8 0.4 Write 1700 0.0 1600 1800 1900 2000 Pulse number b / (nA) 0.4 0.0 , -2.0 0.0 +2.0 Ew,te (V) Fig. 16.27. {a) A perturbing {"write") potential is applied across the device, the state of which is then observed by measuring the current flow at the {"read") potential of 200 mV. {b) Plot of the "read" current as a function of the "write" voltage [74, 75].

16. 6 Interfacing Catehanes with Surfaces and Solid Supports [453 addressable individually (Fig. 16.26). The mechanism of conduction was electron tunneling through the single-molecule thick layer between the junction electrodes. Thus any change in the electronic characteristics of the interelectrode medium was expected to affect the tunneling efficiency and change the resistance of the junc- tion. It should be noticed that such devices are conductors, not capacitors. Experi- ments were performed by applying a series of voltage pulses (between 3-2.0 and -2.0 V) and reading, after each pulse, the current through the device at 200 mV, a potential that does not affect switching (Fig. 16.27a). The results obtained, in the form of a current-voltage curve (Fig. 16.27b), were interpreted on the basis of the mechanism illustrated in Fig. 16.28. Note that this mechanism is somewhat dif- ferent from that which explains the behavior of the same catenane in solution [49, 50] (Section 16.3). Conformation I is the "switch operf' state and conformation IV the "switch dosed" state of the device. When 144+ is oxidized (+2 V), the TTF unit is ionized in state II and experiences Coulombic repulsion inside the tetracationic cydophane component, resulting in circumrotation of the crown ether and forma- tion of conformation III (note that in solution at 3.2 V TTF undergoes two-electron oxidation and the dioxynaphthalene unit is also oxidized). When the voltage is reduced to near-zero bias conformation IV is obtained; this, however, does not return to conformation I, in contrast with what happens in solution. The initial E(V) +2 -2-- H III IV Fig. 16.28. Proposed molecular-level mechanism for operation of the device based on catenane 144+ [74, 75].

16 Motions in Catenanes conformation would, in fact, be restored only via state V in which the bipyridinium units of the cyclophane component are reduced (at the potential value used, -2 V, the bipyridinium units undergo two-electron reduction, in solution). The current (read)-voltage (write) curve has a highly hysteretic profile (Fig. 16.27b). Thus, the catenane junction device operates as a system with potential for use in random access memory (RAM) storage. It is claimed that solid-state devices of this type are close to application. Their design seems, however, to be largely empirical in nature, because the working mechanism of the chemical switching element in the solid state is not yet fully understood. References G. SCHILL, Catehanes, Rotaxanes and Knots, Academic Press, New York, 1971. Molecular Catehanes,

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459 Appendix Glossary The definitions given are not general, but related to the content of this book absorption spectrum: a diagram of the wavdength distribution of the absorption of light by a substance actin: a thread-like protein involved in the linear movement of myosin adduct: a supramolecular species resulting from the association, driven by inter- molecular forces, of two simpler components allosteric effect: modification of the binding ability (or another property) of one site in a molecule or supramolecular species derived from a conformational rearrangement induced by binding at another remote site; allosteric effects can be positive or negative amphiphile: a molecule that

has two distinct zones, one water-soluble (hydrophilic) and the other soluble in organic media (hydrophobic or lipophilic) antenna (molecular-level): see light-harvesting antenna aspartate carbamoyltransferase: an enzyme involved in the synthesis of thymine and cytosine in bacteria assembler: a general purpose building nanorobot atomic force microscopy (AFM): see scanning probe microscopy ATP synthase: the enzyme that synthesizes ATP (see also FoF-ATP synthase) attenuation parameter (fi): a parameter related to the decrease of the rate of an electron-(fie), hole-(fiht), or energy-(fi e) transfer process with increasing dis- tance azacrown ether: a crown ether in which one or more oxygen atoms are replaced by nitrogen azobenzene: a molecular unit containing an N=N double bond that can exist as two different geometrical isomers called cis and trans; see also cis-trans isomers back electron-transfer: a term often used to indicate thermal reversal of a photo- induced electron-transfer reaction which restores the donor and the acceptor in their original oxidation levels; see also charge recombination battery (molecular-level): a molecule capable of accumulating charge beacon (molecular-level): a hairpin-shaped oligonucleotide bearing an intra- molecularly quenched fluorophore whose fluorescence is restored upon binding Molecular Devices and Machines -A Journey into the Nano World. V. Balzani, A. Credi, M. Venturi Copyright � 2003 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim ISBN: 3-527-30506-8

460 I Appendix to a target nucleic acid; it is used to report the presence of specific nucleic acids in solution bilayer membrane: a membrane composed of two monolayers of amphiphilic molecules (typically, phospholipids); the monolayers touch each other with their hydrophobic sides whereas the hydrophilic zone is exposed binary logic: an algebraic representation in which variables can assume only two values (1 or 0, yes or no, true or false) binary number system: a means of representing numbers using only the digits 0 and 1 in which successive digits are interpreted as coefficients of successive powers of the base 2 biomolecular switch: a molecular-level switch that controls a biological function biphotochromic supramolecular system: a supramolecular species containing two photochromic components bistable molecule: a molecule that can be reversibly switched between two different stable states by some external stimulus block copolymer: a polymer whose chain is composed of different segments, each composed of identical repeating units bottom-up approach (to miniaturization): the construction of nanometer objects,

devices, and machines starting from atoms or molecules bridge (molecular-level): a molecular component in a supramolecular system that is not directly involved in the function performed by the system but plays the role of connector between active components bridging ligand: a ligand capable of linking two metal ions Brownian motion: the random movement of molecules caused by collisions related to thermal energy caged biomaterial: a biological material whose function has been blocked by chemical modification calixarene: an aromatic macrocyclic molecule having the shape of a calix carotenoids: derivatives of carotene (a natural pigment) often used as electron donors in multicomponent systems catalyst: a substance which accelerates a chemical reaction, but which is not itself altered in form or amount at the end of the reaction catenan& a catenane-type ligand catenane: a supramolecular species consisting of two or more interlocked macro- cyclic components catenate: a catenane-type metal complex charge pool (molecular-level): see battery charge recombination: the back electron-transfer reaction that can follow charge separation; see also back electron-transfer charge separation: a chemical reaction, usually photoinduced, involving the trans- fer of an electron in a supramolecular species from a neutral component to another neutral component, leading to a species made of a positively and a neg- atively charged moleties charge shift: a chemical reaction, usually photoinduced, involving transfer of an electron (or hole) in a supramolecular species from charged to uncharged molecular components

charge transfer (CT): an electronic transition (and the related absorption band and excited state) between orbitals predominantly localized in different components of a supramolecular species charge transport: a process in which a charge (either an electron or a hole) is moved along a wire-type supramolecular species chemical computer: a computer based on the properties of suitably designed and appropriately integrated molecular components chemical stimulation: the stimulation of a function of a molecular or supra- molecular species by addition of an appropriate chemical reagent (e.g., a metal ion) chemiluminescence: light emitted from an excited state originating from a chemi- cal reaction chiral molecule: a molecule that can exist as two isomers that cannot be super- imposed (mirror images) chiroptical switch: a bistable chiral molecule; see also switch chromophore: a light-absorbing molecular unit chronoamperometry: an electrochemical technique particularly useful for measur- ing the number of electrons exchanged in a redox process circular dichroism: a phenomenon related to the different absorption of left and right circularly polarized light by chiral compounds cis-trans isomers: two structures of the same molecule differing in the relative positions of the substituents around a double bond; also called geometric isomers cofactor: a small non-protein molecular unit linked to the protein chain of an enzyme which determines or improves catalytic activity colloid: an heterogeneous system consisting of small (1-100 nm) partides sus- pended in a solution combinational logic circuit: switching circuit the outputs of which are determined only by the concurrent inputs; its logic function can be obtained by a suitable combination of basic logic operations complex: 1. in coordination chemistry, a compound made of a metal atom or a metal ion surrounded by ligands; 2. in organic chemistry, a host-guest system; 3. in biological chemistry, a receptor-substrate adduct complexes as metals/complexes as ligands strategy: a synthetic strategy based on the use of suitably designed metal complexes as building blocks for the con- struction of metal-based dendrimers; a complex can be used as a metal when the metal coordination sphere is not saturated, and as a ligand when the metal is coordinated to a bridging ligand carrying free coordination sites conjugated molecule: a species containing alternating single and double bonds, in which z electrons are delocalized over the entire molecule convergent synthesis: a synthetic procedure used to construct a dendrimer by appending preformed dendrons to a core coordination bond: a bond between a metal or metal ion and a molecule or an ion; see also ligand and complex copolymer: a polymer made of different repeating units core: the central unit in a dendrimer

462 I Append& coulombic mechanism: a mechanism for electronic energy transfer based on cou- lombic interaction (also called resonance, through-space or F6rster mechanism) covalent bonds: strong atom-atom bonds which determine the structure of a mol- ecule CPK molecular models: space-filling Lego-type models for molecules (scale, 1.25 cm = 1 A) crown ether: a macrocyclic molecule containing oxygen atoms linked by organic spacers (typically -CH2CH2- units) cryptand: a macrobicydic host capable of surrounding a guest species; the result- ing complex is called cryptate cucurbituril: a macrocyclic barrel-shaped compound prepared by acidic condensa- tion of glycoluril and formaldehyde cyclic voltammetry (CV): a very popular electrochemical technique for investigating the redox behavior of molecular and supramolecular species cyclodextrin (CD): a cyclic

oligosaccharide shaped like a truncated cone; -CD, -CD, and 7-CD contain 6, 7, and 8 glucopyranoside units, respectively cyclometalated complex: a metal complex in which a heterocyclic aromatic ligand is coordinated to a metal atom or a metal ion via carbon and nitrogen atoms cyclophane: a macrocyclic organic molecule with a bridged aromatic ring cytochromes: a family of electron-transfer proteins with one or several heine groups denaturation: structural changes of a protein (or of a nucleic acid) from the original native state without alteration of the amino acid (or nucleotide) sequence dendrimer: a well-defined macromolecule with a tree-like structure dendron: a dendrimer branch Dexter mechanism: see exchange mechanism diastereoisomers: stereoisomers which are not mirror images of each other differential pulse voltammetry: an electrochemical technique for investigating the redox behavior of molecular and supramolecular species diode (molecular-level): a two-terminal molecular switch that can turn a current on or off as it attempts to pass through the diode; molecular rectifiers are one type of molecular-level diode ditopic receptor: a supramolecular species with two binding sites capable of host- ing two similar or different guests divergent synthesis: a synthetic procedure used to construct a dendrimer starting from its core by successive repetitive additions of building blocks driving force: term used to indicate the negative of the standard Gibbs energy change (AG �) of a reaction; reactions with a positive driving force (i.e., negative AG �) are spontaneous; see also free energy change dumbbell: a molecular structure consisting of a thread-like component with two bulky groups at its extremities dye: term often used to denote an organic molecule with absorption bands in the visible spectral region dynein: a family of linear motor proteins in charge of intracellular transport efficiency {of a step, t/l: the ratio of the rate of a step to the sum of the rates of all the parallel steps that cause the disappearance of a species

electrochemical sensor: see sensor electrochemical stimulation: the stimulation of a function of a molecular or supra- molecular species by an electrochemical input electrochemiluminescence: light emitted by an excited state originating from a redox reaction between electrochemically generated reactants electrochromic molecule: a molecule that can be reversibly interconverted, by redox processes, between two or more forms with distinct absorption spectra electrolysis: exhaustive electrochemical reduction or oxidation of an ion, molecule, or molecular component electromotive force: a driving force based on an electrical potential difference electron acceptor: an electron-deficient molecule (or molecular component in a supramolecular species) electron donor: an electron-rich molecule (or molecular component in a supra- molecular species) electron injection: the transfer of a negative charge to a molecular or supra- molecular species or to a semiconductor electron transfer: a process that involves transfer of an electron from one molecule (or a molecular component in a supramolecular species) to another; such a pro- cess is often called a redox reaction; it can be photoinduced, i.e. induced by absorption of light by one of the two reaction partners; when the two partners are neutral the process results in a charge separation into positively and nega- tively charged molecules (or molecular components) electron-transfer photosensitization: see photosensitized process electronic coupling (H): see electronic factor electronic energy transfer: see energy transfer electronic factor: the electronic term in Fermi "golden rule" expressions for the rate constants of energy-(H e) and electron-(H el) transfer processes electronic rearrangement: a change in the electronic distribution caused by an external stimulus (e.g., light absorption) electronically excited molecule: a molecule in which absorption of a photon has caused a rearrangement in its electronic structure; see also excited state emission: the radiative deactivation of an excited state emission spectrum: a diagram of the wavelength distribution of the light emitted by a substance enantiomers: stereoisomers that are mirror images of each other energy barrier (AG#): the activation energy of a chemical reaction energy concentrator: see light-harvesting antenna energy-level diagram: see state energy-diagram energy migration: the transfer of electronic energy among identical molecular components in a supramolecular species or among monomeric units in a poly- mer; see also energy transfer and hopping mechanism energy transfer: a process that causes transfer of electronic energy from an excited state of a molecule (or a molecular component in a supramolecular species) to a another molecule (or molecular component) enzyme: protein capable of catalyzing biological processes

exchange mechanism: a mechanism for electronic energy transfer, based on exchange interaction, that requires overlap of the wavefunctions of the energy donor and the energy acceptor excimer: an excited dimer, dissociative in the ground state, resulting from the reaction of an excited molecule with a ground state molecule of the same type exciplex: an excited complex, dissociative in the ground state, resulting from the reaction of an excited molecule with a ground state molecule of a different type excited state: a higher energy state of a molecule (see also electronically excited molecule) exciton: a term used for polymers and solid-state systems to indicate an excited state (electron-hole pair) FoF-ATP synthase: a natural molecular-scale machine which consists of two rotary molecular motors (F0 and F) attached to a common shaft; see also ATP syn- thase fatigue: term used for indicating the lack of reversibility, particularly with reference to photochromic systems Fermi "golden rule" expression: a quantum mechanical expression for the rate constant of energy- and electron-transfer processes Fermi level: the average between the highest occupied and lowest unoccupied levels in a solid state material ferrocene: an organometallic molecule that undergoes reversible one-electron oxi- dation, often used as a reference in electrochemical experiments flash photolysis: a pulsed irradiation technique used to produce and investigate transient species fluorescence: the light emitted as a result of spin-allowed radiative deactivation of an excited state fluorescent sensor: see sensor fluorescent switch: a compound existing in two forms with different fluorescence properties fluorophore: a fluorescent molecular unit F6rster mechanism: see coulombic mechanism Franck-Condon factor (FC): the nuclear term in the Fermi "golden rule" expres- sions for the rate constants of energy (FC e) and electron (FC ei) transfer free-base porphyrin: see porphyrin free energy change (AG�): the thermodynamic quantity associated with a chemical reaction that establishes whether the reaction can occur (AG � < 0); see also driving force full adder: a logic element which operates on two binary digits and a carry digit from a preceding stage, producing as output a sum digit and another carry digit fullerene: a family of spherical molecules consisting of carbon (C) atoms; the most common fullerene is C60. fuzzy logic: a type of logic in which propositions are not required to be either true or false, but may be true or false to different degrees (in contrast with classical binary logic)

glucose oxidase: an enzyme which catalyzes the oxidation of glucose ground state: the lowest energy, stable electronic state of a molecule guest: an ion or a convex molecule capable of being hosted by a concave molecular or supramolecular species half adder (molecular-level): a molecular device capable of adding two one-digit binary numbers heme group: the complex between an iron(II) ion and a porphyrin ligand which constitutes a cofactor of many enzymes (e.g., cytochromes) hemicarceplex: a host-guest complex in which the host (hemicarcerand) is a spe- cies whose internal cavity is accessible only at high temperature heterosupramolecular system: a system consisting of molecular or supramolecular species linked to a nanoscopic solid state component (e.g., to a nanoparticle) hole burning: the photobleaching of a feature within an inhomogeneous absorption or emission band caused by the disappearance of resonantly excited molecules as a result of a photochemical or photophysical process hole injection: the transfer of a positive charge to a molecular or supramolecular species or to a semiconductor hole transfer: the transfer of a positive charge from a molecule (or a molecular component in a supramolecular species) to another; see also electron transfer holography: a technique used to form three-dimensional optical images hopping mechanism: an energy, electron, or hole transfer occurring among identical molecular components in a supramolecular species or among monomeric units in a polymer host: a molecular or supramolecular species, usually with a concave structure, capable of hosting an ion or a molecule host-guest system: see host and guest hydrogen bond: a relatively weak chemical bond arising when a hydrogen atom covalently linked to an atom X forms an additional bond with another atom Y either in the same or in another molecule; strong hydrogen bonds are formed when X and Y are electronegative atoms (e.g., N, O) induced fit: extensive rearrangement of a receptor aimed at optimization of a host-guest interaction inhibitor: a substance which reduces the rate of a chemical reaction, but which is not itself altered in form or amount at the end of the reaction intermolecular forces: weak attractive forces such as hydrogen bonds, electron donor-acceptor and -interactions, and van der Waals forces that are responsible for molecular assembly internal conversion: a spin-allowed radiationless deactivation of an excited state intersystem crossing: a spin forbidden radiationless deactivation of an excited state intervalence transfer: the transfer of an electron between two species with the same chemical nature but different oxidation state; see also mixed-valence state ion channel: a supramolecular system (in Nature, an allosteric protein) which enables ions to cross a membrane in a thermodynamically allowed direction

ion pump: a supramolecular system (in Nature, an allosteric protein) which enables ions to cross a membrane against a thermodynamic gradient, by using a source of energy such as ATP or light isoemissive point: the wavelength at which the intensity of emission does not change during a chemical reaction or physical change isomerization: the interconversion between isomers isomers: molecules having the same composition but different structure isobestic point: the wavelength at which the absorbance does not change during a chemical reaction or physical change kinesin: a family of linear motor proteins in charge of intracellular transport Langmuir-Blodgett (LB) film: a molecular mono- or multi-layer obtained by orga- nization of amphiphilic molecules at an air-water interface and deposited on to a solid surface large-downward approach: see top-down approach large molecule: a large chemical compound in which it is not possible to identify distinct molecular components, in contrast with supramolecular species laser: (acronym from light amplification by stimulated emission of radiation): a source of monochromatic coherent light used in photochemistry for pulsed excitation on very short time scales Lewis acid: a chemical compound capable of accepting an electron pair lifetime (): the time needed by intrinsic, first-order deactivation processes to reduce the concentration of a transient species (e.g., an excited state) to 1/e of its initial value ligand: a molecule or an ion capable of binding to a metal ion or a metal atom ligand centered: the orbitals, electronic transitions, excited states, and absorption bands of a ligand in a metal complex light-emitting diode (LED): a device converting electric power into light by electro- luminescence light-harvesting antenna (molecular-level): an organized array of molecular com- ponents (i.e., a supramolecular species) capable of absorbing light and delivering the resulting electronic energy to a predetermined component of the array; this function is often called the antenna effect linker: see bridge liposome: an aqueous compartment enclosed within a bilayer membrane liquid crystal: a liquid which is not isotropic because of preferential orientation of molecules in large domains; depending on the type of molecule and organi- zation, liquid crystalline phases can be nematic, smectic, cholesteric, discotic or lyotropic logic gate (molecular-level): a molecular or supramolecular species capable of per- forming a logic operation logic operation: an operation on logical quantities (0, 1; yes, no; true, false) luminescence: the light emission caused by radiative deactivation of an excited state luminophore: a luminescent molecular unit macrocycle: a molecule or supramolecular species with a closed, ring-type structure

Marcus inverted process: an electron- or energy-transfer process occurring in the Marcus inverted region, i.e., in a kinetic regime in which the rate constant decreases with increasing driving force Marcus theory: a classical theory for electron- and energy-transfer processes in which the energy barrier (/XG #) is related to the standard free energy change (AG �) and the nuclear reorganizational energy (,t) by a quadratic equation. According to this theory, on increasing the driving force the reaction rate increases when -AG�< ; (normal region) but decreases when -AG�> ; (inverted region) memory (molecular-level): a molecule that can be switched between forms (write) with different properties (read); see also bistable molecule mesogenic molecule: a chemical species capable of generating a liquid crystal metal-to-ligand-charge transfer (MLCT): the electronic transitions (and related excited states and absorption bands) that in metal complexes transfer electronic charge from metal to ligand(s) methylviologen: the common name for the 1,1'-dimethyl-4,4'-bipyridinium dica- tion microtubule: a thread-like protein-based structure, 18-25 nm in diameter, related to the linear movement of kinesin and dynein mixed-valence state: an excited state arising from an intervalence transfer transi- tion; it can be related to an absorption band modular approach: the use of repeating units to construct a supramolecular (mod- ular) system molecular device: an assembly of a discrete number of molecular components (i.e., a supramolecular species) designed to perform a specific function molecular electronics: electronics based on molecular-level components molecular machine: a particular type of molecular device in which the component parts change their relative positions as a result of an external stimulus molecular recognition: the ability of a molecule to recognize and associate with another molecule on the basis of the presence of complementary chemical functionalities molecular-wire behavior: a kinetic regime of electron-transfer reactions in supra- molecular species characterized by a very small decrease in the rate constant on increasing distance monolayer: a one-molecule-thick layer motor protein: a complex biological species that plays the role of a motor inside cells multicomponent system: see supramolecular system multiplexing optical system: a system capable of processing two or more optical signals simultaneously multistate-multifunctional system: a system capable of existing in three or more forms that can be interconverted by means of different stimuli myosin: a family of linear motor proteins nanopartide: a solid particle of nanometer size, usually a metal or semiconductor nanocrystal

nanostructured electrode: an electrode made of syntherized nanopartides nanotechnology: a new branch of technology, dealing with objects at the nano- meter (10 -9 m) scale nanotube: a carbon tube made of graphite sheets, a few nanometers in diameter and up to millimeters long neural-type system: an artificial system capable of mimicking some elementary properties of neurons non-linear optics: the study of a particular class of phenomena dealing with the interaction between light and matter, such as multiphoton processes and second harmonic generation non-radiative deactivation: see radiationless decay nuclear factor: see Franck-Condon factor nuclear rearrangement: a change in the relative positions of atoms in molecules or components in supramolecular species caused by an external stimulus (e.g., light absorption) nudeophile: an electron-rich compound nucleotide: a chemical species formed by a heteroaromatic base, a sugar, and a phosphate unit oligonudeotide: a polymer formed by a few nucleotides, essentially a fragment of a nucleic acid optical tweezer: a laser technique used to control the position of a small bead optoelectronic device: a device transducing an optical input into an electrical output orbital: a one-electron wavefunction which explicity depends on spatial coordinates and defines the region of space in which the electron is likely to be found oxidation: the half reaction of a redox process involving the release of one or more electrons by a reactant perceptron: the artificial intelligence unit used to mimic the behavior of a neuron pH jump: a large change in the pH of a solution caused by rapid addition of acid or base phase isomers: the isomers generated in a supramolecular system by concerted conformational motion of its components phosphorescence: light emission caused by a spin-forbidden radiative deactivation of an excited state photochemical stimulation: stimulation with light of a function of a molecular or supramolecular species photochemistry: the branch of chemistry dealing with the interaction of light (far UV to IR) with matter; the absorption of light by a molecule causes the formation of an electronically excited state photochromic molecule: a molecule that can be reversibly interconverted between two forms with different absorption spectra, with at least one of the reactions being induced by absorption of light photocurrent: an electric current generated by absorption of light photoinduced electron transfer (PET): see electron transfer

photoinduced redox reaction: see electron transfer photoisomerization: photoinduced interconversion between isomers photolitography: a photochemical technique used in the top-down approach to miniaturization photonic stimulation: see photochemical stimulation photonics: the branch of science dealing with the use of light signals for information processing photophysical processes: photoexcitation and subsequent events which lead from one state of a molecular unit to another via radiative and radiationless tran- sitions photorefractive material: a material that undergoes a change in refraction index when stimulated with light photoresponsive polymer: a polymer that undergoes a change in some of its prop- erties (e.g., its length) when stimulated with light photosensitized process: a reaction of a non-absorbing species induced by an electron- or energy-transfer process involving an excited state of a light- absorbing species photosensitizer: a molecular unit capable of being photoexcited and of inducing excitation or reaction in another molecular unit photostationary state: a chemical equilibrium reached in the presence of light excitation photosynthesis: a process that converts light energy into chemical energy polymer: a chemical compound made of many covalently linked identical or dif- ferent repeating units polynudear complex: a complex containing several metals or metal ions in its structure polypeptide: a chain of amino acids; see also protein polypyridine ligand: a ligand consisting of many pyridine units porphyrins: a class of molecule based on the quadratic arrangement of four basic nitrogen-containing pyrrole units. In free-base porphyrins two nitrogen atoms are linked to hydrogen atoms; on deprotonation a metal ion can be coordinated by the four nitrogens t-tt interactions: weak, noncovalent interactions involving aromatic units preorganization: an arrangement of functional groups or molecular units designed to facilitate the occurrence of a specific process or function protein: a natural polymer made of a sequence of amino acids protein folding/unfolding: spontaneous (folding) or stimulated (unfolding) rear- rangements of protein chains related to their functional three-dimensional ter- tiary structure proton: a positively charged hydrogen atom; in solution it is the species transferred in so-called acid-base reactions proton-motive force: a driving force based on a proton energy gradient proton pump: an ion pump for protons pseudorotaxane: an inclusion complex in which a molecular thread is encircled by a macrocyclic component; see also rotaxane

P-type photochromic system: a photochemically reversible photochromic system quantum yield (O): the ratio of the number of light-generated events to the num- ber of absorbed photons; for example, in fluorescence, the ratio of the numbers of emitted to absorbed photons quencher: a molecule or molecular component in a supramolecular species that deac- tivates (quenches) an excited state of another molecule or molecular component quenching: the deactivation of an excited state and, as a consequence, of all its processes (e.g., luminescence) by a quencher quinones: electron-deficient aromatic molecules that can be reversibly reduced by one and two electrons racemization: a reaction that converts an enantiomer into its mirror image, even- tually leading to equal populations of the two enantiomers radiationless decay: the deactivation of an excited state via radiationless transitions without emission of a photon or a chemical change radiationless transition: an isoenergetic transition between two states of a molecu- lar unit radiative decay: see luminescence radiative transition: a transition between two states of a system, the energy differ- ence being emitted or absorbed as a photon rate constant: a parameter used to express the specific rate of a process reaction center (RC): a supramolecular structure of natural photosynthetic systems in which electronic energy is converted into chemical energy by means of a charge-separation reaction receptor: a term commonly used in biology to indicate a host species rectifier (molecular-level): a type of molecular-level diode in which current flow in one direction is more difficult than in the opposite direction redox reaction: a process resulting from coupled oxidation and reduction (half) reactions redox switch: a compound that can be interconverted between two different forms by a reversible redox reaction reduction: the half reaction of a redox process; the process involves uptake of one or more electrons by a reactant relay: a chemical compound playing the role of charge carrier in a redox process reorganizational energy: the energy (; in the Marcus equation) required for all the structural adjustments (in reactants, 2, and in the surrounding solvent mole- cules, ;o) which are needed to obtain the reactive configuration for electron- and energy-transfer processes resonance mechanism: see coulombic mechanism rotacatenane: the combination of a rotaxane and a catenane in the same supra- molecular structure rotaxane: a supramolecular species consisting of a dumbbell-shaped component and a macrocyclic component which surrounds the linear portion of the dumb- bell and is trapped mechanically by bulky stoppers; when at least one of the stoppers is absent, the macrocyclic component can dethread and the supra- molecular species is called pseudorotaxane

saccharides: organic compounds made of carbon, oxygen and hydrogen, also known as carbohydrates or sugars sacrificial acceptor: a compound capable of scavenging, by means of an irreversible reaction, the electron donor species generated in a photoinduced electron- transfer reaction, thereby preventing back-electron transfer sacrificial donor: a compound capable of scavenging, by means of an irreversible reaction, the electron acceptor species generated in a photoinduced electron- transfer reaction, thereby preventing back-electron transfer scanning probe microscopy (SPM): a range of techniques used to study the struc- ture of surfaces based on an atomically sharp probe which scans above the sample surface with subnanometer resolution while monitoring some interac- tion between the probe and the surface. Most common SPM techniques are scanning tunneling microscopy (STM) and atomic force microscopy (AFM). SPM techniques can also be employed for the positional control of objects on the nanometer scale (nanomanipulation) scanning tunneling microscopy (STM): see scanning probe microscopy scanning tunneling spectroscopy (STS): a technique, derived from STM, used to investigate the local electronic distribution of the surface of a sample scavenger (reductant or oxidant): see sacrificial donor or sacrificial acceptor self-assembled monolayer (SAM): a molecular monolayer which forms sponta- neously on a surface self-assembly: spontaneous aggregation of molecular components self-organization: spontaneous formation, by self-assembly, of an organized supra- molecular system capable of performing a function semiconductor: a solid material with a relatively small gap between the valence and conduction bands sensor: a molecular or supramolecular species that undergoes a change in some of its properties (e.g., fluorescence spectrum, redox potential) on interaction with a specific molecule or ion single-molecule spectroscopy: a range of techniques aimed at optical detection and spectroscopic characterization of a single molecule singlet: the spectroscopic multiplicity of an electronic state with overall spin value of zero singlet-singlet energy transfer: energy transfer from an electronically excited sin- glet donor to produce an electronically excited acceptor in a singlet state slipping process: the threading/dethreading of a macrocycle through the stopper of a dumbbell-shaped component small-upward approach (to miniaturization): see bottom-up approach sol-gel process: the preparation of a three-dimensional porous solid network (gel) starting from colloidal partides dispersed in a liquid (sol) spacer: see bridge spectral sensitization: the sensitization of a photoinduced process in a semicon- ductor by a molecular species capable of absorbing low-energy radiations that the semiconductor is unable to absorb spin-allowed transition: the transition between states of the same multiplicity

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different multiplicity spin multiplicity: a spectroscopic parameter of an electronic state, with a value of 28 + 1, where $ is the total spin quantum number of the system; a state of sin- glet multiplicity has $ = O, a state of triplet multiplicity has $ = 1 spin selection rules: the rules that govern the probability of an electronic transition on the basis of the spin values of the states involved spin-transition material: a material undergoing switching between two different spin states, e.g. on changing the temperature or upon light excitation stacking interactions: a particular type of z-z interaction state energy diagram: a diagram showing the relative energies of the (relevant) electronic states of a molecular or supramolecular species stereogenic center: an atom bound to four different substituents; a molecule with one stereogenic center is chiral stereoisomers: isomers that differ from one another only in the way atoms are ori- ented in space stopped flo a technique based on rapid mixing of solutions used to investigate the kinetics of chemical reactions stopper: a bulky group at the end of a thread-like compound substrate: a term commonly used in biology to indicate a guest species superexchange mechanism: a tunneling mechanism for electron- or energy- transfer processes which is based on the participation of virtual states of molec- ular components or of the medium intervening between the two reaction partners supramolecular chemistry: 1. classical definition by J.-M. Lehn: 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; 2. more general definition used in this book: the chemistry of systems made of two or more molecular components (see also supramolecular system) supramolecular system (or supramolecular species): a chemical species in which it is possible to identify molecular components, in contrast with a large molecule; see also supramolecular chemistry switch (molecular-level): 1. a molecular device, incorporated in a molecular wire, that can reversibly interrupt the movement of electrons or electronic energy across it as a consequence of an external stimulus; 2. a species that can be reversibly interconverted between two (or more) different states by means of an external stimulus template synthesis: a synthetic strategy which relies on the presence of molecular recognition sites between the components to be assembled terminal ligand: a ligand of a polynudear metal complex or dendrimer that does not bridge metal ions and thereby occupies a peripheral position thermochromic molecule: a molecule that can be reversibly interconverted, by heating or cooling, between two forms with different absorption spectra through-bond interactions: the interactions between remote components as a result of the mixing with orbitals of connector units; see also superexchange mechanism

through-space interactions: the interactions that result from direct spatial overlap of orbitals of the active components, in contrast with through-bond interaction time resolved spectroscopy: the recording of spectra at a series of time intervals after excitation of the system with a light pulse top-down approach (to miniaturization): the construction of miniaturized devices starting from macroscopic materials topology: in a supramolecular species it concerns the relative spatial distribution of components trans-cis isomers: see cis-trans isomers transient: a short-lived species (e.g., an excited state) transient dc conductivity: a technique based on pulsed excitation for measuring the conductivity of excited states or other transient species transient spectroscopy: see time resolved spectroscopy triplet: the spectroscopic multiplicity of an electronic state with overall spin value of one triplet-triplet energy transfer: the energy transfer from an electronically excited triplet donor to produce an electronically excited acceptor in the triplet state tritopic receptor: a supramolecular species with three binding sites, thus capable of hosting three equal or different guests truth table: a table that correlates input and output values of a logic function and lists all its possible states T-type interaction: a particular type of - interaction T-type photochromic system: a thermally reversible photochromic system turnover number: a parameter measuring the resistance to fatigue two-photon excitation: the excitation resulting from the successive or simultaneous absorption of two photons tylakoid membrane: the structure contained in the chloroplasts which embeds all the main molecular components of the photosynthetic process unsaturated molecule: see coniugated molecule van der Waals interactions: weak, noncovalent interactions caused by dipole-dipole and dispersion forces viologen: a common name for 4,4t-bipyridinium derivatives water deavage reaction: the splitting of water into hydrogen and oxygen wire (molecular-level): a common name to indicate a long, highly coniugated mol- ecule write-lock-read-unlock-erase cycle: a cyclic process in a multistate/multifunc- tional system that can be used for optical memory purposes zeolite: a family of crystalline microporous aluminosilicate compounds with a well defined structure zero-zero spectroscopic energy {E�-�): the energy difference between the zero vibrational levels of two electronic states zwitterionic structure: a structure with opposite charges in two different regions of a molecule or supramolecular species

4,4[List of Abbreviations The same abbreviaton may have dijrent meanings, as indicated ACA: ADP: AFM: AMI: ANI: apo-GO: AQ: ATCase: ATP: ATPase: B800: B850: BC: BChls: BDPY: BP: BPTTF: bpy: Bu: fid: fien: flht: CBPQT4+: CD: CPK: CPL: CT: CTP: CV: 9-anthracenecarboxylic acid adenosine diphosphate atomic force microscopy Austin Model 1, a semiempirical molecular calculation method 4-aminonaphthalene monoimide apo-glucose oxidase anthraquinone aspartate transcarbamoylase adenosine triphosphate ATP synthase bacteriochlorophyll molecules with absorption maximum at 800 nm bacteriochlorophyll molecules with absorption maximum at 850 nm bacteriochlorophyll toohomer bacteriochlorophylls boron-dipyrromethene bacteriopheophytin bis(2,S-dimethylpyrrolo[3,4-d])tetrathiafulvalene 2,2'-bipyridine butyl attenuation parameter of an electron-transfer process attenuation parameter of an energy-transfer process attenuation parameter of a hole-transfer process cydobis(paraquat-p-phenylene) cydodextrin Corey-Pauling-Koltun molecular models circularly polarized light charge transfer cytidine triphosphate cyclic voltammetry

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Cy: cydam: DABCO: dansyl: DB24C8: DHA: DMA: DMF: DMN: DMPA-: DMSO: DNA: 1/5DN38C10: DTP: AG�: AG#: E0'0: EDTA: EPR: F: FAD: Fc: FCd: Fce: FMN: G: GTP: Hel: Hen: HBD: HIV: HOMO: HPLC: qen.conv: In: ras s: List of Abbreviations 1 475 cytochrome 1,4,8,11-tetraazacydotetradecane 1,4-diazabicyclo[2.2.2] octane the common name for the 5-dimethylamino-l-naphthalenesul- phonamido unit dibenzo[24] crown-8 dihydroazulene N,N-dimethylaniline N,N-dimethylformamide dimethoxynaphthalene dimyristoylphosphatidyl anion dimethylsulfoxide deoxyribonucleic acid 1,5-dinaphtho[3 8] crown- 10 5,15-ditolylporphyrin dianion free energy change energy barrier zero-zero spectroscopic energy ethylenediaminetetraacetate anion electronic paramagnetic resonance, also known as electron spin resonance (ESR) molar absorption coefficient, a parameter used to measure the capacity of a molecule to absorb light of a specific wavelength fluorescein fraction of the excited-state energy conserved in the final charge- separated state of a photoinduced dectron-transfer reaction flavin adenine dinudeotide ferrocene Franck-Condon factor for electron-transfer processes Franck-Condon factor for energy-transfer processes flavin mononudeotide quantum yidd guanine guanosine triphosphate electronic couplig factor in electron-transfer processes electronic couplig factor in energy-transfer processes hexa-t-butyldecacydene human immunodeficiency virus highest occupied molecular orbital high pressure liquid chromatography energy conversion efficiency input signal F6rster overlap integral between the luminescence spectrum of the donor and the absorption spectrum of the acceptor equilibrium constant of an association process

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SCE: SDS: STM: STS: T: T, T2: TCB: TEE: TET: THF: TTF: Tyrz: UV: VHF: ZnP: List of Abbreviations 1 477 saturated calomel dectrode sodium dodecyl sulfate scanning tunneling microscopy scanning tunneling spectroscopy thymine the first two triplet excited states of a molecule with dosed shell configuration tetracyanobenzene tetraethynylethene tetracene tetrahydrofuran tetrathiafulvalene a redox active tyrosine aminoacid lifetime ultraviolet vinylheptafulvene zinc porphyrin symbol used to indicate the inclusion of the chemical entry that preceeds the symbol into the one that follows it symbol used to indicate the inclusion of the chemical entry that follows the symbol into the one that preceeds it

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