Springer Theses

Design, Synthesis and Characterization of new Supramolecular Architectures

schnell und portofrei erhältlich bei

Chapter 2
Supramolecular Architectures

2.1 Dendrimers

Dendrimers [1, 2] are globular size, monodisperse macromolecules in which all bonds emerge radially from a central focal point or core with a regular branching pattern and with repeating units constituting the branching points. The term *dendrimer* refers to its characteristic tree-like structure and it derives from the Greek word *dendron* (tree) and *meros* (part). From a topological viewpoint, dendrimers contain three different regions: core, branches and surface. Each repetition synthetic cycle leads to the addition of one more layer of monomers in the branches, called *generation*. Therefore, the generation number of the dendrimer is equal to the number of repetition cycles performed and to the number of branching points present from the core towards the periphery.

The first example of an iterative synthetic approach toward dendrimers has been reported in 1978 by Vögtle [3], who called it "cascade synthesis". In the mid-1980s, Tomalia [4] and Newkome [5] independently reported the divergent synthesis of two new families of dendrimers: poly(amidoamine) and the so-called "arborols", respectively. A growing interest on these macromolecules lead in 1990 to the convergent synthesis of aromatic polyether dendrimers by Fréchet [6]. The two different synthetic approaches can be explained as follows:

(a) In the divergent method, dendrimers are built from the core out to the periphery and in each step a new layer of branching units is added.
(b) The convergent method follows the opposite path: the skeleton of a dendron, defined as an entire branch, is built up step by step and finally reacted with the core moiety.

Dendrimer chemistry is nowadays a rapidly expanding field, as testified by the exponentially increasing number of papers published on this topic per year. Dendrimers keep attracting the attention of the scientific community because of their fascinating structure and unique properties: indeed the field of dendrimer

chemistry has evolved from the initial pursue of synthesizing new large and aesthetically pleasant molecules, to their characterization and finally it has now moved towards functionality. Today dendrimers are used or are planned to be exploited in a variety of applications, taking advantage of the great number of functional units that can be incorporated inside them, their tree-like structure containing internal dynamic cavities, their well-defined dimensions close to that of important biological molecules (Fig. 1.1), like proteins and bioassemblies, the presence of an internal microenvironment different from the bulk of the solution, and their endo- and exo-receptor properties. As a result, applications ranging from the biological and medical field (artificial enzymes, drug-delivery and diagnostics systems) to nanoengineering (molecular wires, light-emitting diodes), optical data transport (fiber optics), catalysis, energy-harvesting devices and mimics of natural photosynthesis are foreseen (for some recent reviews, see: [7–13]).

2.2 Dendrimers and Light

Currently, dendrimer research is developing swiftly in the direction of highly functional materials. Also in the field of photoactive dendrimers the complexity of the systems has increased enormously. The investigation of dendritic structures functionalized with luminescent groups [14], photoswitchable units [15], energy and/or electron donor–acceptor components and the implementation of such functionalized dendrimers in devices [16], provide insight in the fundamental processes occurring in such complex systems and in their future applications.
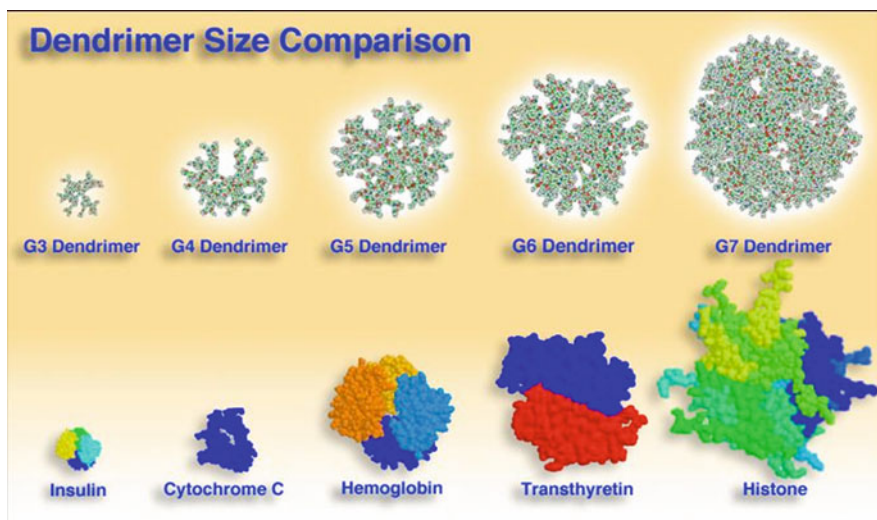

Fig. 1.1 Dendrimer size in comparison with important biological molecules

Since dendrimers can be functionalized with multiple chromophoric groups, that are in very close proximity, novel properties can arise compared to the single chromophoric system. Due to the stepwise synthesis, either divergent or convergent, chromophores can be implemented in the dendritic structure with high precision. The number of chromophores and the size of the dendrimer are very well controlled, which is of very great importance for some biological and biomedical applications. The presence of multiple chromophores in the same molecule enables the detection of single dendrimer via single molecule spectroscopy (SMS), which is particulary interesting for nanotechnology. Furthermore, an increased sensitivity with respect to specific classes of molecules can be established, enabling the detection of very low concentrations of these molecules. This is of great interest for the field of molecular recognition, e.g. for the development of biosensors (immuno-diagnostic).

A specific advantage of the dendritic framework is that a microenvironment can be crated around a single chromophore. By placing such protective environment around a chromophore its luminescence can be dramatically improved. Dendritic substituents can also promote supramolecular organization of chromophores, e.g. inducing the formation of fibers or doughnut-like structures.

The possibility to functionalize chromophores with large dendritic substituents is particularly interesting for the development of light emitting diodes (LEDs). The dendritic wedges do not only prevent the aggregation of chromophores, thereby reducing the amount of self quenching, but they also provide a way to improve the solubility of the chromophores in polymers, rendering a more homogeneous blend.

The introduction of photoisomerizable groups, such as azobenzene derivatives, in dendrimers enables the controlled induction of a structural change, especially when those units are attached to the core or implemented in the branches. If attached at the periphery, these photoisomerizable groups, can be used to "close" the surface of a dendrimer by means of a photoinduced increase of steric hindrance at the periphery. This type of dendrimers can be used as carriers of small molecules, while a controlled release of those guest molecules is possible using light, which induced the isomerization from *cis* to *trans*. In addition, azobenzene-functionalized materials are widely used in the field of datastorage.

The implementation of chromophores in dendritic structures can also provide more insight in the structural features of dendrimers. Dyes can be used as internal probes to investigate the microenvironment created by dendritic branches. At the same time the influence of external factor, e.g. the solvent or ions, on the microenvironment can be studied. This may concern a change in the conformation of the dendritic structure, but also the accessibility of the dendritic structure by other molecules. The implementation of multiple chromophores within one dendrimers allows the investigation of internal interactions between the chromophores, such as the formation of excimers and energy and electron transfer processes. To what extend these interactions take place will depend on the flexibility of the dendritic framework and the position of the chromophores within the dendritic structure.

2.3 Molecular Machines

What would be the utility of such machines? Who knows? I cannot see exactly what would happen, but I can hardly doubt that when we have some control of the arrangement of things on a molecular scale we will get an enormously greater range of possible properties that substances can have, and of the different things we can do.[17, 18].

2.3.1 The Concept of a Machine at the Molecular Level

In everyday life we make extensive use of (macroscopic) machines. A machine is [19] an apparatus for applying mechanical power, having several parts each with a definite function. When a machine is working, at least some of its components display changes in their relative positions. A machine is characterized by (1) the kind of energy input supplied to make it work, (2) the type of movements performed by its components, (3) the manner in which its operation can be monitored and controlled, (4) the possibility to repeat the operation at will and establish a cyclic process, (5) the timescale needed to complete a cycle of operation, and (6) the function performed by the machine. The concept of a machine can be extended to the molecular level. A molecular-level machine can be defined as an assembly of a discrete number of molecular components designed to perform mechanical-like movements (output) as a consequence of appropriate external stimuli (input). Although there are many chemical compounds whose constitutions and/or shapes can be modified by an external stimulus—for example, molecules capable of undergoing photoinduced cis/trans isomerizations of their C=C, C=N, or N=N bonds—the term molecular-level machine will only be used for systems whose component parts undergo movement with relatively large amplitudes. Furthermore, systems in which the molecular movements are not controlled by some easily identifiable and well-characterized external stimulus will not be considered to be molecular-level machines. The extension of the concept of a machine to the molecular level is of interest not only for the sake of basic research, but also for the growth of nanoscience and the subsequent development of nanotechnology. The concept of a machine at the molecular level is not a new one. Our bodies can be viewed as very complex ensembles of molecular-level machines that power our physical motions in a multitude of different guises, repair tissue damage in a wide spectrum of situations and circumstances, as well as preside over our innermost worlds where we are preoccupied by our sensory perceptions, emotional states, and thought processes. The idea of constructing artificial molecular-level machines, however, is quite a recent one. The first time the topic was seriously contemplated was in 1959 by Richard Feynman in his historic address There is Plenty of Room at the Bottom to the American Physical Society in December of that year. The earliest examples of synthetic molecular-level machines, based on the photoisomerization of azobenzene, were reported [20] in the early 1980s. In the last 15 years research in the field of artificial molecular-level machines

has been stimulated by several major scientific breakthroughs and paradigm shifts: they include (1) the rapid development of probe microscopies [21, 22] following the award of the Nobel Prize in Physics to Binnig and Rohrer in 1986; (2) a growing interest in supramolecular chemistry [23–28] after the award of the 1987 Nobel Prize in Chemistry to Pedersen, Cram, and Lehn; (3) the elucidation and unraveling of the working mechanisms of some key biological devices and machines [29–38], such as those involved in photosynthesis (Deisenhofer, Huber, and Michel recognized by the 1988 Nobel Prize in Chemistry) and in the ATP synthesis (leading to the 1997 Nobel Prize in Chemistry to Boyer, Skou, and Walker); (4) the great progress in understanding the mechanisms of the homogeneous and heterogeneous thermal and photoinduced electron-transfer reactions [39, 40] provided by Marcus who was awarded the Nobel Prize in Chemistry in 1992; and (5) the realization that the (physical) top-down approach to miniaturization in the electronics industry, for example, has intrinsic limitations and the increasing confidence that it can be replaced profitably by a (chemical) bottom-up approach [41]. In the past few years interest in artificial molecular machinery has grown exponentially and several short reviews covering specific aspects of the field are now available [42–44]. The aim of this article is to present a unified view of the field by focusing in on past achievements, present limitations, and future perspectives.

2.3.2 Defining Molecular-Level Machines

We have already identified the features and characteristics of macroscopic machines in, and have also established that one of the operational requirements of a molecular machine will be that the movement of its component parts will have relatively large amplitudes—a property which implies the occurrence of chemical reactions. In his 1959 address to the American Physical Society, Feynman noted that an internal combustion engine of molecular size is impossible. Other chemical reactions, liberating energy when cold, can be used instead. Even relatively cold chemical reactions, however, can destroy the molecules constituting a machine. Since such a machine works by repeating cycles (Point 4), an important requirement is that any chemical change or reaction taking place in the system has to be reversible. Within this constraint, any kind of chemical process that causes motions of a machine's component parts—for example, isomerizations, acid/base reactions, oxidation/reduction processes, complexation/decomplexation equilibria involving, for example, the making and breaking of hydrogen bonds—can be useful. Most chemical reactions occur as a result of thermal activation on mixing the reactants. If a molecular-level machine has to work by thermal activation it will need the addition of reagents at all steps in its working cycle, since the added reagents play the role (Point 1) of chemical energy inputs. Although such kinds of input can be useful, clearly the repeated addition of reagents will result in the

accumulation of by-products that, after a relatively small number of cycles, will compromise the operation of the machine unless the products can be removed from the system, which is not an easy task to perform. In principle, the best energy inputs to make a molecular machine work (Point 1) are photons and electrons (or holes). Indeed, with appropriately chosen photochemically or electrochemically driven reactions, it is possible to design interesting and intriguing molecular machines. The motions performed by the component parts of a molecular-level machine (Point 2) depend to some extent on whether the machine is molecular or supramolecular in nature (the most authoritative and widely accepted definition (see Sect. 1.1 and [45, 46]) of supramolecular chemistry is the chemistry beyond the molecule, bearing on the organized entities of higher complexity that result from the association of two or more chemical species held together by intermolecular forces. On the basis of this definition, it is tempting to classify molecular machines as either molecular or supramolecular. However, it is not as simple and straightforward as one might think and so we avoid this classification. The fundamental nature of all the systems we discuss is their multicomponent nature. For any kind of device—be it macroscopic or otherwise—the observed function results from the cooperative interactions between the various component parts). Movements of component parts within classical molecules will necessarily involve changes in their conformations and/or configurations around covalent bonds that are formally single or double, respectively, in their orders, although these changes in molecular structure are accompanied by the making and breaking of intramolecular noncovalent bonds. Movements of the component parts within supermolecules (complexes) may be accompanied by conformational and/or configurational changes within their covalently linked molecular components; however, it will be largely the reorganization of intermolecular noncovalent bonds between the molecules that will usually reflect and constitute the movements within these kinds of molecular-level machines. In nonclassical so-called interlocked molecules the mechanical bonds that link the component parts together offer the close to unique opportunity, within relatively small molecules at least, to effect movements with large amplitudes upon their components, mainly as a result of the making and breaking of intercomponent noncovalent bonds. In order to monitor and control the operation (Point 3) of a molecular machine the motions of the component parts should bring about readable changes in some properties of the system. Any kind of chemical or physical probe can be useful in providing read-outs, particularly the various different types of spectroscopies that are currently available to us. In this regard, it should be pointed out that photochemistry and electrochemistry are often very useful since both photons and electrons can play the dual role of writing, that is, causing the change in the system, and reading, that is, reporting the resulting state of the system. The operating timescale (Point 5) of molecular machines is that of nuclear motions, which can range from nanoseconds to seconds depending on the nature of the components involved and the type of motions that are happening. We would like to point out that the description of a motion implies the definition of a fixed reference system. In the case of molecular machines, this matter is not so

trivial. Finally, the functions that can be performed by exploiting the movements of the components in artificial machines (Point 6) are largely unpredictable.

2.4 Molecular Logic

The realization of computers with very small size, low power consumption, and computing performance that may be hard to reach with silicon-based technology ([47], see also [48]) is a strong motivation for the search for information-processing strategies based on molecules. The rational basis for this research stems from the fact that in living organisms information is transported, elaborated, and stored by molecular or ionic substrates [49, 50]. Although the components of a molecular computer will not necessarily have to operate analogously to microelectronic circuits [51], several efforts have been devoted to the design, synthesis, and characterization of chemical systems that mimic the operation of semiconductor logic gates [52]. As molecular switches convert input stimulations into output signals [53], the principles of binary (Boolean) logic [54] can be applied to the signal transduction operated by molecules under appropriate conditions (a large number of chemical switches exhibiting interesting properties, from a binary-logic viewpoint, have been reported in the literature. In many cases, the authors were either not aware of such behavior in their systems or published the work before the notion of molecular logic gates became popular. For the first explicit description of the analogy between molecular switches and logic gates, see: [55]). Implementation of the most common Boolean functions (PASS, YES, NOT, AND, NAND, OR, NOR, XOR, XNOR, and INH) with chemical systems is now possible. A critical issue of molecular logic gates is the interconnection of basic elements to create complex circuits. In contrast, electronic logic gates can be easily interconnected, owing to full input/output homogeneity. However, rather than relying on extensive physical connection of elementary gates, the construction of molecular logic networks can take advantage of functional integration and reconfiguration within a single molecule, which can be achieved by rational chemical design [56]. The fact that a relatively simple, commercially available dye molecule in aqueous solution can perform both the full-adder and full-subtractor functions—which in silicon-based systems require circuits made of five interconnected gates—is a demonstration of this idea. Recent reports on the first molecular versions of a digital multiplexer [57] and of a keypad access device have taken molecular logic one step further.

The development of novel computational architectures constitutes the main scientific driving force for the imitation of Boolean logic functions with molecular systems. Aside from futuristic speculations related to the construction of a chemical computer, recent work has shown that molecular logic gates could lead to practical applications in the not-too-distant future. Molecular devices that control protein folding [58] or release a chemical species [59] by processing chemical inputs according to programmed logic functions have been reported. They can be

regarded as precursors of systems operating in vivo that are capable of autonomously diagnosing a disease and effecting a therapy. Moreover, a method based on molecular logic gates for tagging and identifying small objects in a large population has been proposed as a ready-to-use application for combinatorial chemistry [60, 61]. It should be noted that computing devices based on (supra)molecular species and soft matter represent a radically different approach to information processing with respect to computers made from solid-state semiconductors. Therefore, comparisons between these types of systems should be made with care and, for certain aspects, may not make much sense. It seems fair to state, however, that the examples mentioned in the previous paragraph are simple computational tasks that molecules can do and silicon cannot. Certainly, the investigation of intelligent molecules capable of elaborating signals introduces new concepts in the field of chemistry and stimulates research in the bottom-up approach to nanodevices.

References

1. Fréchet JMJ, Tomalia DA (eds) (2001) Dendrimers and other dendritic polymers. Wiley, Chichester
2. Newkome GR, Moorefield C, Vögtle F (2001) Dendrimers and dendrons: concepts, syntheses, perspectives. VCH, Weinheim
3. Buhleier EW, Wehner W, Vögtle F (1978) Synthesis 2:155
4. Tomalia DA, Baker H, Dewald JR, Hall M, Kallos G, Martin S, Roeck J, Ryder J, Smith P (1985) Polym J 17:117
5. Newkome GR, Yao Z-Q, Baker GR, Gupta K (1985) J Org Chem 50:2003
6. Hawker CJ, Fréchet JMJ (1990) J Am Chem Soc 112:7638
7. Mery D, Astruc D (2006) Coord Chem Rev 250:1965
8. Tomalia DA, Fréchet JMJ (eds) (2005) Special issue: dendrimers and dendritic polymers. In: Prog Polym Sci 30 (3–4)
9. Scott RWJ, Wilson OM, Crooks RM (2005) J Phys Chem B 109:692
10. Chase PA, Klein Gebbink RJM, van Koten GJ (2004) Organomet Chem 689:4016
11. Ong W, Gomez-Kaifer M, Kaifer AE (2004) Chem Commun 1677
12. Ballauff M, Likos CN (2004) Angew Chem Int Ed 43:2998
13. Caminade A-M, Majoral J-P (2004) Acc Chem Res 37:341
14. Ceroni P, Bergamini G, Marchioni F, Balzani V (2005) Prog Polym Sci 30:453 and reference therein
15. Liao L-X, Stellacci F, McGrath DV (2004) J Am Chem Soc 126:2181
16. Thomas KRJ, Thompson AL, Sivakumar AV, Bardeen CJ, Thayumanavan S (2005) J Am Chem Soc 127:373
17. Feynman RP (1960) Eng Sci 23:22–36
18. Feynman RP (1960) Saturday Rev 43:45–47
19. Hawkins JM (1979) The Oxford paperback dictionary. Oxford University Press, Oxford
20. Shinkai S, Manabe O (1984) Top Curr Chem 121:76–104
21. Binnig G, Rohrer H (1987) Angew Chem 99:622–631
22. Binnig G, Rohrer H (1987) Angew Chem Int Ed Engl 26:606–614
23. Lehn J-M (1988) Angew Chem 100:91–116
24. Lehn J-M (1988) Angew Chem Int Ed Engl 27:89–112
25. Cram DJ (1988) Angew Chem 100:1041–1052

26. Cram DJ (1988) Angew Chem Int Ed Engl 27:1009–1020
27. Pedersen CJ (1988) Angew Chem 100:1053–1059
28. Pedersen CJ (1988) Angew Chem Int Ed Engl 27:1021–1027
29. Deisenhofer J, Michel H (1989) Angew Chem 101:872–892
30. Deisenhofer J, Michel H (1989) Angew Chem Int Ed Engl 28:829–847
31. Huber R (1989) Angew Chem 101:849–871
32. Huber R (1989) Angew Chem Int Ed Engl 28:848–869
33. Boyer PD (1998) Angew Chem 110:2424–2436
34. Boyer PD (1998) Angew Chem Int Ed 37:2296–2307
35. Walker JE (1998) Angew Chem 110:2438–2450
36. Walker JE (1998) Angew Chem Int Ed 37:2308–2319
37. Skou JC (1998) Angew Chem 110:2452–2461
38. Skou JC (1998) Angew Chem Int Ed 37:2320–2328
39. Marcus RA (1993) Angew Chem 105:1161–1172
40. Marcus RA (1993) Angew Chem Int Ed Engl 32:1111–1121
41. Nalwa HS (ed) (2000) Handbook of nanostructured materials and nanotechnology. Academic Press, New York
42. Balzani V, Credi A, Venturi M (1999) In: Ungaro R, Dalcanale E (eds) Supramolecular science: where it is and where it is going. Kluwer Academic, Dordrecht, pp 1–22
43. Balzani V, Credi A, Venturi M (2000) In: Shibasaki M, Stoddart JF, Vögtle F (eds) Stimulating concepts in chemistry. Wiley-VCH, Weinheim, pp 255–266
44. Balzani V, Gómez-López M, Stoddart JF (1998) Acc Chem Res 31:405–414
45. Lehn J-M (1990) Angew Chem 102:1347–1362
46. Lehn J-M (1990) Angew Chem Int Ed Engl 29:1304–1319
47. International Technology Roadmap for Semiconductors (ITRS) 2005 Edition and 2006 Update. http://www.itrs.net
48. Thompson SE, Parthasarathy S (2006) Mater Today 9:20
49. Goodsell DS (2004) Bionanotechnology: lessons from nature. Wiley, Hoboken
50. Jones RAL (2004) Soft machines: nanotechnology and life. Oxford University Press, New York
51. Tullo A (2006) Chem Eng News 84:22
52. Balzani V, Credi A, Venturi M (2003) Molecular devices and machines: a journey into the nanoworld. Wiley-VCH, Weinheim, Chap 9
53. Feringa BL (ed) (2001) Molecular switches. Wiley-VCH, Weinheim
54. Gregg JR (1998) Ones and zeros: understanding boolean algebra, digital circuits, and the logic of sets. Wiley, New York
55. de Silva AP, Gunaratne HQN, McCoy CP (1993) Nature 364:42
56. de Silva AP (2005) Nat Mater 4:15
57. Andréasson J, Straight SD, Bandyopadhyay S, Mitchell RH, Moore TA, Moore AL, Gust D (2007) Angew Chem 119:976
58. Muramatsu S, Kinbara K, Taguchi H, Ishii N, Aida T (2006) J Am Chem Soc 128:3764
59. Amir RJ, Popkov M, Lerner RA, Barbas III CF, Shabat D (2005) Angew Chem 117:4452
60. de Prasanna Silva A, James MR, McKinney BOF, Pears DA, Weir SM (2006) Nat Mater 5:787
61. Webb R (2006) Nature 443:39