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Synthesis of Nanostructures by Self-Assembly

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4.2 SYNTHESIS OF NANOSTRUCTURES BY SELF-ASSEMBLY

B.L. Feringa²

If nature is considered as the ultimate example of how to construct nanosize molecular systems one cannot escape the fascinating way by which the biological machinery relies on self-organization, self-assembly and self-replication. One well-studied example is the assembly of the tobacco mosaic virus. In its assembled form, the virus is 300-nm long and has a width of 18 nm. It consists of about 2000 identical protein molecules forming a coating around an RNA molecule of about 6400 nucleotides (RNA is genetic material normally serving for the transcription of information from the DNA to the protein synthesizing machinery of cells). It can be assembled and de-assembled *in vitro*. This implies that all the components of the system contain all the information necessary to form a structural aggregate. The amount of information is surprisingly small. A remarkable feature of the assembly process is that the virus is constructed from sub-assemblies. Large and extremely complex natural products have challenged the synthetic

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chemist for many decades and the tremendous progress in this field has cumulated recently in the total synthesis of nanosize multifunctional natural products such as vitamin B12, palytoxin and brevetoxin (potent toxins produced by a coral and an algae, respectively). The construction of unnatural materials with nanoscale dimensions is limited only by the imagination of the synthetic chemist. Key problems in fabricating nanostructures are the design of efficient assembly processes with perfect control over molecular size and geometry. Also the synthesis of monodisperse systems is often a major challenge. Important tasks are also the introduction of appropriate functionalities to control molecular and supramolecular properties and to incorporate these in such a way that one can access the functions in the nanoscale constructs, for instance enabling the communication with these functions at the molecular level.

To achieve efficient synthesis of functional nanoscale systems, new construction methods will be required. It will be evident that complicated multistep synthesis is best avoided. An emerging new methodology includes covalent or non-covalent bond formation strategies using 'preprogrammed' molecules. In this chapter two major approaches will briefly be outlined: covalent assembly (also called the 'molecular construction kit' approach) and self-assembly.

Covalent assembly

The use of molecular building blocks for the construction of larger covalent assemblies implies that stereoelectronic information is preprogrammed in the molecular units. With the proper design a minimum of external instruction is required to construct structurally complex systems with well defined and rigid two- or three-dimensional architectures and precise positioning of functional groups. An example is the synthesis of a molecular tape by cycloaddition (figure 4.2.1).

Figure 4.2.1

Scheme of a molecular tape. Its construction is realized by simple domino-like sequential cycloadditions (addition to a carbon-carbon double bond in which a ring is generated) that are completely controlled by the stereoelectronic information preprogrammed in the bisdiene and the bisdienophile units.

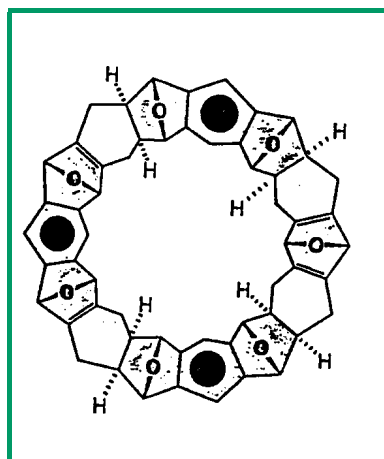
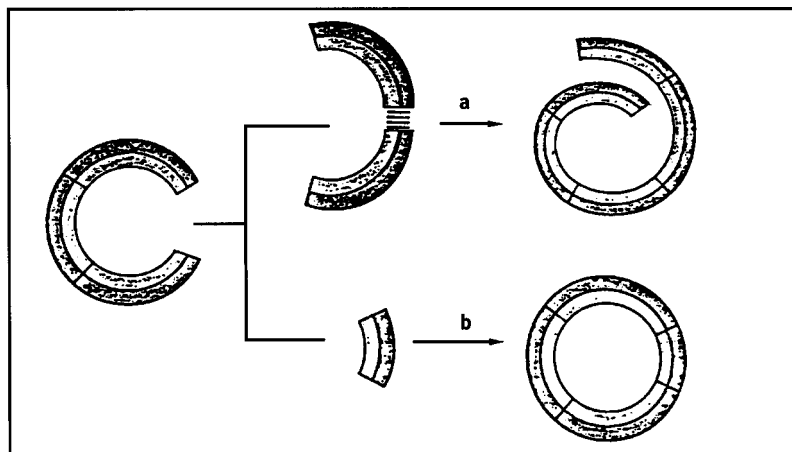


Figure 4.2.2

Schematic representation of the construction principle of molecular spirals (a) and belts (b) by a sequence of cycloaddition reactions of preprogrammed building blocks.



Similar sequences of repetitive cycloadditions (figure 4.2.2) led to the assembly of molecular belts, spirals and cages. The construction of kohnkene (about 1 nm in size, figure 4.2.3a) encapsulating benzene in the interior and of a container molecule (figure 4.2.3b) is also illustrative.

It should be noted that numerous other container-type molecules have been assembled in recent years that can encapsulate smaller functional guest molecules. These approaches pave the way to prepare a large variety of well-organized robust molecular constructs that ultimately could be used to assemble molecular machinery. The photoelectron transport systems constructed of five functional subunits (figure 4.2.4a), a photoswitchable molecular wire (figure 4.2.4b) and a molecular turnstile (figure 4.2.4c) are just a few examples of the numerous fascinating systems that can be readily constructed.

Figure 4.2.3

a Molecular belt constructed following the principle shown in figure 4.2.2; benzene is encapsulated.

b Molecular container compound.

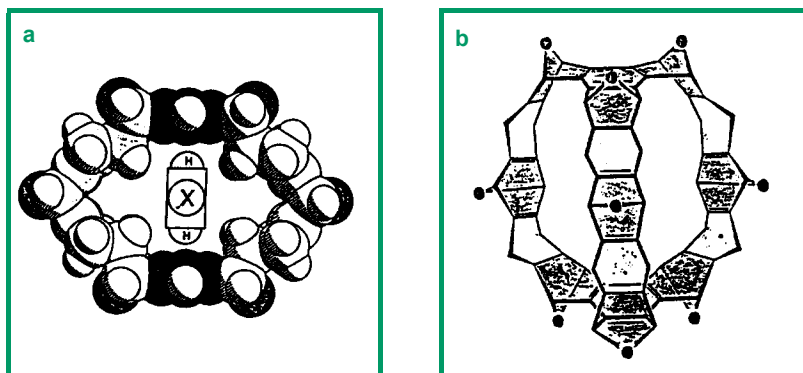
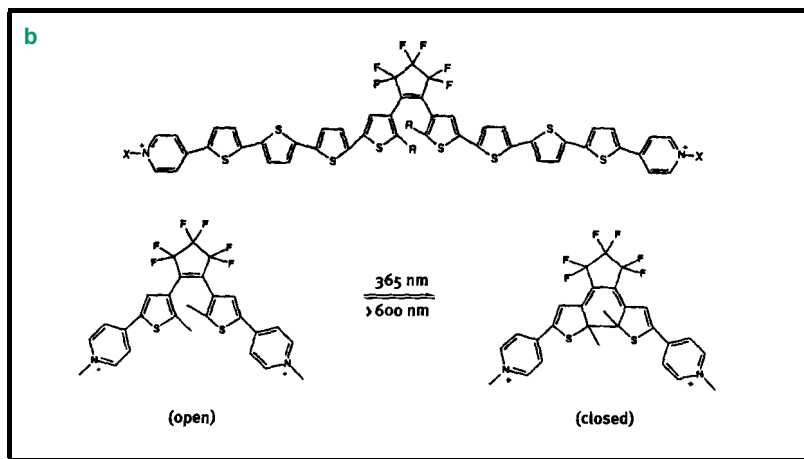
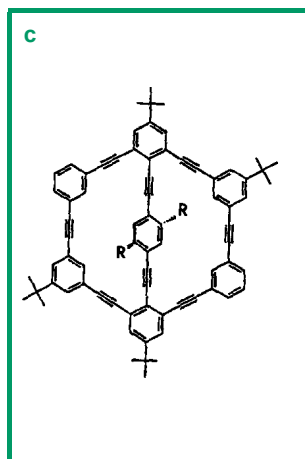
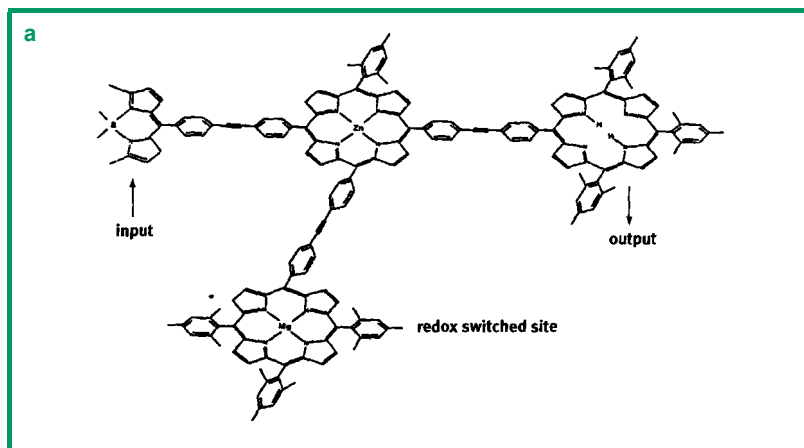


Figure 4.2.4.

- a Electron transport system with five subunits containing porphyrins.
- b Photoswitchable wire; the electronic communication between the outer parts is blocked in the open form.
- c Molecular turnstile.

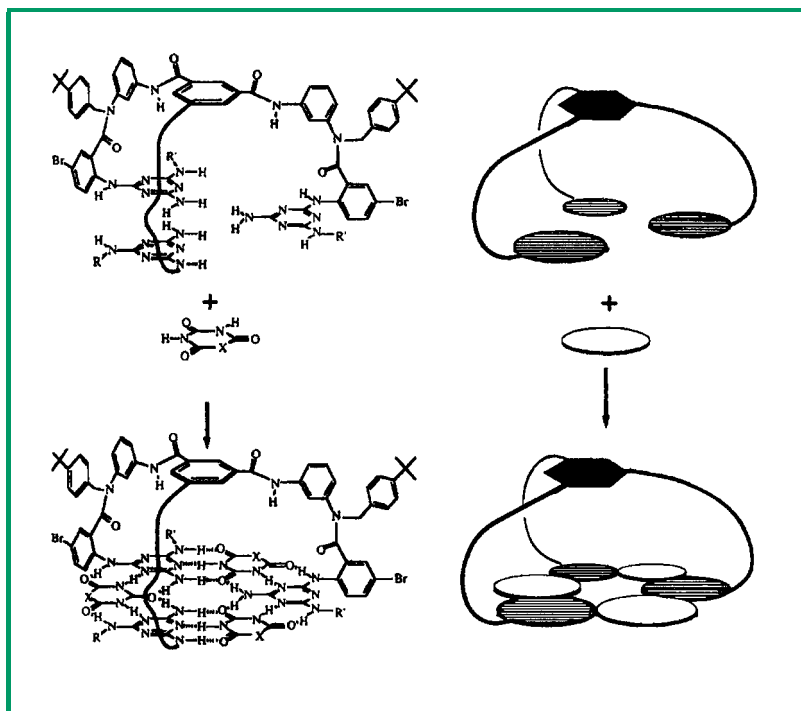


Self-assembly

Self-assembly has been defined as “the spontaneous association of molecules under equilibrium conditions into stable, structurally well-defined aggregates joined by non-covalent bonds” [Whitesides, 1991]. The synthesis of molecular structures that undergo self-assembly lies at the heart of future nanosystem design [Philp, 1996]. The information necessary for the organization process to occur must be embedded in the components and is expressed through selective molecular interactions. A distinction can be made between self-organization like the formation of crystals, vesicles or liquid crystalline phases and the much broader principle of self-assembly that governs the spontaneous generation of even very large systems capable executing complex functions. In approaches to generate molecules that are pre-programmed to undergo self-assembly the major intermolecular forces that can be exploited are ionic, hydrogen bond and coordinative interactions. Other interactions that can be beneficial to the assembly process are Van der Waals interactions and hydrophobic interactions. Technology for the generation of self-assembled structures has been developed

Figure 4.2.5

Molecular rosettes formed upon self-organization of melamine ($C_3H_6N_6$) derivatives

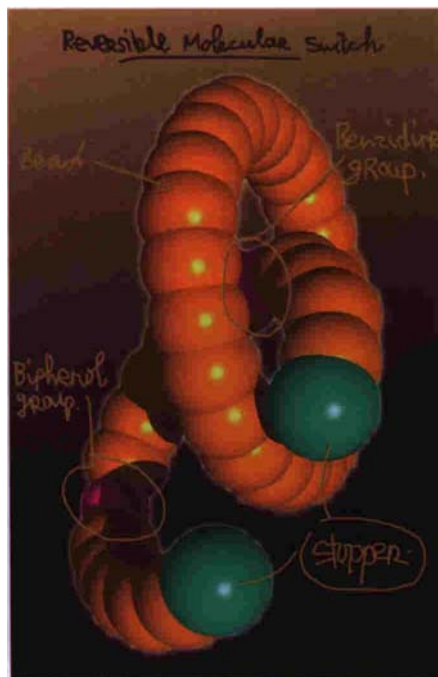


based on crystal engineering and patterning of monolayers (self-assembled monolayers (SAMs), section 2.2.2, see e.g. [Allara, 1996]). Organization through multiple hydrogen bonding and the formation of coordination complexes (section 4.3) has been investigated for the synthesis of large soluble ensembles. The lattices, tapes and three-dimensional structures shown in figure 4.2.5 are reminiscent of the self-organization of natural nanostructures such as DNA and proteins through multiple hydrogen bond formation. Highly efficient self-organization to stable systems with a large variety of architectures is possible due to the planar structure with multiple hydrogen bonding acceptor and donor functionalities. Further exploration of these principles allows the formation of numerous new materials with nanoscale structures including polymers, membranes, containers, wires, tapes, ladders and other equivalents of macroscopic constructs. That self-assembled structures can obtain micrometer dimensions is illustrated by the synthesis of porphyrin wheels with diameters up to $50 \mu\text{m}$ [Schenning, 1996].

Fascinating examples of new strategies for making more complex systems, in which the assembly process allows also the design of specific functions, are the mechanically interlocked structures such as catenanes (interlocked rings) and rotaxanes including the molecular shuttle shown in figure 4.2.6. In these cases the self-organization is mainly governed by multiple electrostatic interactions.

Figure 4.2.6

Artist's impression of a reversible molecular shuttle consisting of a rotaxane (a ring-shaped molecule around a linear molecule) that is formed by self-assembly. The ring slides along the chain until it encounters a functional group with a favorable specific interaction, where it finds a stable position. This switch is bistable and reversible: the two positions represent '1' and '0'. The ring is prevented from sliding off the chain by large end groups. Adapted from [López, 1996].

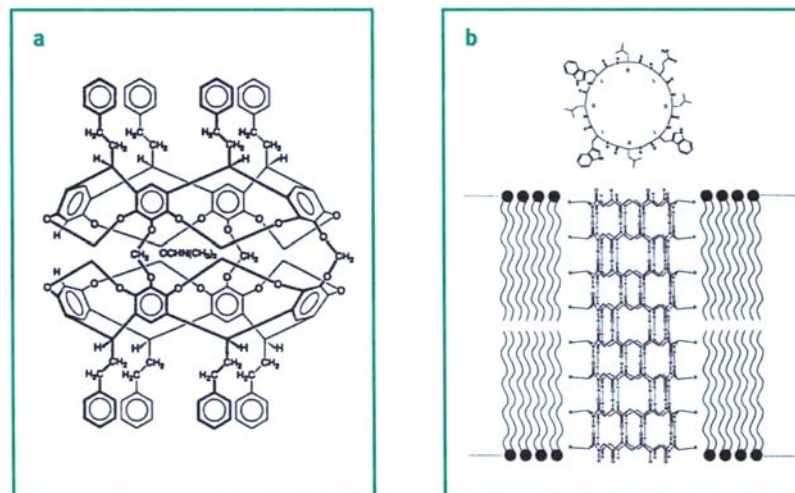


Recently a number of approaches have been studied in which several complementary groups are present in the molecular component with precise geometrical constraints. This is illustrated in the formation of molecular container molecules (figure 4.2.7a) suitable for acting as catalysts and nanosize tubes (figure 4.2.7b).

Figure 4.2.7

a Molecular container assembled through aggregation of two complementary parts.

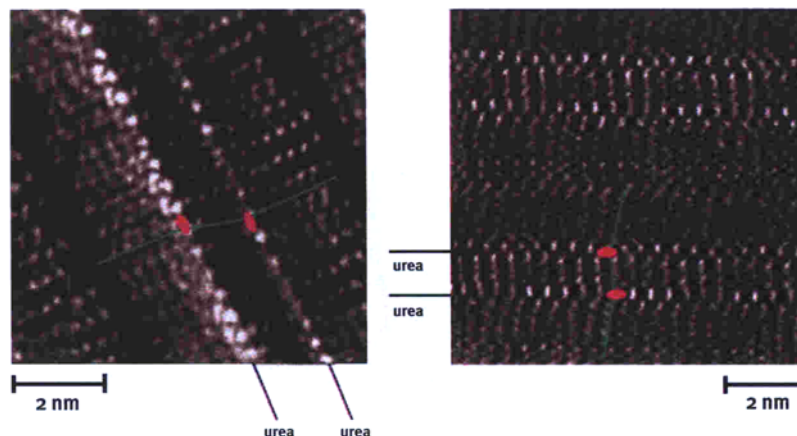
b Cyclic aminoacid-based peptide-type tubes synthesized through self-assembly.



The organization process can readily be controlled by the shape of the organic building blocks and the number of 'intelligent components' included. The ease of structural modification and thus tuning of these features is a key advantage of nanofabrication based on organic molecules. The formation of nanosize tapes (figure 4.2.8) using bis-urea compounds is illustrative. Due to the 'robust' organization such systems are highly suitable to incorporate a diversity of functions. The external control of self-organized systems - the possibility to trigger

Figure 4.2.8.

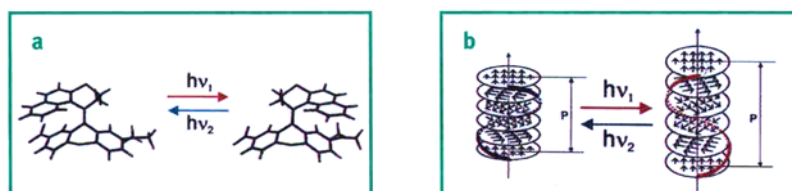
Scanning tunneling microscope (STM) image of molecular tape formed through self-organization of bis-urea ($\text{CO}(\text{NH}_2)_2$) compounds. The highly directional multiple hydrogen bonds control the linear organization while the shape of the molecule determines the aggregates that are formed.



changes in the assembly after its formation - is another major challenge. The architecture and properties of nanostructures can be reversibly modulated by external signals (mechanical, optical or electronic). In this way it is possible to 'talk' with the system at a molecular level. An example is seen in the reversible control of the organization - and thereby of the physical properties - of liquid crystalline (LC) matrices using chiral optical molecular switches as guests (figure 4.2.9).

Figure 4.2.9

Switching of liquid crystals for optical recording: A molecular switch (a) is incorporated as a guest within the host molecule of a liquid crystalline (LC) material (b). The organization and chirality of the liquid crystal phase is changed by photochemical control of the chirality of the switch.



An ultimate challenge in the construction of nanomaterials and devices will be the design of autoreplicating and autorepair systems. Successful approaches will not only require control of assembly but also precise control of molecular recognition, (auto)selection of components to be assembled and control of reactivity of several functional groups. The incorporation of such complex tasks in model systems (the first primitive systems have been reported recently) will set the stage to design nanoscale molecular machinery.