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DESIGN AND SYNTHESIS OF MACROMOLECULAR STRUCTURES
FROM SELF-ASSEMBLING BUILDING BLOCKS

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Abstract: The self-assembling properties of a variety of building-blocks are used to generate different types of nanostructures, e.g. molecular golfballs, molecular tubes, and molecular braids.

INTRODUCTION

Molecular Chemistry involves the design and construction of molecules from atoms and simple low molecular weight building blocks with the help of strong covalent bonds. This field began with the synthesis of the first organic compound (urea) by Wöhler in 1827. At the beginning of this century Staudinger performed experiments that laid the basis for *Macromolecular Chemistry*, a word coined by him to describe a new research area, viz. that of molecules with unusually large dimensions. More recently, Lehn together with Cram and Pedersen introduced the field of *Supramolecular Chemistry*, which concerns the synthesis and study of supermolecules and ensembles of molecules held together by weak non-covalent bonds (hydrogen bonds, van der Waals interactions, electrostatic interactions). Input, knowledge, and experience from these three fields of chemistry are required to design and construct the next generation of molecular structures, viz. those having nanometer sized dimensions (nanostructures, see Fig. 1). Such structures are of great interest and potential for areas such as materials science and catalysis.¹ In the following we will report our recent efforts to design nanostructures from different building blocks by the process of self-assembly and self-organization.

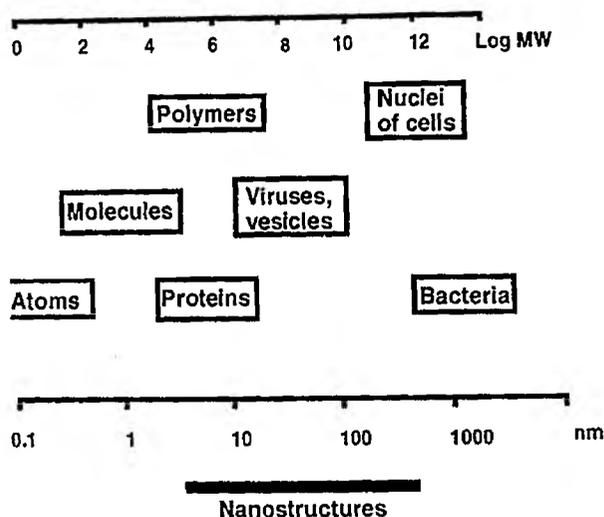
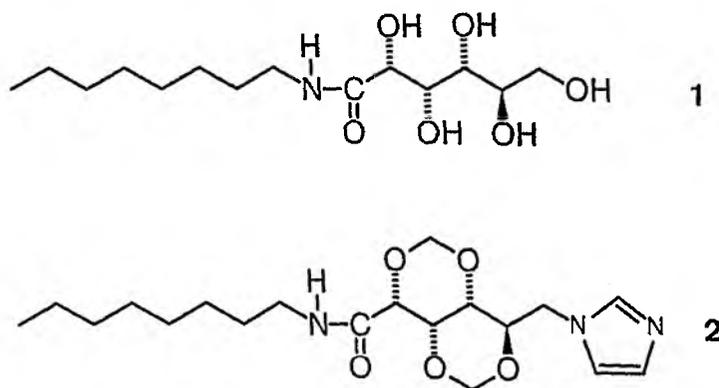


Fig. 1. A comparison of the dimensions of structures in biology and synthetic chemistry

GLUCONAMIDE BUILDING BLOCKS

Following initial studies by Fuhrhop² and others³ we investigated the possibility of synthesizing functionalized nanostructures from carbohydrate building blocks, *e.g.* gluconamides of type **1**.



Compound **1** was protected with methylene groups and provided with a metal-coordinating imidazole function (see **2**). Dispersion of **2** in buffered solutions of pH 8 led to the formation of hollow tubules with diameters of 3000 nm and lengths of several micrometers. Electron microscopy revealed that the tubules are built up from smaller

fibers which are also hollow and composed of multilayers (Fig. 2). In water at pH < 4 compound **2** self-assembles to yield vesicles with diameters ranging from 150-800 nm. UV-vis titrations showed that **2** easily forms complexes with different metal ions. For instance, with $\text{Cu}(\text{ClO}_4)_2$ a 4/1 ligand to copper complex is obtained. Dispersion of this complex in a buffered solution of pH 8 gave a molecular braid consisting of 4 bundles of fibers (Fig. 3).⁴

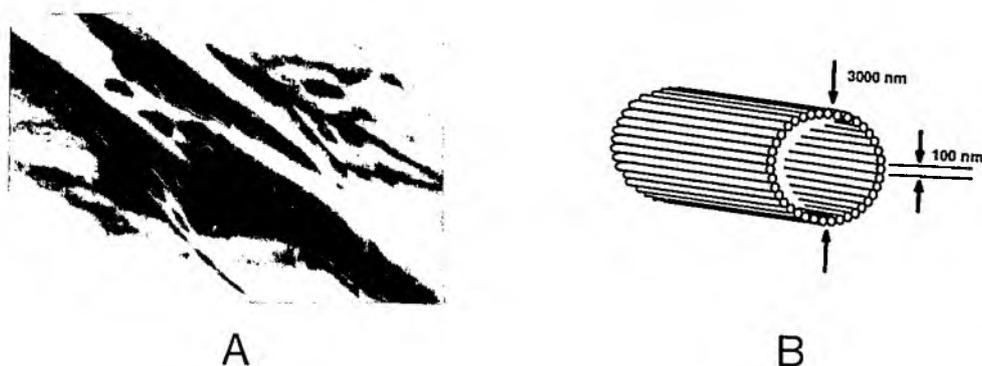


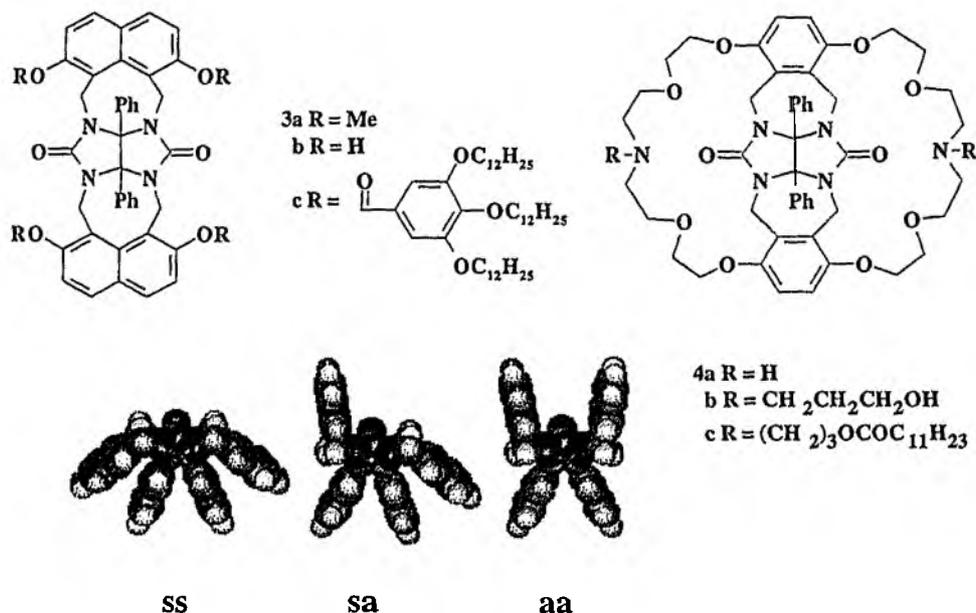
Fig. 2. Scanning electron micrographs of hollow tubules formed from **2** at pH 8 (A). Schematic drawing of a tubule (B).



Fig. 3. Transmission electron micrograph of a molecular braid obtained by dispersing the copper(II) complex of **2** in water at pH 8 (A). Schematic drawing of the molecular braid (B).

BOWL-SHAPED BUILDING BLOCKS

Previous studies in our group have shown that molecular clips derived from diphenylglycoluril (e.g. **3a**) can act as host molecules for aromatic guest molecules. Their crown-ether derivatives (e.g. **4a**), which are bowl-shaped, bind dihydroxybenzenes as well as alkalimetal ions.



Clip **3b** was modified with 12 long aliphatic chains to give compound **3c**, which in chloroform solution exists as a mixture of 3 conformers with *sa* being the predominant conformer (66%). When the guest molecule 3,5-dihydroxybenzoic acid methyl ester (**5**) was added the conformation of **3c** changed into *aa* and the guest was bound with an estimated binding constant of $K_a=5000 \text{ M}^{-1}$. Compound **3c** displayed monotropic liquid-crystalline behavior. In the presence of **5** different nematic and smectic phases were formed.⁵ The type of phase depended on the molar ratio of host and guest (Fig. 4).

Molecular bowl **4c** was synthesized from **4b** by an esterification reaction. When this compound was dispersed in 0.1 N aqueous HCl nanotubes with diameters of 100 nm were formed (Fig. 5). Interestingly, K^+ and Na^+ ions induced the formation of vesicles from **4b**, whereas Rb^+ ions gave a mixture of vesicles and tubes. Cs^+ ions yielded nanotubes exclusively.⁵ Bowl molecules with long aliphatic tails and quaternary ammonium groups in the crown ether rings also formed stable vesicles in water.⁶ The nanospheres obtained from **4** and related molecules have dimples on their surfaces. Because of this feature the name molecular golfball was proposed for these molecular objects.⁶ In the dimples guest molecules can be bound with high binding constants ($K_a=10^5 \text{ M}^{-1}$).⁶

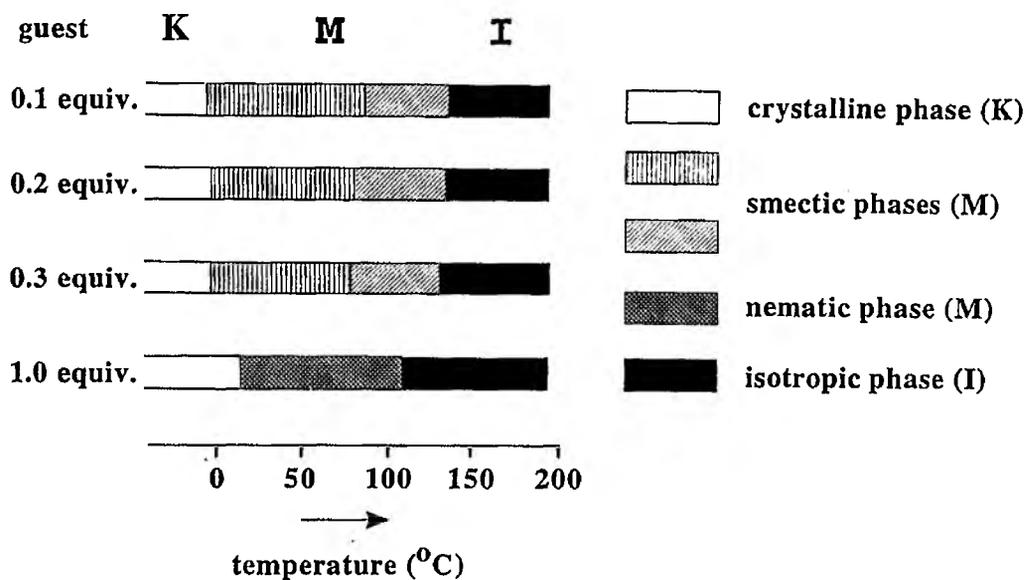


Fig. 4. Thermotropic liquid-crystalline behavior of clip 3c in the presence of different amounts of guest 5.

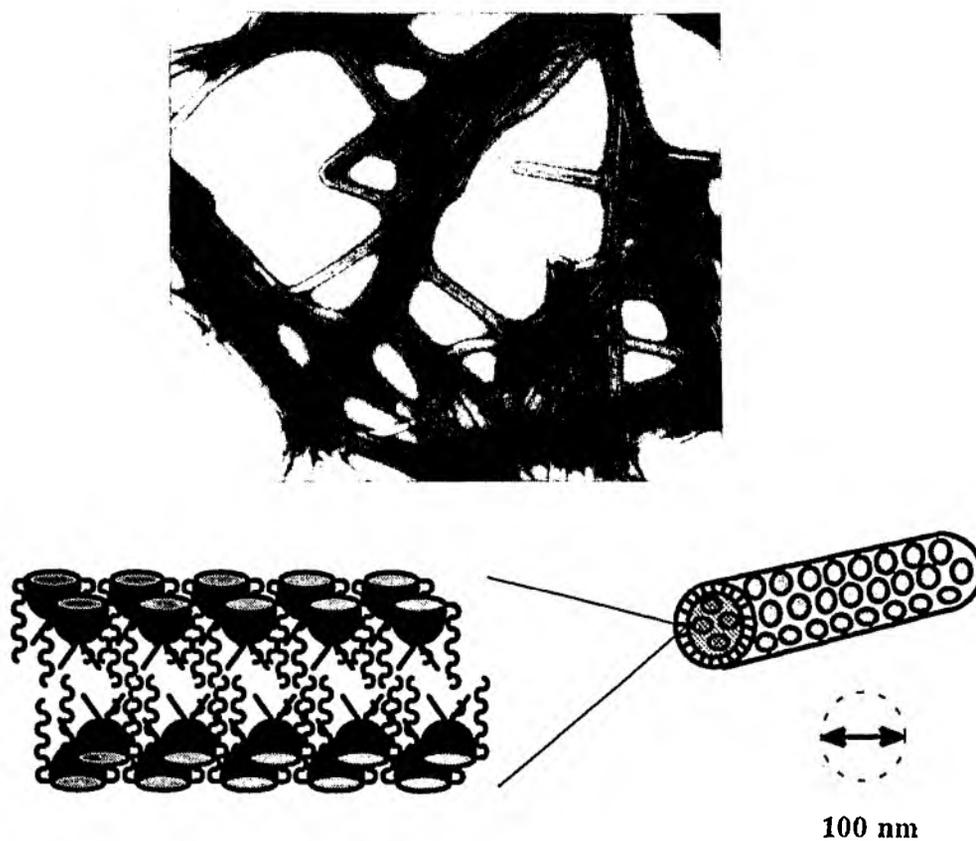


Fig. 5. Electron micrograph (negative staining technique) of nanotubes derived from 4c (A). Schematic drawing of a nanotube (B).

PHTHALOCYANINE BUILDING BLOCKS

Interesting nanometer-sized structures are accessible from phthalocyanine molecules containing crown ether rings. 18-Crown-6 phthalocyanine **6** self-assembles in the presence of metal salts to form different types of aggregates. For instance, with Rb^+ and Cs^+ ions linear stacks are obtained, whereas with Ba^{2+} ions sheet structures are generated (Fig. 6). The electrical conductivities of the aggregates were found to depend on the type of metal ion and increased in the series $(\text{Ba}^{2+})\text{Pc} < (\text{K}^+)\text{Pc} < (\text{Cs}^+)\text{Pc} < (\text{Rb}^+)\text{Pc}$.⁷

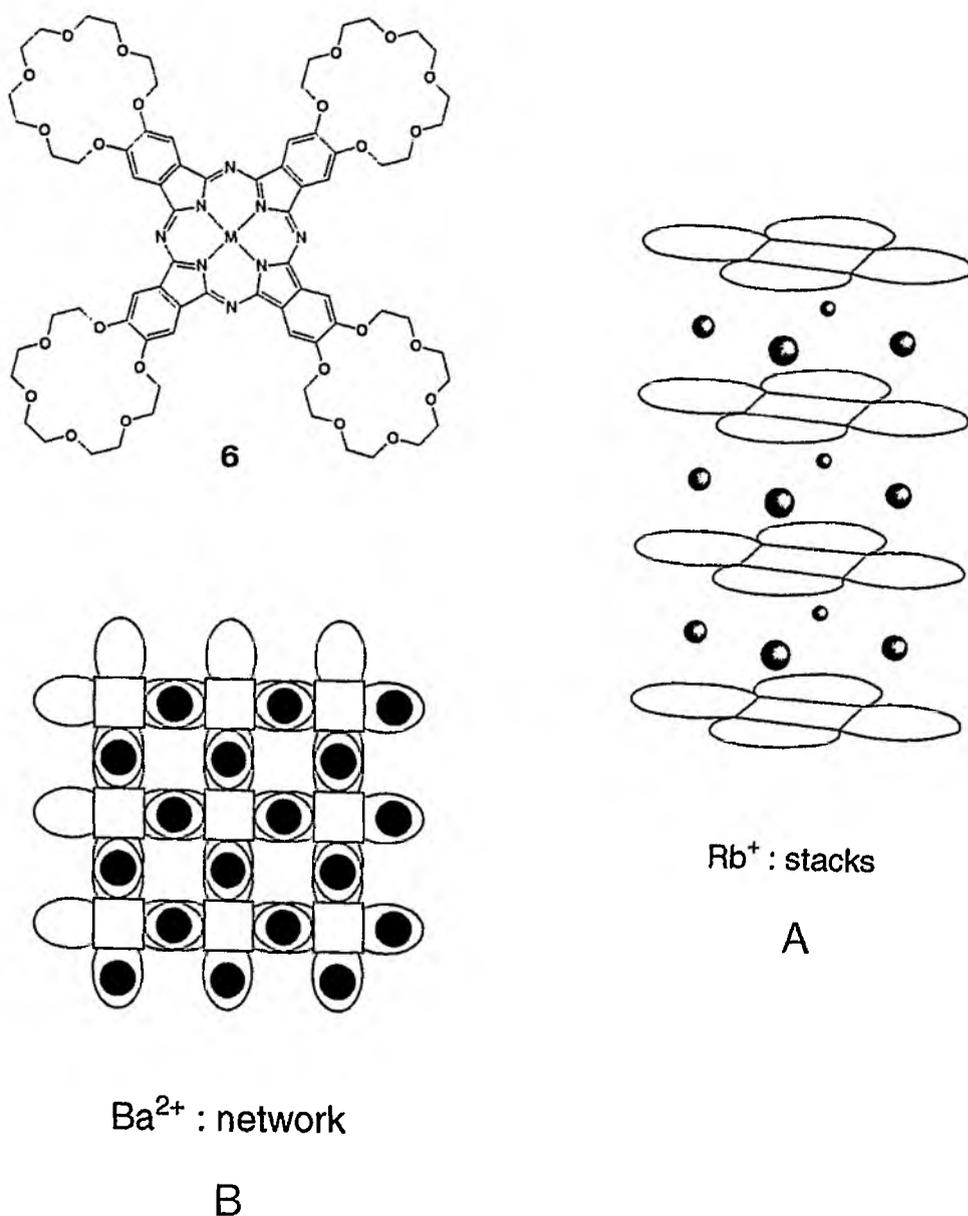


Fig. 6. Nanostructures formed from **6** and Rb^+ picrate (A) and Ba^{2+} picrate (B).

Crown ether phthalocyanines were modified with 8 hydrocarbon chains to give liquid-crystalline building blocks of type 7. In chloroform solution 7 forms extremely long fibers by a self-assembly process. According to electron microscopy the fibers consist of bundles of parallel strands, each of which has a thickness equal to the diameter of a single molecule of 7, *viz.* 60 Å. A schematic representation is shown in Fig. 7. The strand in fact is a molecular cable, containing a central electron wire, 4 ion channels, and a surrounding isolating hydrocarbon mantle. The conductive properties of this cable are currently under investigation.

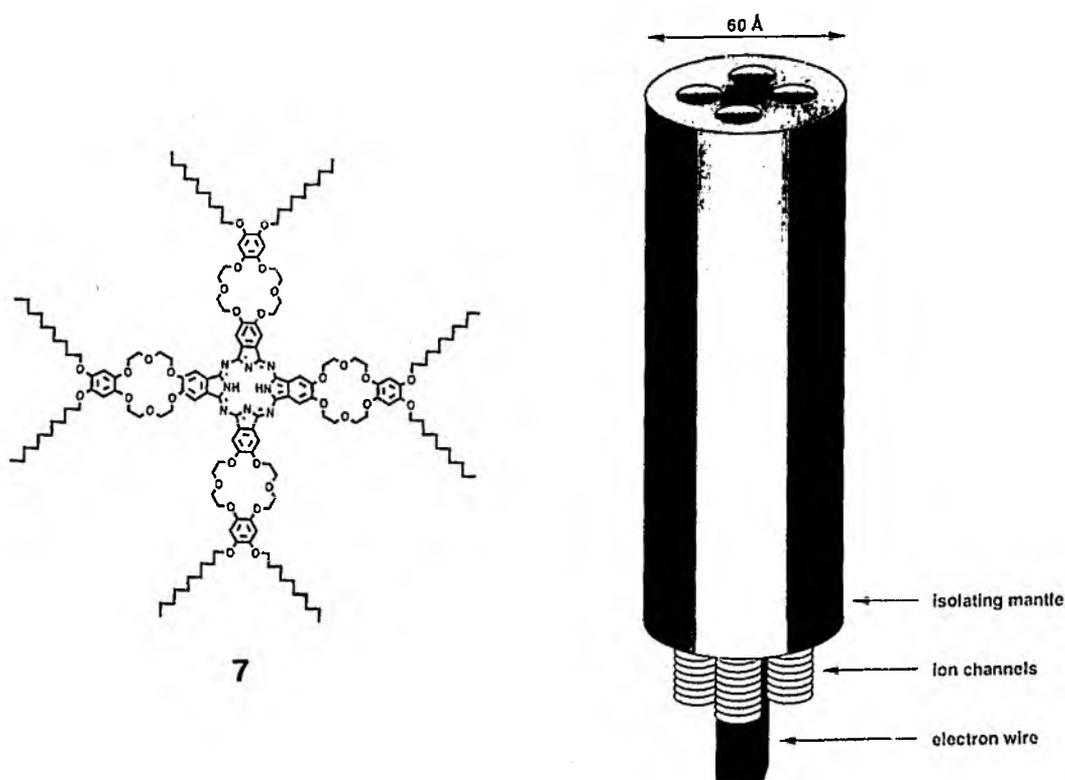


Fig. 7. Schematic representation of the multiwired molecular cable formed by self-assembly from 7.

CONCLUSION

As shown in this paper, nanometer-sized structures are accessible from a variety of building blocks. The procedures to generate these structures make use of the self-assembling properties of the molecular units. Currently our efforts are focussed on gaining better control over the shape of the obtained objects.

ACKNOWLEDGMENT

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