Perspectives in supramolecular chemistry: From molecular recognition towards self-organisation

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Abstract: Self-assembly processes generate spontaneously defined supramolecular architectures on the basis of specific molecular information and recognition features. Several types of organic and inorganic self-assembled structures are described.

Supramolecular chemistry has relied on more or less preorganised molecular receptors for effecting molecular recognition, catalysis and transport processes. A step beyond consists in the design of systems undergoing *molecular self-organisation*, i.e. systems capable of spontaneously generating a well-defined supramolecular architecture by *self-assembling* from their components in a given set of conditions.

The *molecular information* necessary for the process to take place and the *algorithm* that it follows must be stored in the components and operate through selective molecular interactions. Thus, these systems may be termed *programmed supramolecular systems*, that generate organised entities following a defined plan based on molecular recognition events (1). Several approaches to self-assembling systems have been pursued.

Self-assembly of organic supramolecular structures

Molecular information expressed through molecular recognition events provides means for directing the spontaneous formation of supramolecular species from complementary components. It may allow the design and engineering of supramolecular materials, in particular of liquid crystalline and of polymeric nature.

1) *Mesophases* and *liquid crystalline polymers* of supramolecular nature have been generated from complementary components, amounting to macroscopic expression of molecular recognition (Figure 1) (2).
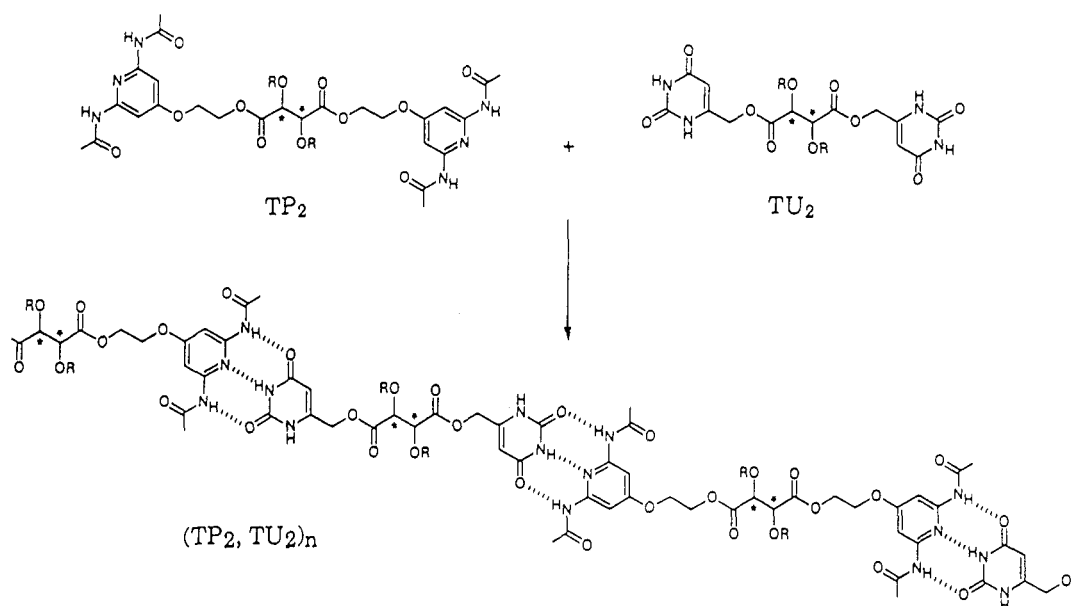
Figure 1   Self-assembly of the polymolecular supramolecular species $(TP_2, TU_2)_n$ from the complementary chiral components TP_2 and TU_2 via hydrogen bonding; T represents L–, D– or meso(M)–tartaric acid; $R=C_{12}H_{25}$.

The self-assembly of complementary ditopic components through hydrogen bonding yields liquid crystalline "polymers" of supramolecular nature; it takes place by a progressive growth revealed by electron microscopy: from nuclei, to filaments, to tree-like species, to strings and fibers that present helicity induced by the chirality of the subunits derived from tartaric acid (3).

2) A *bis-porphyrin supramolecular cage* is obtained by self-assembly of two porphyrin components bearing uracil type units that interact through hydrogen bonding with two complementary triaminopyrimidine units (Figure 2) (4).

3) *Ordered solid state structures* are formed through molecular recognition directed self-assembly of complementary hydrogen bonding components (Figure 3) (5, 6).

A rich variety of structures and properties may be expected to result from the blending of supramolecular chemistry with polymer chemistry and materials science (7).
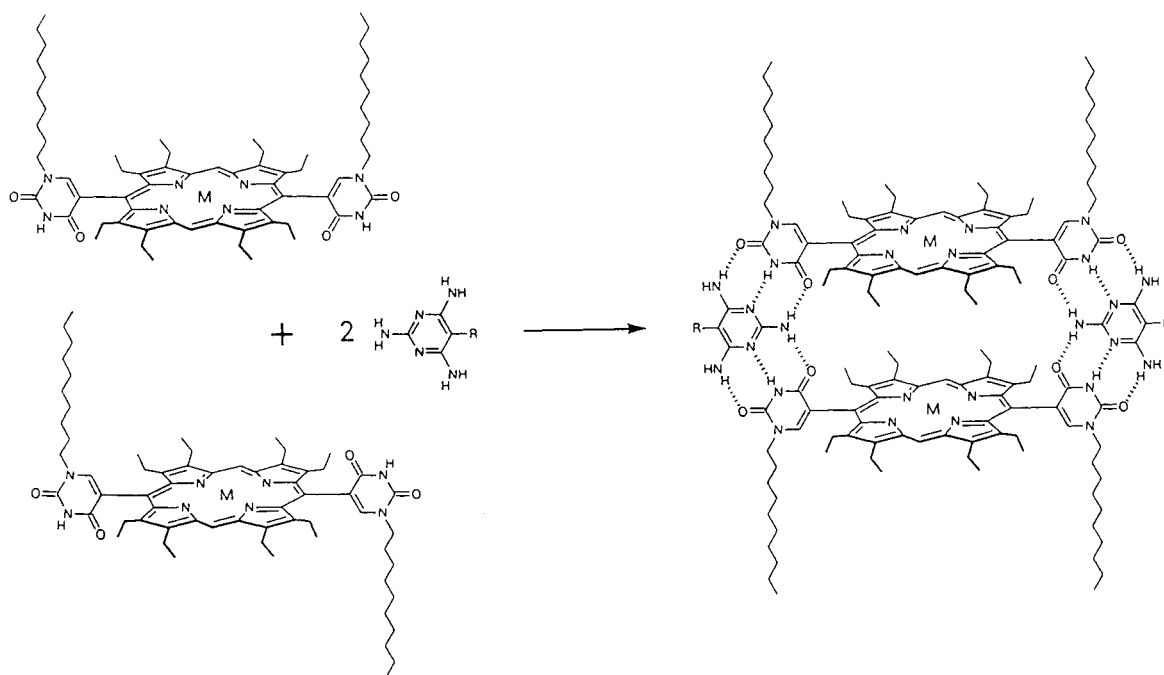
Figure 2   Supramolecular cage-like structure formed by the self-assembly of two porphyrins, containing 5-alkyluracil recognition groups, and two alkyltriaminopyrimidine (TAP) units. R=decyl, R'=octyl or decyl, M=2H$^+$, Fe^{III}Cl or Zn^{II}.
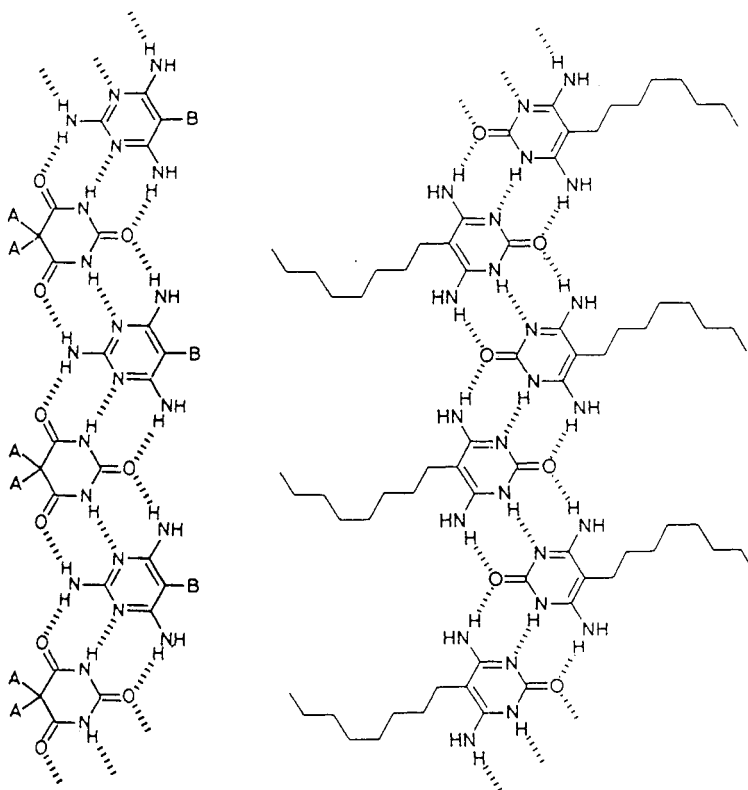

Figure 3   Self-assembled supramolecular strands derived from components bearing side-chains and containing heterocomplementary (left) or self-complementary (right) recognition sites; A and B: aliphatic chains; for the corresponding crystal structures see ref. 5, 6.

Self-assembly of inorganic structures

The self-assembly of inorganic structures of several types has been achieved, based on ligand design and on the use of suitable coordination geometries that act as the assembling algorithm.

1) *Double-stranded* and *triple-stranded helicates*. Double helical and triple helical metal complexes are formed by the spontaneous assembly of two or three linear polybipyridine ligands of suitable structure into a double or a triple helix by binding of specific metal ions displaying respectively tetrahedral (Cu^I) and octahedral (Ni^{II}) coordination geometry. These species are illustrated by the trinuclear double and triple helicates shown below (Figure 4) (8-10).
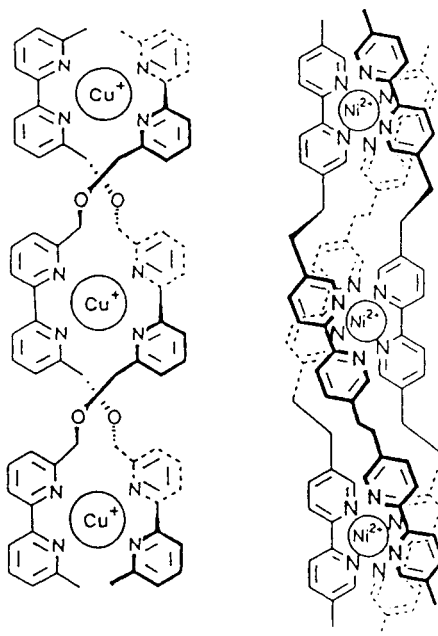

Figure 4

2) *Self-recognition* occurs in helicate self-assembly. Thus, on treatment with copper(I) ions, mixtures of the [oligo(2,2')-bipyridine] strands yield spontaneously the homostrand double helicates without significant crossover. Similarly, when a mixture of two tris-bipyridine ligands containing different substitutions is allowed to react with copper(I) and nickel(II) ions, only the expected double and triple helicates are formed (Figure 5). The process represents a self/nonself-discrimination involving the preferential binding of like metal ions by like ligand strands in a mixture to selectively assemble into the corresponding helicates. In a broader perspective, these results point to a change in *paradigm* from pure compounds to *instructed mixtures* — that is from seeking chemical purity to designing programmed systems composed of mixtures of instructed components capable of spontaneously forming well-defined superstructures through self-processes (11).
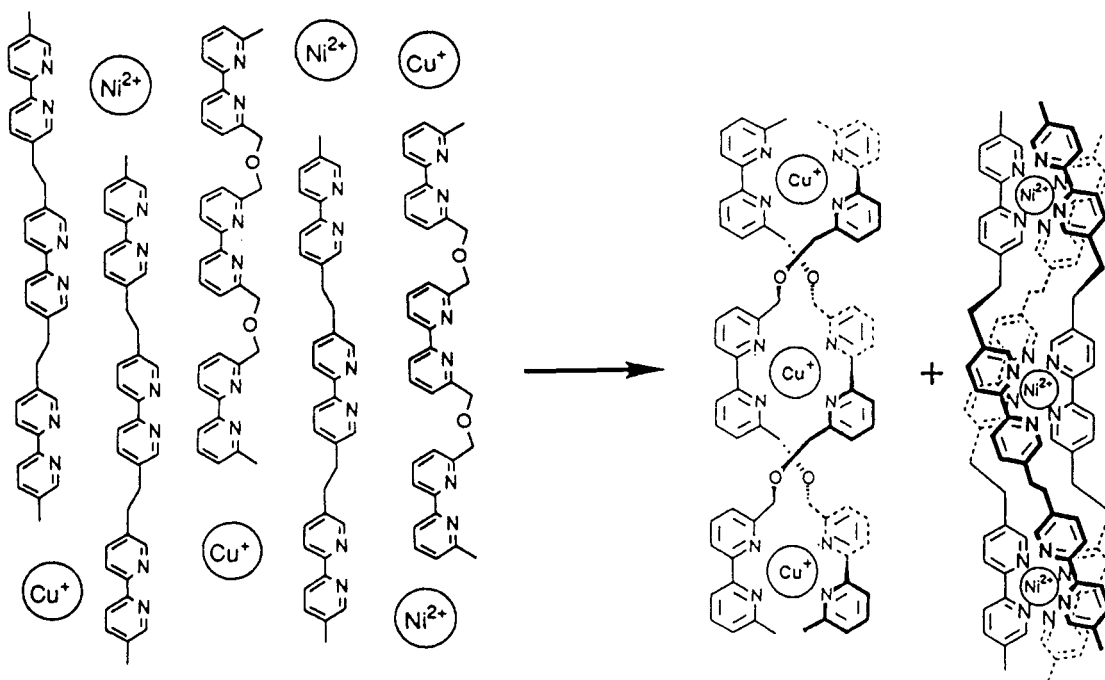
Figure 5   Self-recognition in the self-assembly of a double helicate and a triple helicate from a mixture of oligobipyridine strands and of Cu^I and Ni^{II} ions (ClO$_4^-$ anions omitted).

3) A *circular complex* is formed by the assembly of a trinucleating ligand, three 2,2'-bipyridine units and three Cu^I ions (Figure 6, left) (12). A capped structure has also been obtained (Figure 6, right).
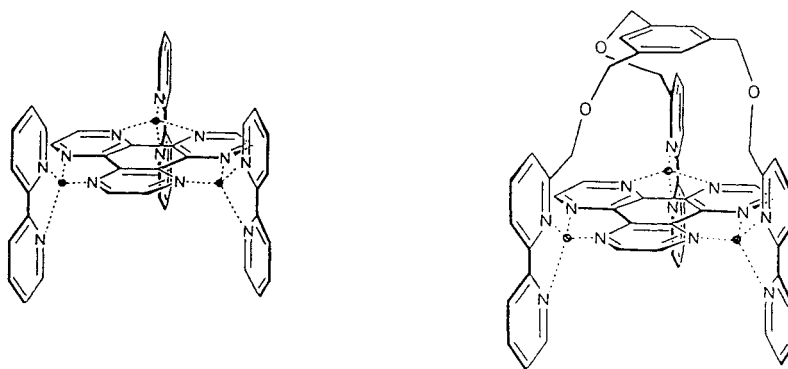

Figure 6

Multiple component self-assembly leads to the generation of cylindrical structures such as that shown on Figure 7 which builds up spontaneously from five ligands of two different types and six Cu^I ions (12).

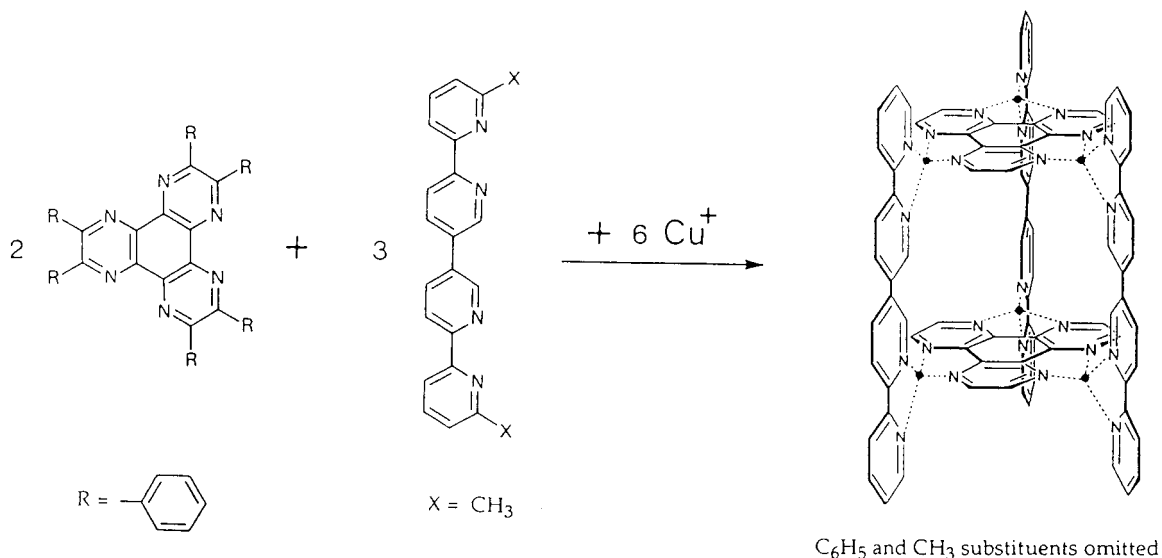C_6H_5 and CH_3 substituents omitted

Figure 7   Self-assembly of a cylindrical superstructure from five ligands
of two different types and six metal ions.

This process represents the remarkable self-organisation of a closed inorganic architecture from multiple components by the spontaneous and correct assembly in one stroke of altogether eleven particles belonging to two types of ligands an one type of metal ion. The operation of this instructed supramolecular systems fulfills the three levels of molecular programming and of information input, *recognition, orientation* and *termination*, that determine the generation of a discrete supramolecular architecture. The steric and binding information contained in the ligand is read out by the metal ions following a tetrahedral coordination algorithm. This process represents a further step in the control of the self-organisation of large and complex supramolecular architectures through molecular programming.

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