

CHEMICAL SYNTHESIS OF NANOSTRUCTURES

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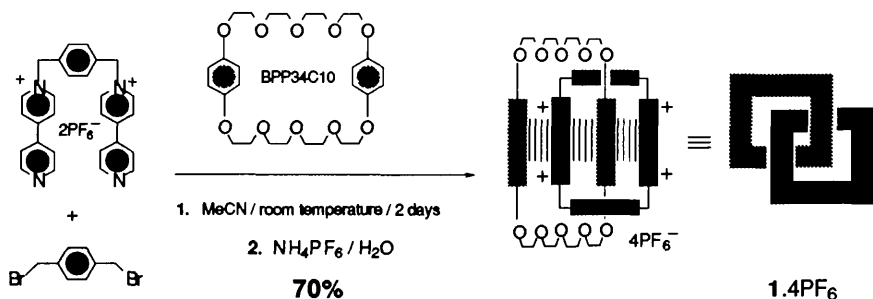
ABSTRACT

Molecular recognition is central to the self-assembly of catenanes and rotaxanes. The design criteria for efficient formation of these compounds is gradually becoming clear. Self-assembly of mechanically-interlocked compounds is heading apace towards the nanometre scale.

SELF-ASSEMBLY OF UNNATURAL MATERIALS

Supramolecular chemistry¹ as it occurs in the biological world provides molecular designers with a plethora of functions and processes from which to gain inspiration. Self-organisation, self-assembly and self-replication are necessary concepts for chemists to appreciate and tame before the chemical synthesis of large, well-defined and functioning molecular nanostructures can be achieved.

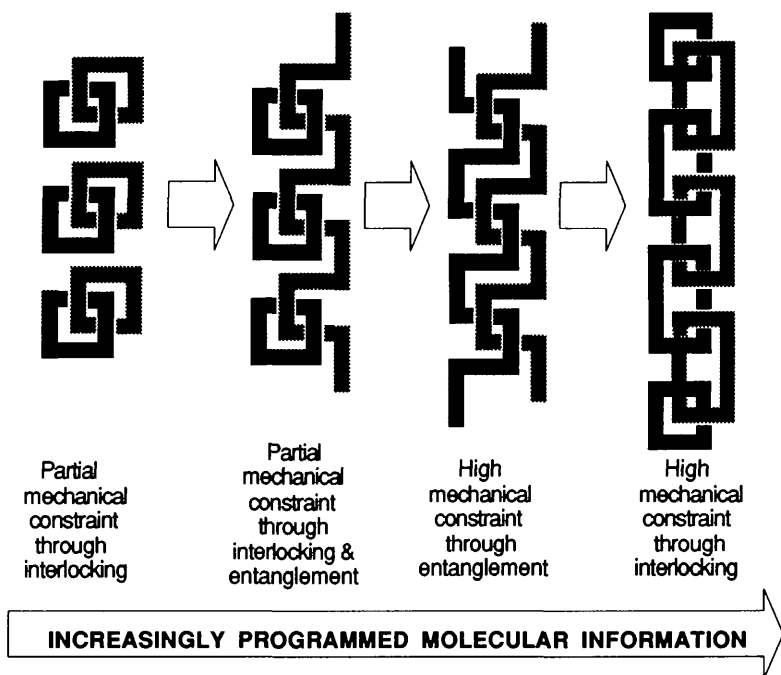
The tremendous physical strength and flexibility of cables, ropes, knots and chains in the world around us poses an intriguing question to the chemist - can we reproduce the features of mechanical entanglement at the molecular level, and if so, what are the consequences in terms of the properties and functions of the materials? Mechanical interlocking in relatively small synthetic chemical systems has already been demonstrated. Self-assembly processes² have revolutionized the construction of interlocked molecules,³ and have made possible the preparation of the knots⁴ and helices⁵ by template-directed methods. Nanostructures incorporating entangled components remain a key goal of this kind of research.



Template-directed self-assembly of a [2]catenane

The complementarity between bisraphenylene-34-crown-10 (BPP34C10) and paraquat, and between cyclobis(paraquat-*p*-phenylene) and guests containing π -electron rich aromatic

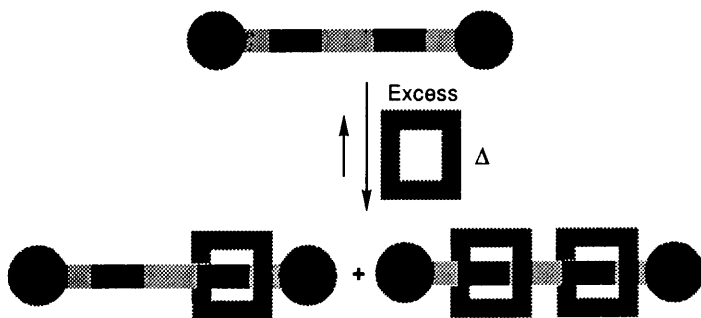
rings, suggested what proved to be the extremely efficient template-directed self-assembly⁶ of the [2]catenane 1.4PF₆. The building blocks contain sufficient molecular information to induce formation of continuously ordered stacks in their crystals. This donor-acceptor stack can be rearranged conceptually to afford pseudorotaxanes and double helices, in a logical sequence. This sequence may be derived from a continuous donor-acceptor stack, by formally connecting the termini of the donors or of the acceptors, respectively. Rearrangement of the stack to an acceptor-donor-donor-acceptor sequence leads to an oligocatenane. Increasingly refined programming of the molecular components in this sequence is necessary with respect to the information which they contain. For example, the preorganised crown ether ring must be prepared before self-assembly of the [2]catenane can be accomplished.



Routes to Rotaxanes

The "intelligent" self-assembly⁷ of a [2]rotaxane by threading may prove to be the prototype for a series of larger well-defined structures. Four pre-programmed building blocks combine to form a [2]rotaxane which contains two binding sites, hence generating a molecular shuttle. In principle, for every n paraquat units in the thread, there will be $n-1$ BPP34C10 rings incorporated between the two stoppers. Alternatively, by fine-tuning the size of the stopper, macrocycles can be slipped on to the dumbbell at elevated temperatures in solution. Cooling

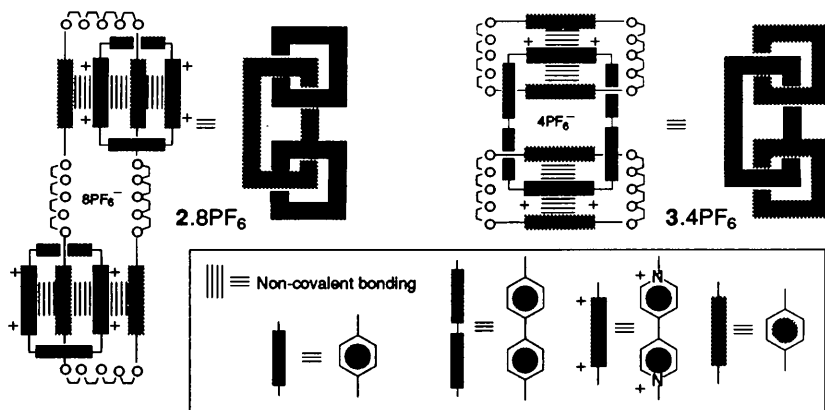
down the solutions affords the thermodynamically-stable rotaxanes after chromatography. We have recently demonstrated the high-yielding slippage⁸ of BPP34C10 on to dumbbells incorporating paraquat residues as recognition sites.



Self-assembly of a [2]rotaxane and [3]rotaxane by slippage

Towards Molecular Chains

Polycatenanes are perhaps one of the most appealing and challenging nanostructures whose synthesis remains as yet untamed by polymer scientists and nature. The increased number of interactions that are required for the chain construction of a polycatenane means that much more recognition information is necessary than that needed for the formation of polyrotaxanes, or even helices. We have already characterized⁹ the [3]catenanes **2.8PF₆** and **3.4PF₆**, from which one could conceive of planning a route to polycatenanes. The reduced preorganisation of TPP68C20, when compared with that of BPP34C10, resulted in this route failing. The recipe is clearly deficient of molecular information.



We have now managed to self-assemble a [4]catenane¹⁰ by using a crown ether incorporating three hydroquinone rings, and all the necessary molecular information to interact with the components of the cyclobis(paraquat-1,1'-[4,4'-biphenylene]) cyclophane. Currently,

we are concentrating our efforts on increasing the efficiency still further in order to address the appealing challenge of oligocatenanes and polycatenanes.

Bigger and Faster Information Stores?

The power to self-assemble large ordered wholly-synthetic nanostructures packed with molecular information is becoming available at a considerable rate of knots! The challenge for the 21st century is to find out how to make use of this information.

Acknowledgements

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