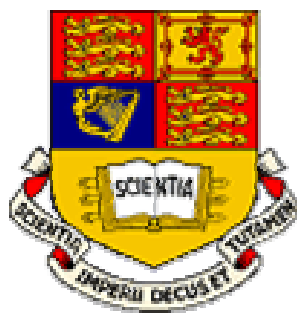


Supramolecular Chemistry of Nanomaterials

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Topics to be covered in the course:

- 1 - Introduction (definition of terms, etc.)
- 2 – Self-assembly
- 3 – Nano-capsules for delivery and reactions
- 4 – Supramolecular Switches
- 5 – Molecular Machines
- 6 – Self assembly in surfaces
- 7 – Supramolecular chemistry of polymeric materials

General references on Supramolecular Chemistry

- J.L. Atwood, J.E.D. Davies, D.D. MacNicol, F. Vogtle (editors), *Comprehensive Supramolecular Chemistry*, Elsevier, Oxford 1996
- J.W. Steed, J.L. Atwood, *Supramolecular Chemistry*, Wiley, 2000
- P.D. Beer, P.A. Gale, D.K. Smith, *Supramolecular Chemistry*, OCP, 1999
- A. Bianchi, K. Bowman-James, E. Garcia-España (editors), *Supramolecular Chemistry of Anions*, Wiley-VCH, New York 1997
- J.F. Stoddart (editor), *Monographs in Supramolecular Chemistry*, RSC
- J.M. Jehn, *Supramolecular Chemistry*, VCH, Weinheim 1995
- J.P. Behr (editor), *The lock and key principle*, Wiley, Guilford 1994

Nanomaterials

Nanoscale materials; materials with structural features (particle size or grain size, for example) of at least one dimension in the range 1-100 nm.

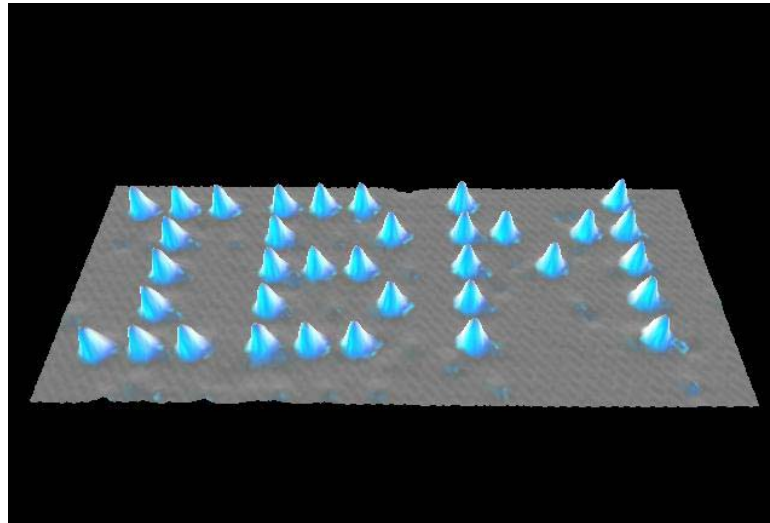
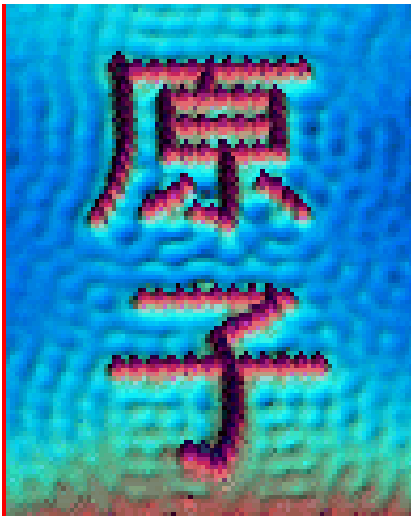
What makes these nanomaterials so different and so intriguing? Their extremely small feature size is of the same scale as the critical size for several physical phenomena.

<http://www.csa.com/hottopics/nano/overview.html>

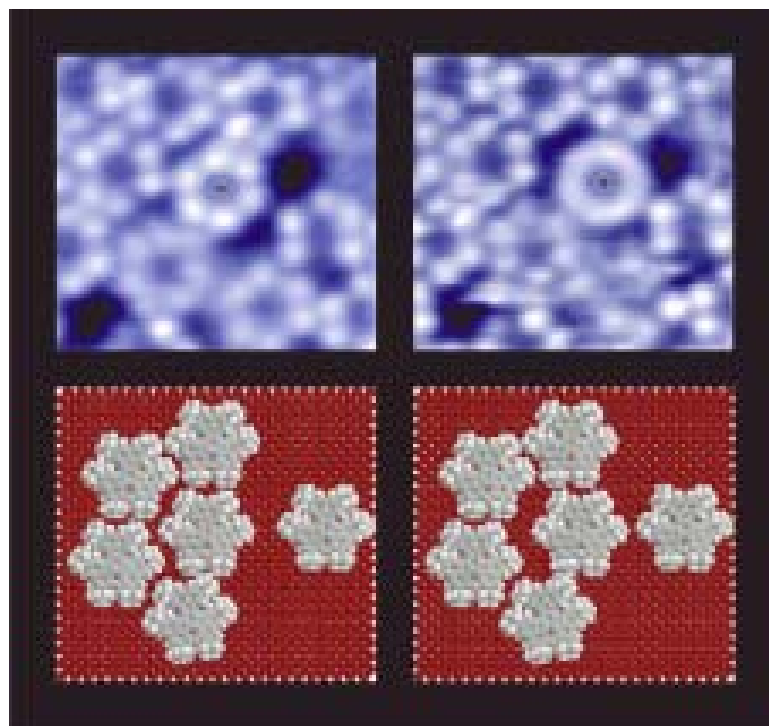
Scientists want to know how simple atoms and molecules come together and arrange themselves to form complex systems, such as living cells that make life possible on earth. This "bottom-up" science, which deals with how complex systems are built from simple atomic-level constituents, spawned nanoscience. It is the study of the properties of tens of or hundreds of atoms or molecules in a space with a diameter of less than 50 nanometers

<http://www.csa.com/hottopics/nano/websites.html>

Top-down approach:



<http://www.almaden.ibm.com/vis/stm/images/stm10.jpg>



Two STM images on top show a six-lobed 'propeller' molecule marked by an inner ring in an immobilized state close to four sister molecules (at left) and in a rotating state when shifted away by one-fourth of a nanometer (at right).

Taken from: <http://www.chem.ucla.edu/dept/Faculty/gimzewski/id2.htm>

The bottom-up approach: supramolecular chemistry

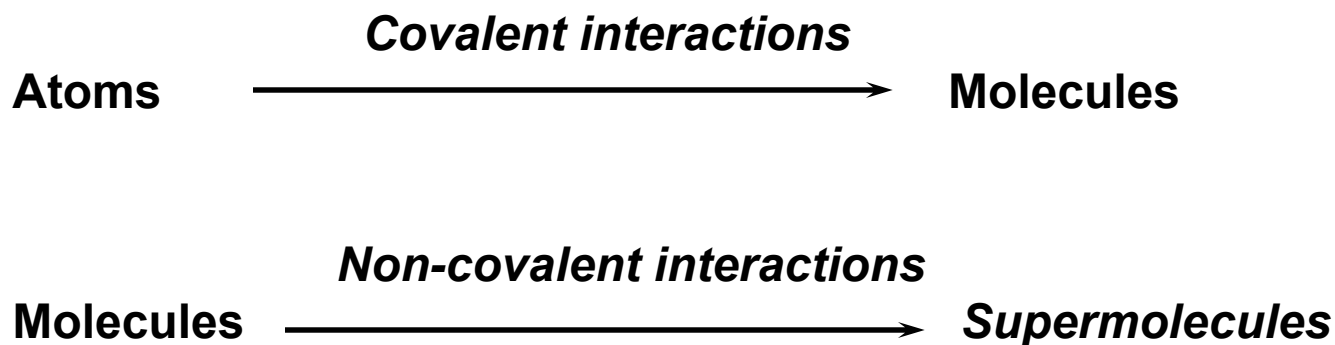
What is supramolecular chemistry?

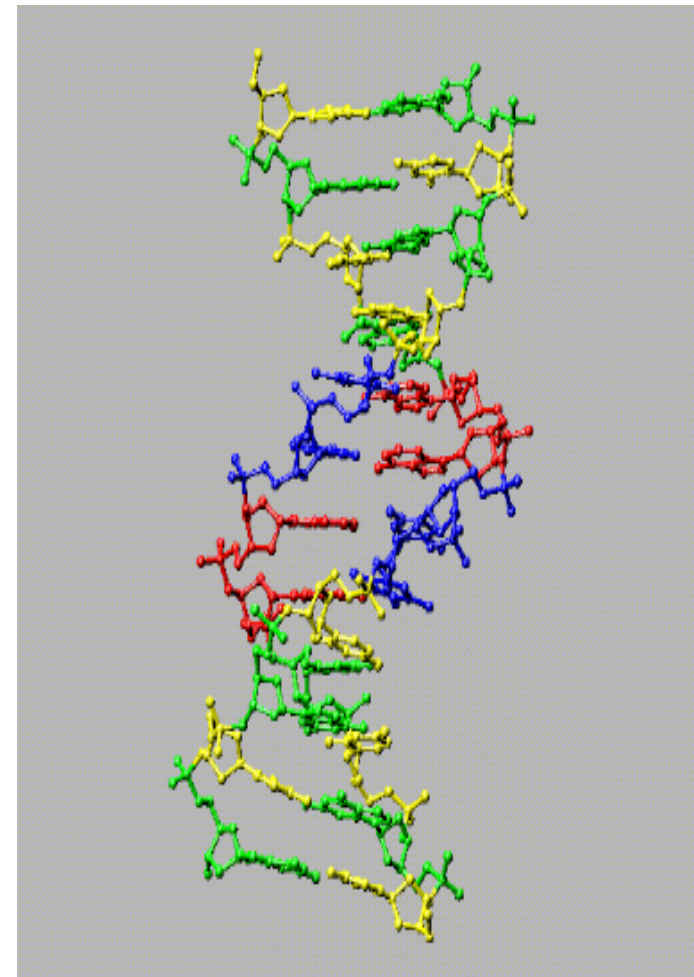
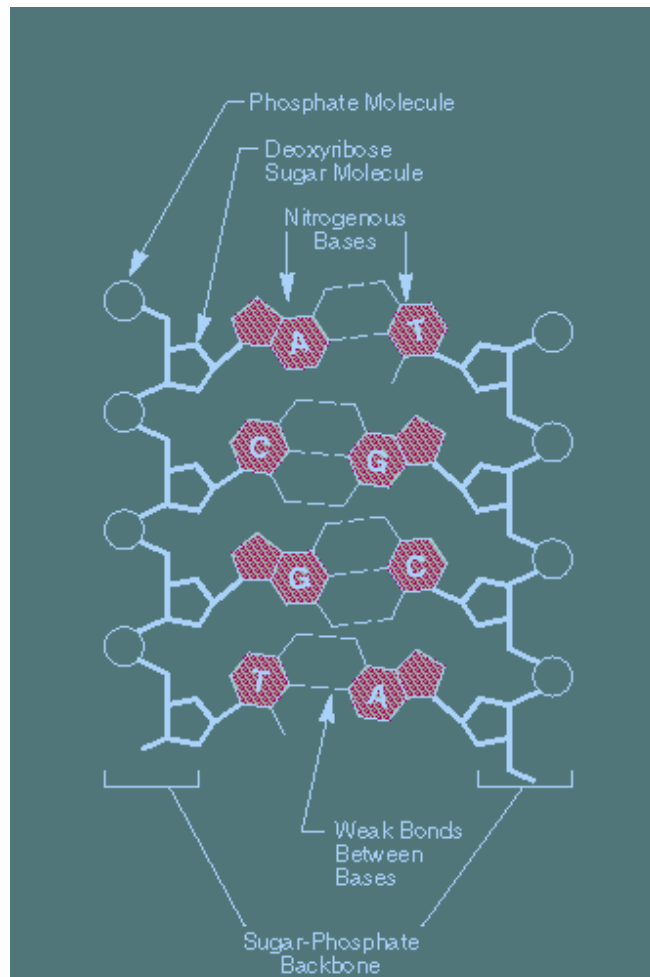
“Chemistry beyond the molecule.”

“Chemistry of molecular assemblies and of the intermolecular bond.”

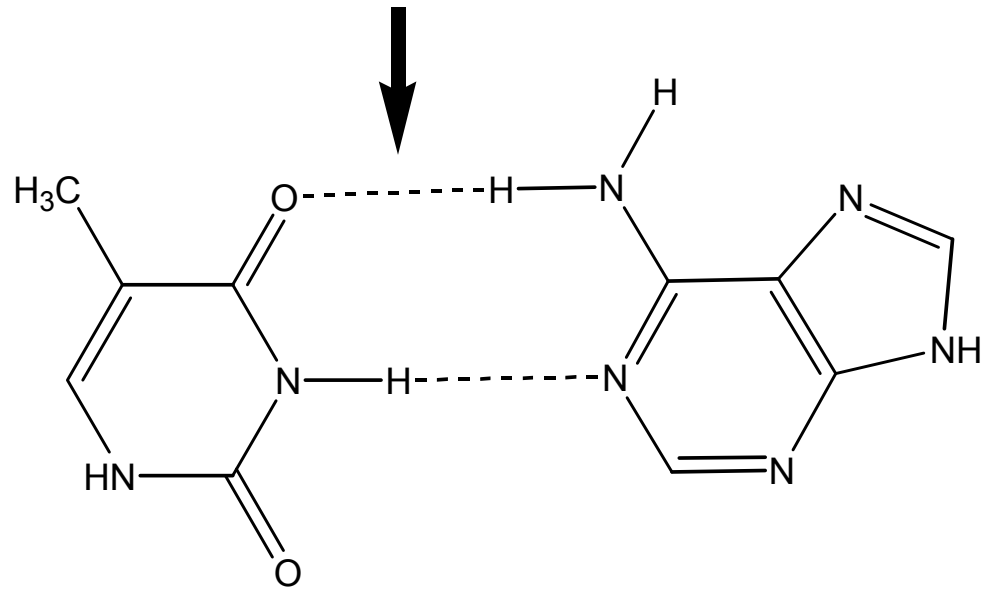
“The chemistry of the non-covalent bond.”

“Supramolecular chemistry involves investigating molecular systems in which the most important feature is that components are held together by intermolecular forces, not by covalent bonds”



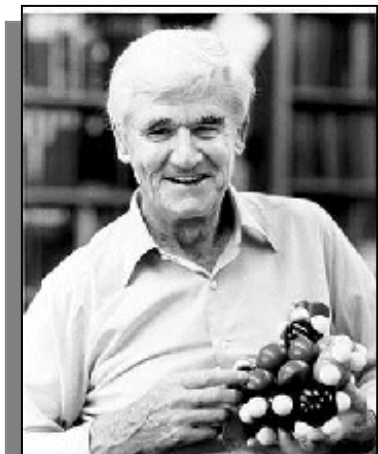


H-Bonding (non-covalent interactions)

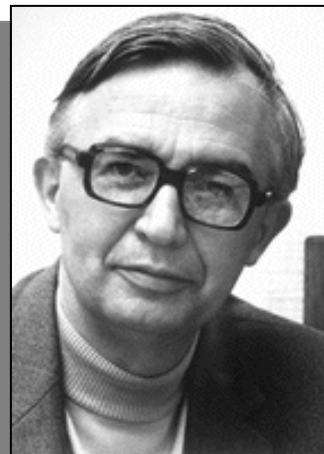


Thymine

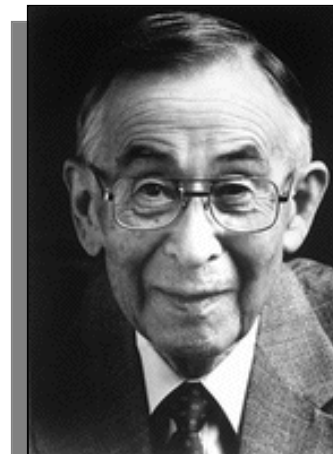
Adenine



Donald J. Cram

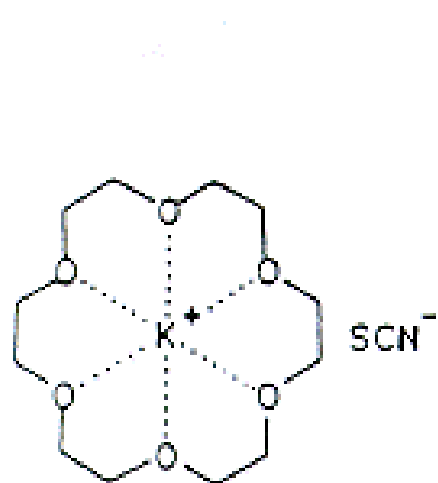


Jean-Marie Lehn

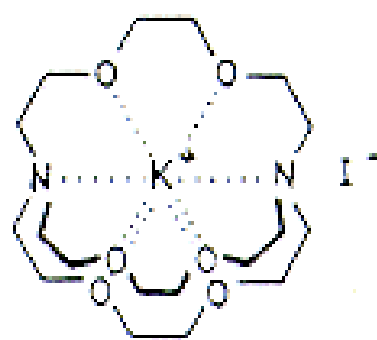


Charles J. Pedersen

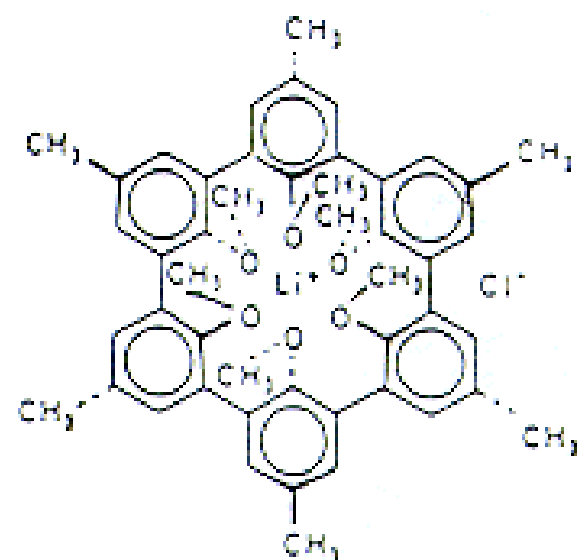
The research developed by Cram, Lehn and Pedersen at the end of the 1960s and beginning of the 1970s established the basis for the development of supramolecular chemistry as a recognised discipline. They were awarded the chemistry Nobel Prize in 1986 due to their work in the area.



Crown ether complex
according to Pedersen



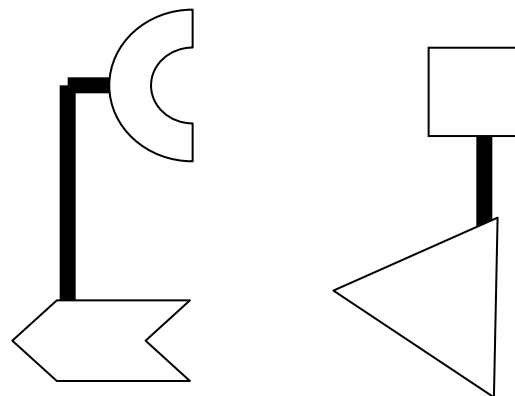
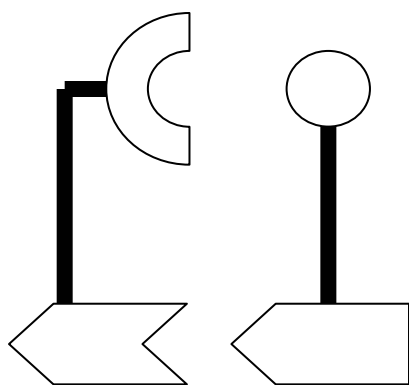
cryptand complex
= cryptate
according to Lehn



host-guest complex
according to Cram

Host-Guest chemistry

In supramolecular chemistry we usually consider a molecule (a host) binding another molecule (a guest) to produce a host-guest complex or supramolecule.



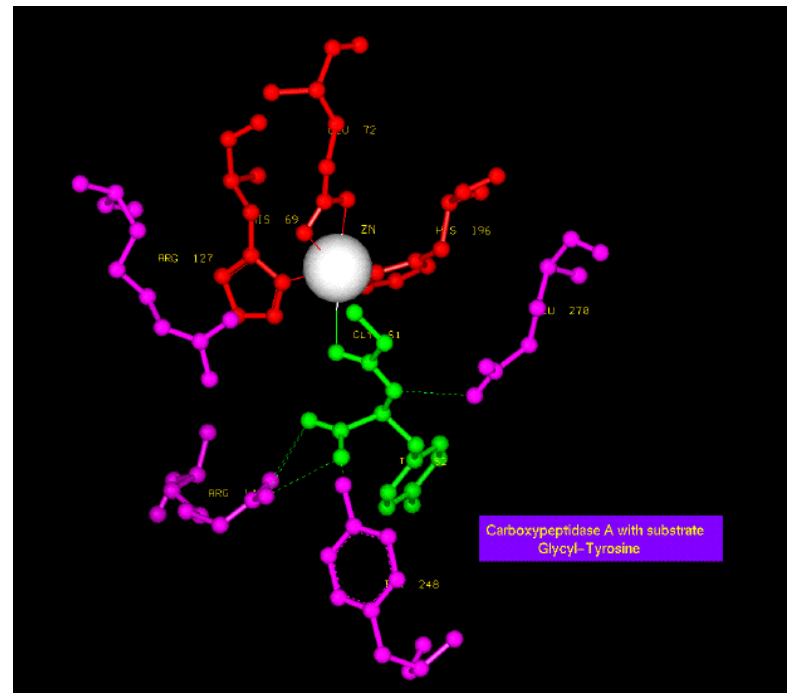
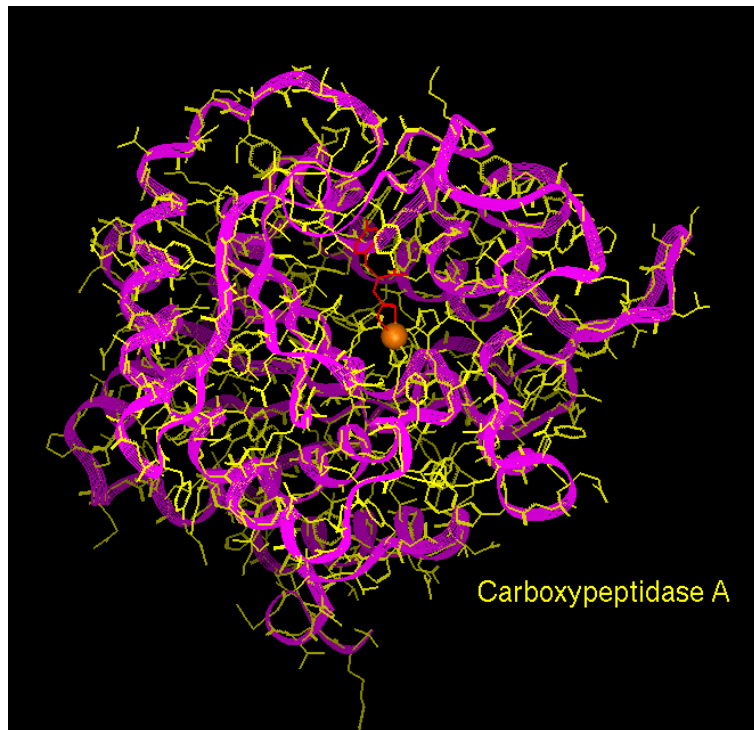
Complementarity:

- In order to bind, a host must have binding sites of the correct electronic character to *complement* those of the guest.
- The binding sites must be spaced out on the host in such a way to make it possible for them to interact with the guest.

The lock-and-key principle:

- The size, shape and position of the binding sites within the active site of a host (e.g. an enzyme) are ideal for *specific* recognition of the guest (e.g. substrate).

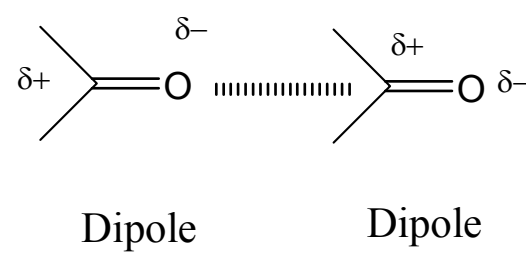
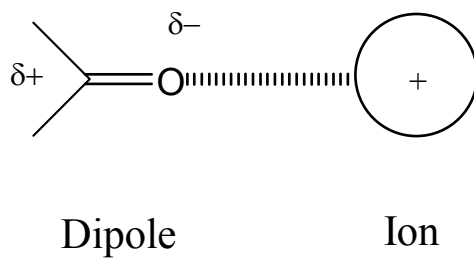
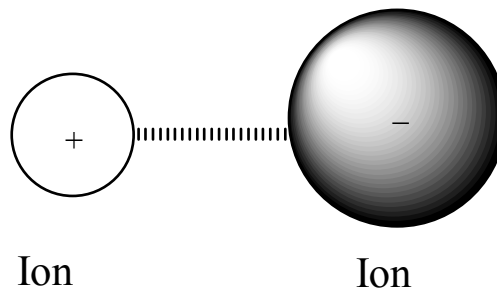
The most striking examples of host-guest complexes (keeping in mind the lock-and-key principle and complementarity) are biological molecules. Here is an example of an enzyme:



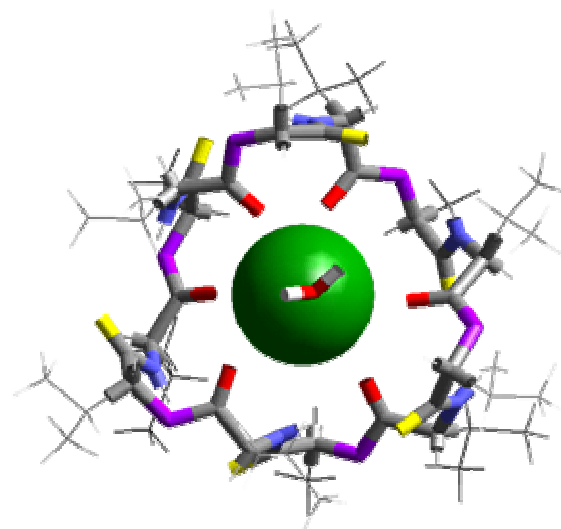
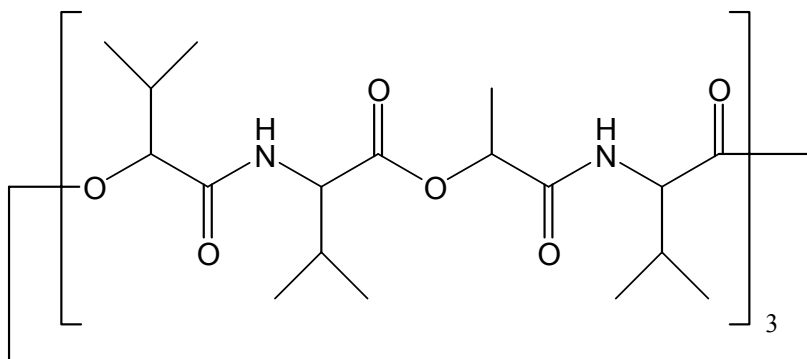
Nature of Supramolecular Interactions

- 1 - Electrostatic (e.g. ion-ion, dipole-dipole)
- 2 - Hydrogen bonding (4 - 120 kJ/mol)
- 3 - π - π stacking interactions (0 - 50 kJ/mol)
- 4 - Cation- π interactions (5 - 80 kJ/mol)
- 5 - Van der Waals forces (< 5 kJ/mol)
- 6 - Hydrophobic effects

1) Electrostatic interactions



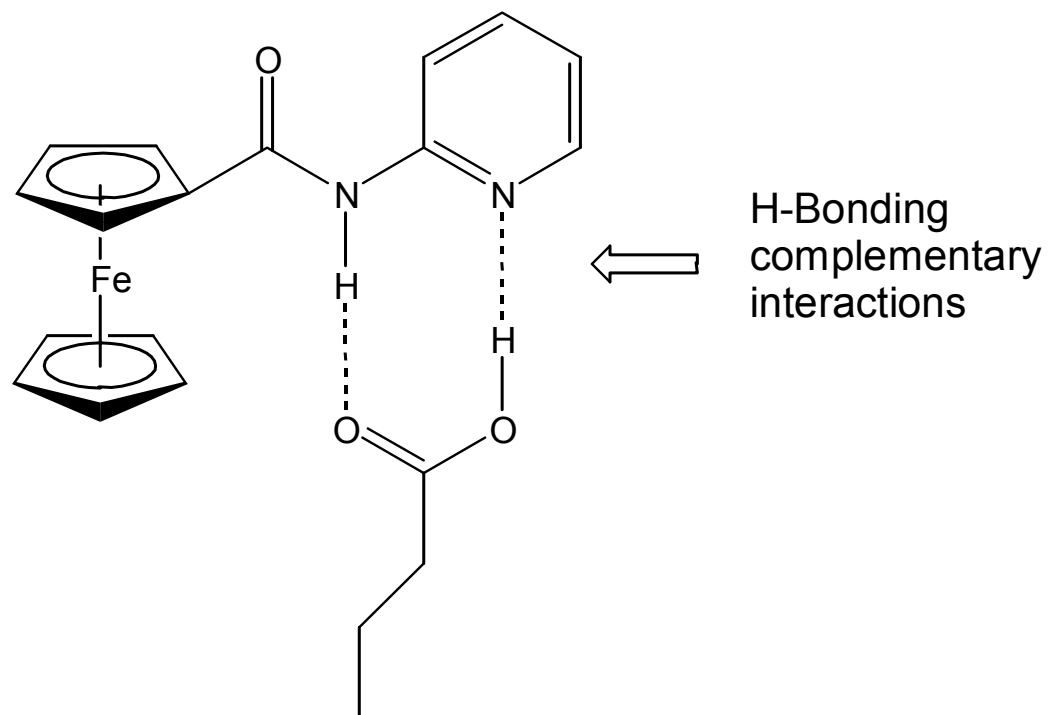
***Valinomycin*: a natural antibiotic which displays ion-dipole (an H-bonding) interactions.**

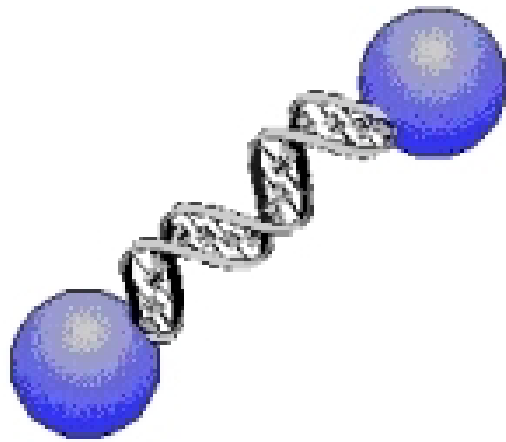


(Taken from: <http://molsim.ch.umist.ac.uk/vm.shtml>)

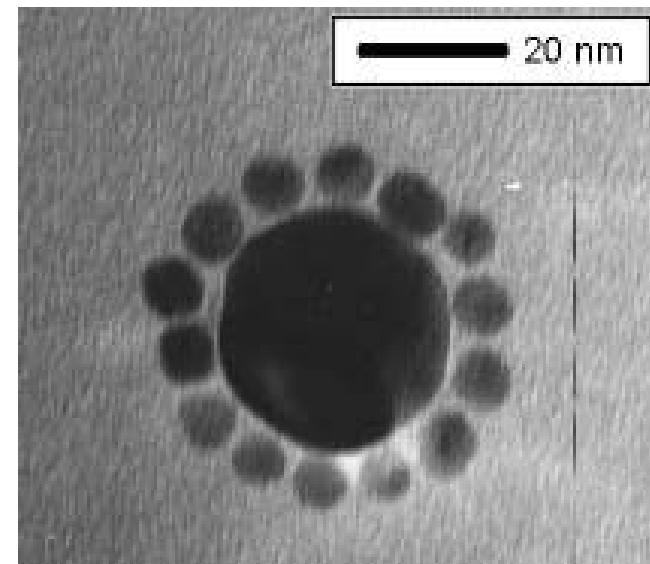
2) *Hydrogen bonding*

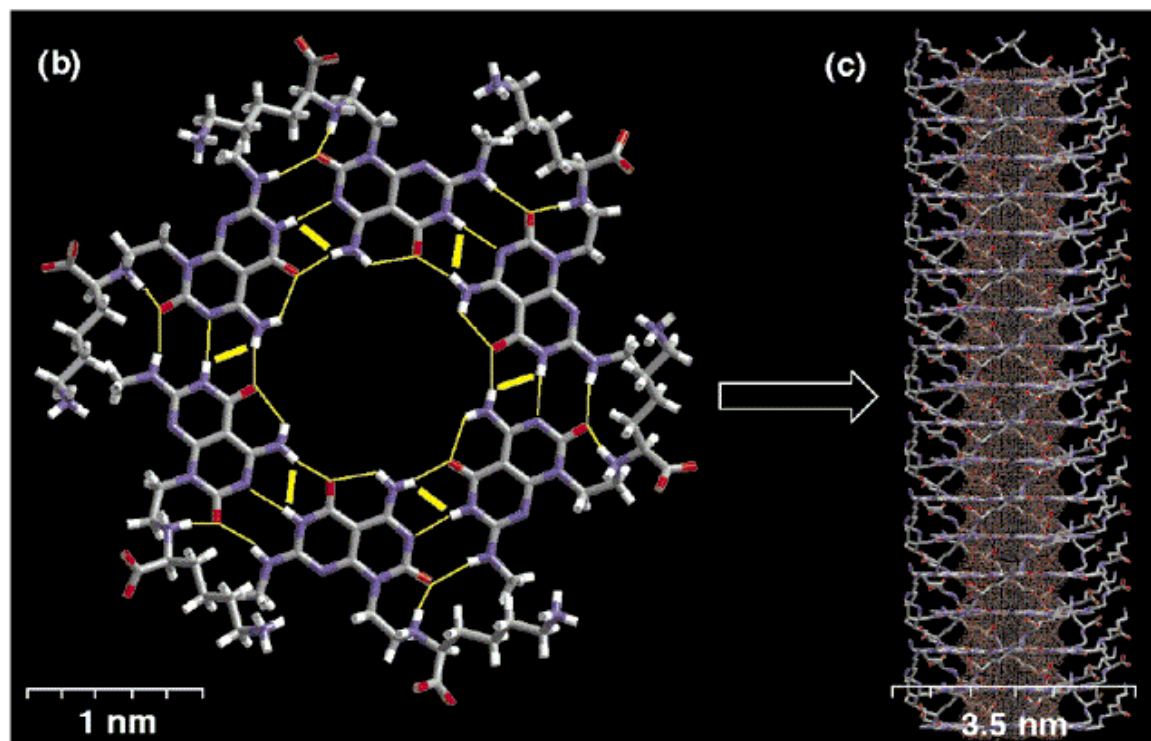
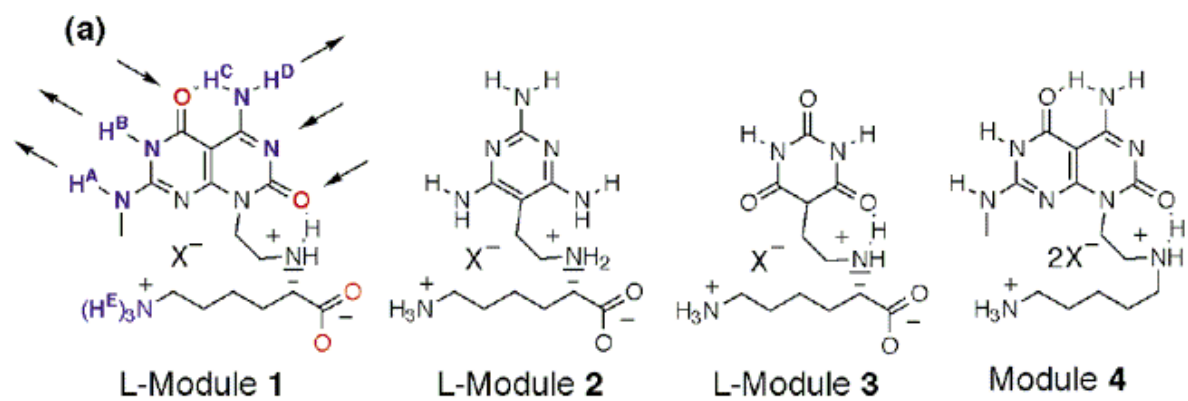
H-bond donor (D) \longrightarrow **A-H** \cdots **B** \longleftarrow H-bond acceptor (A)

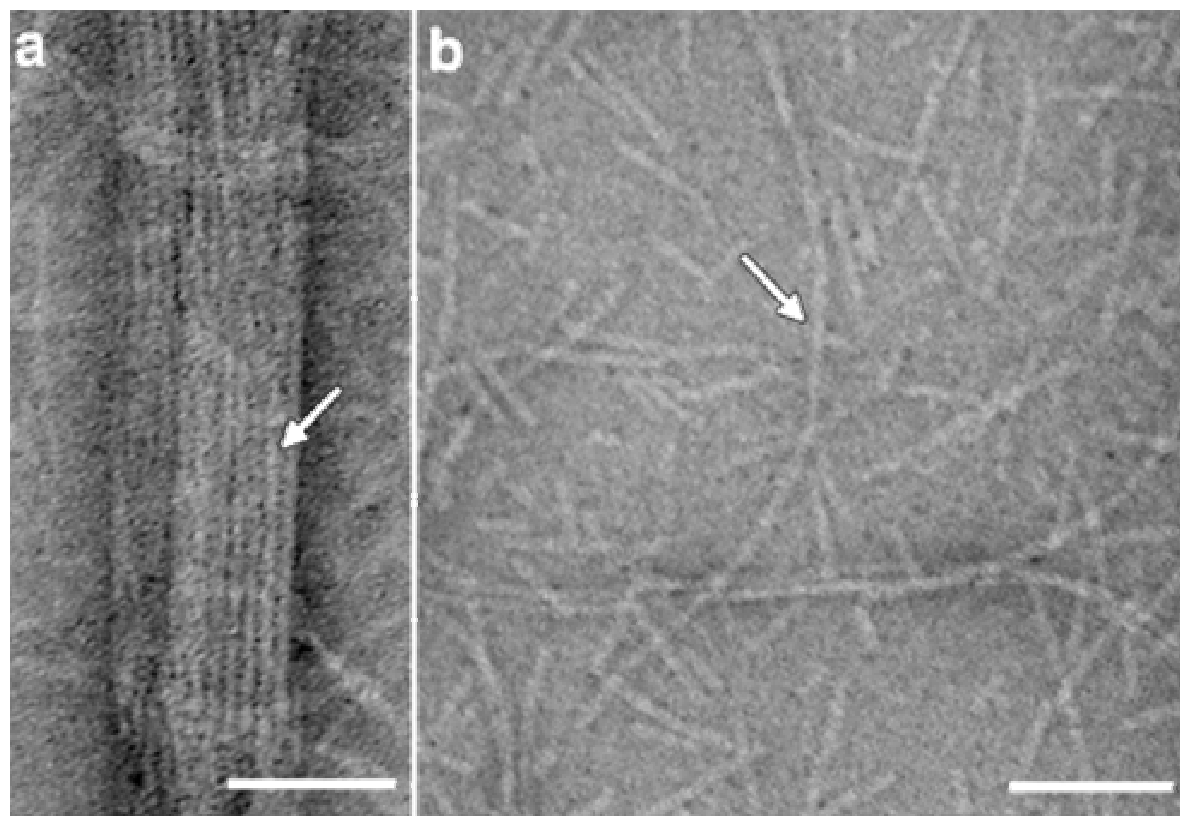




Biomaterials Chemistry

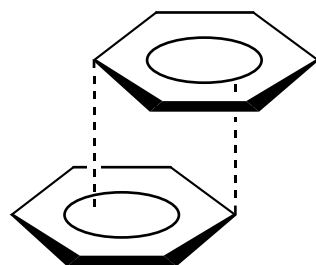




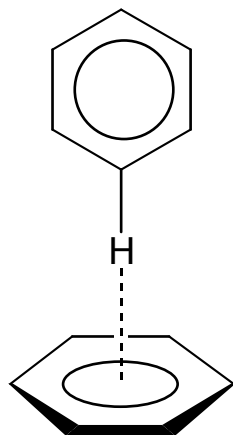


Fenniri, *J. Am. Chem. Soc.*, 123 (16), 3854 -3855, 2001.

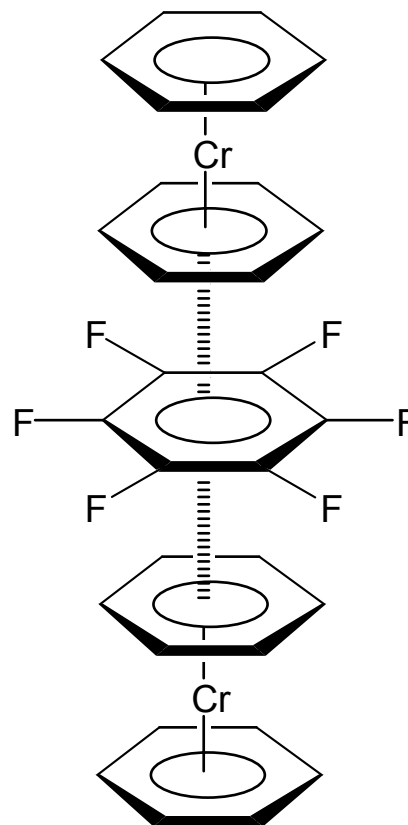
3) π - π stacking interactions



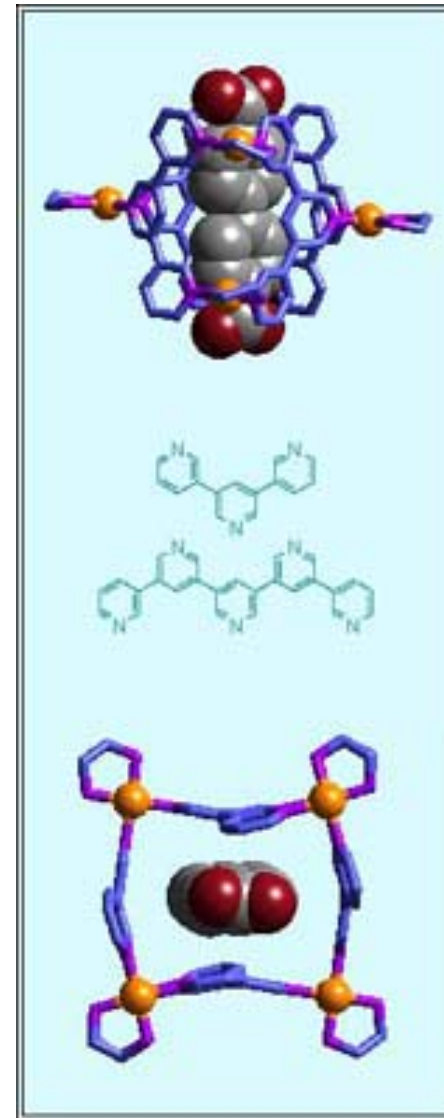
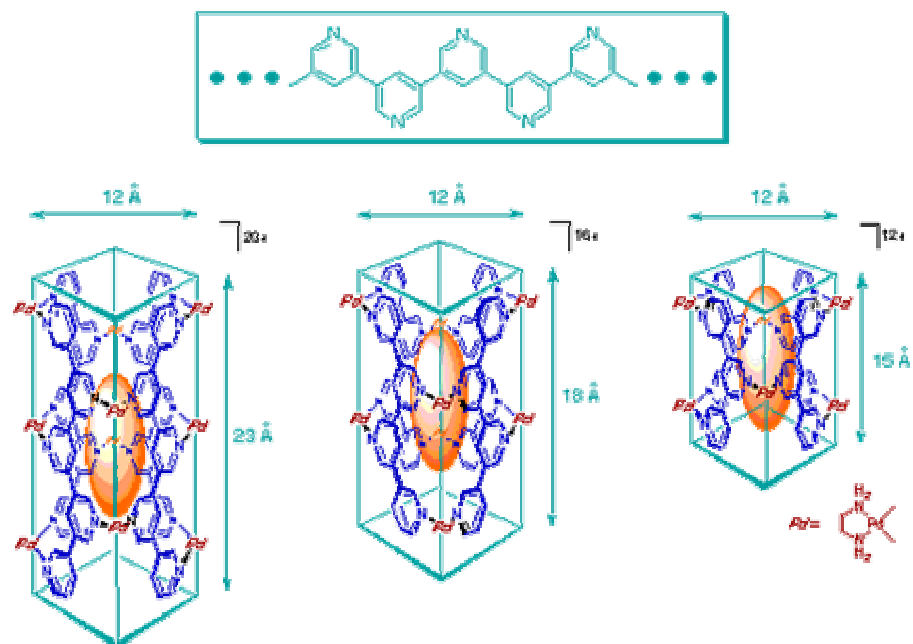
Face-to-face



Edge-to-face



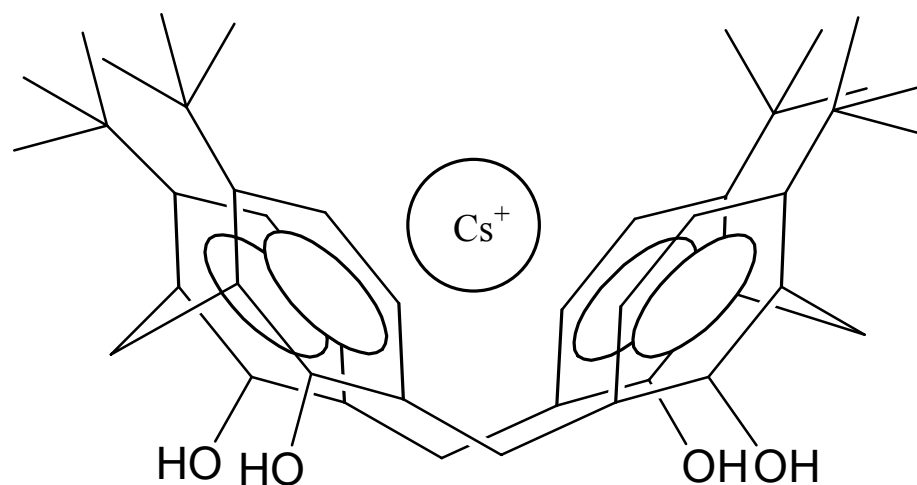
Perutz et al, Chem. Commun. 1999, 1027



Taken from: <http://www.apchem.nagoya-u.ac.jp/butsu2/page3.html>

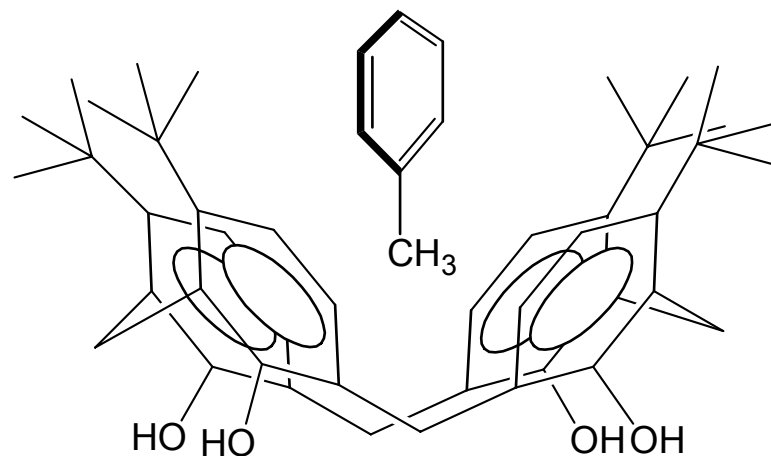
4) *Cation- π interactions*

Organometallic bonds between transition metal and conjugated rings (such as Cp) are not really supramolecular interactions. However, the interaction between alkaline and alkaline earth metals with double bonds are much weaker and can be considered *supramolecular*.

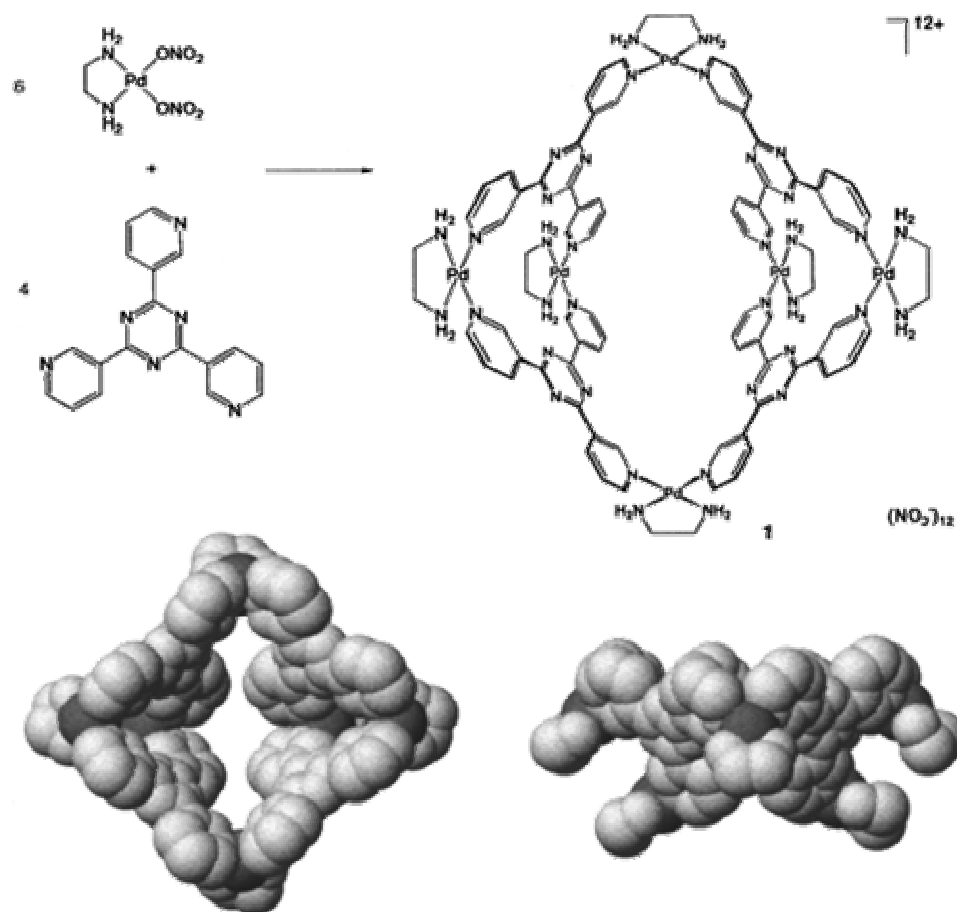


5) *Van der Waals forces*

These forces arise from the polarisation of an electron cloud by the proximity of an adjacent nucleus, resulting in a weak electrostatic interaction. They are not directional and hence they possess little scope in the design of hosts.



6) *Hydrophobic effects*



M. Fujita et al., *J. Am. Chem. Soc.*, 2000, **122**, 2665 -2666

Supramolecular host design

In order to design a host which will bind a particular guest, two important concepts have to be taken into account:

- Complementarity
- Host preorganisation

First step in this process is to define the targeted *guest* we are after. This will set the requirements (electronic, steric, geometrical, etc.) to be incorporated in the host.

Type of guests:

- Cationic: Most of the receptors to bind cations use electrostatic ion-dipole interactions. H-bonds can also be used to enhance the interactions.
- Anionic: In comparison to cation binding, the design of hosts for anionic guests is a relatively new area. To design a host for anions the following have to be taken into consideration: charge, size, pH dependance, solvation and geometry

- Simultaneous cationic and anionic binding: This type of recognition (known as *ditopic*) is particularly challenging since two different receptor sites have to be designed within the same host.
- Neutral species: In order to bind neutral guests, the design of the host has to use non-covalent interactions other than electrostatic. Usually, the design relies on H-bonding, π – π stacking and the hydrophobic effect.

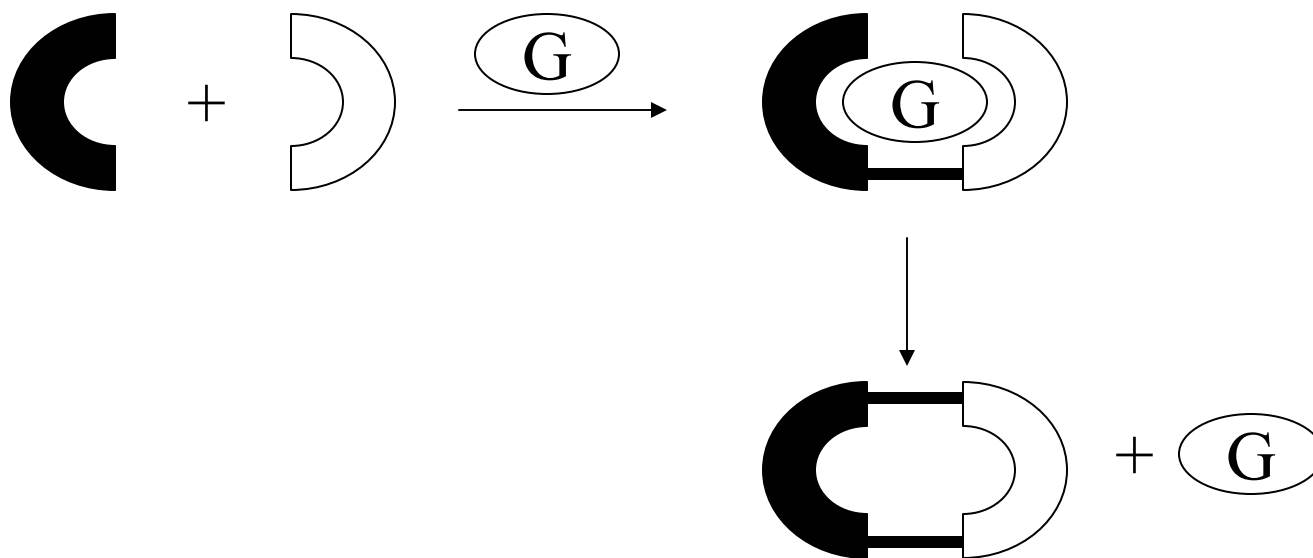
Stability of the host-guest complex

As in any other chemical system, when designing hosts for specific guests, one has to take into account thermodynamic and kinetic factors.

The most stable host-guest complexes are generally obtained with hosts that are pre-organised for ideal guest binding, i.e. where there is no entropically and enthalpically unfavourable arrangements.

The templating effect

“A chemical template organises an assembly of atoms, with respect to one or more geometrical loci, in order to achieve a particular linking of atoms.”



Types of templating agents

Metal cations: The longest known and most frequently employed template syntheses are those based on metal ion chelates (either temporary or permanent).

Neutral molecules: In this case, the templating species will use non-covalent interactions such as H-bonding, π – π stacking and hydrophobic effect to pre-organise the building blocks to assemble.

Anionic species: Even though biological processes make extensive use of anions as templates, it has only been recently that synthetic chemists use anions as templates.

During the last few years both organic and inorganic syntheses have been developed in which the presence of an anion is essential for the formation of the desired assembly.

Current challenges in Supramolecular Chemistry

- Fundamental understanding
- Nanomaterials/Nanotechnology
- Supramolecular catalysis
- Supramolecular chemistry of biological systems