

Supramolecular Chemistry

M. Sc. 4th Sem (402-I)

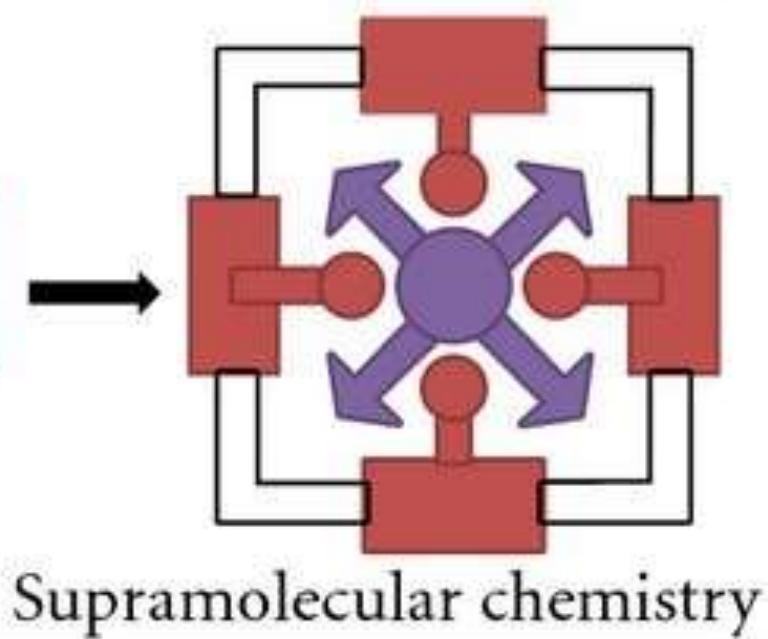
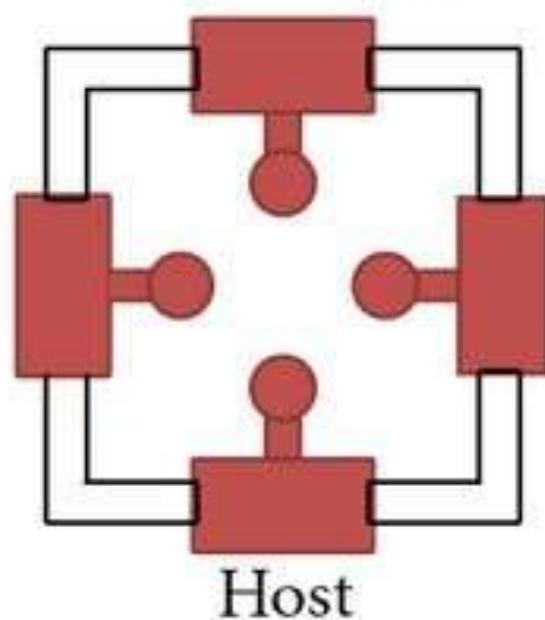
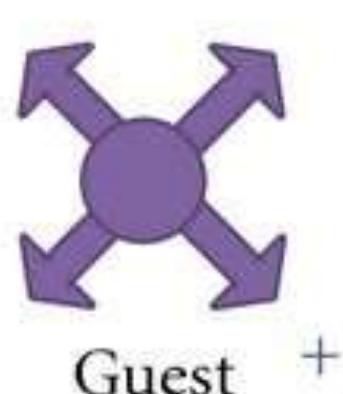
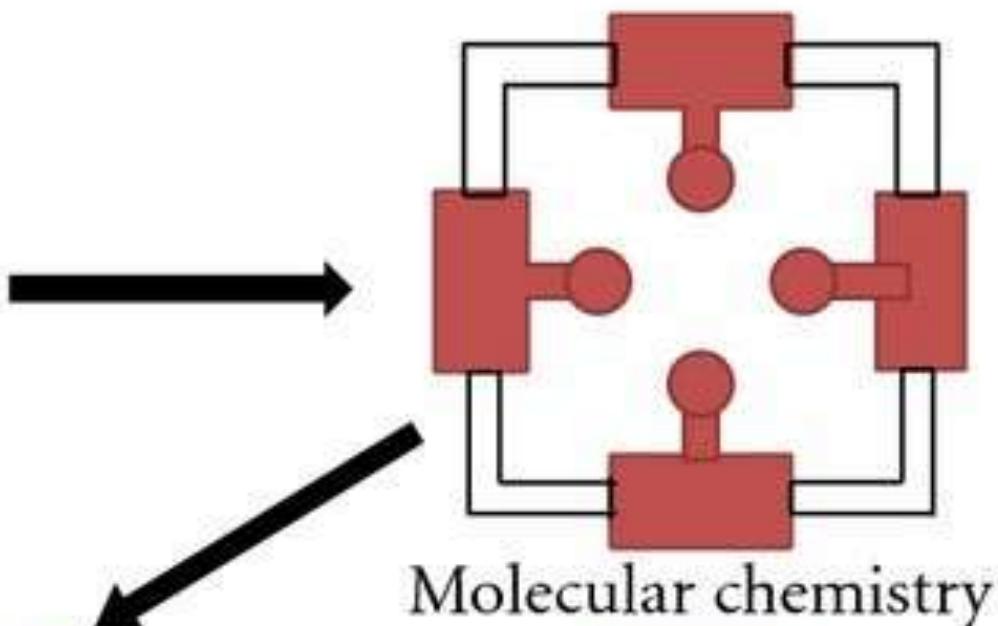
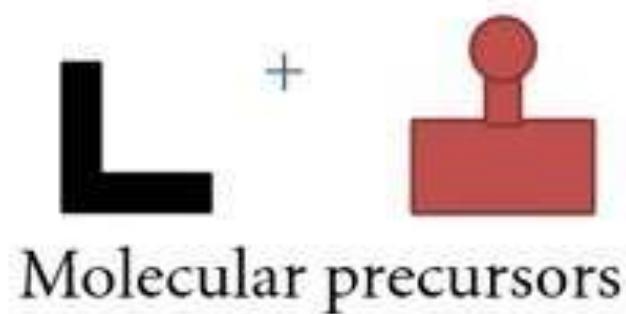
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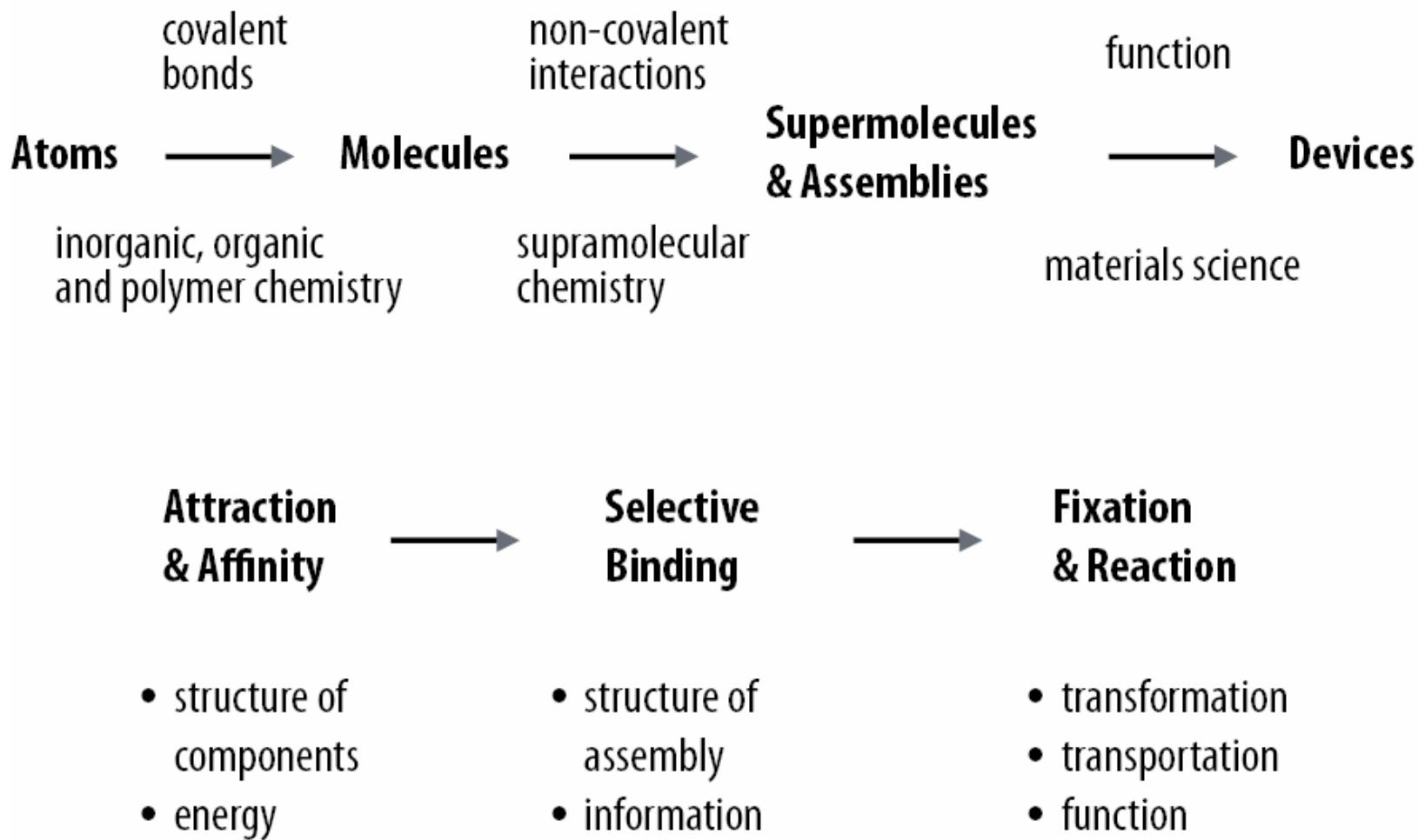
Supramolecular Chemistry

Supramolecular chemistry is the chemistry beyond the molecule. It is a chemistry of the intermolecular bond covering the structure & function of the entities formed by association of two or more chemical species by non-covalent bond i.e. components of molecule are organized by means of non-covalent interactions like ion-ion interaction, dipole-dipole interaction, ion-dipole interaction, pi-pi interaction, cation-pi interaction, vanderwall's interaction, H-bond interaction, hydrophobic interaction etc.

Individual non covalent interactions may be weak, but many of them give stable structure allowing self healing (error correction). It is chemistry of guest & host. It is emerging branch of chemistry.



Interdisciplinary Nature of Supramolecular Chemistry



“molecular recognition is selective binding with a purpose”

Basic Characteristics of Supramolecule

It has important characteristics like

Self assembled structure,

(Self) United through interaction,

(Self) Polymolecular entities by spontaneous process

(self) Reorganization to bind the other molecule,

(self) Association of many molecules to form cooperative society which are thermodynamically Stable.

Supermolecules vs. Supramolecular

Supermolecules

- well-defined, discrete species formed from a defined, finite number of molecules
- the equivalent of low molecular weight organic molecules
- Covalent bonded
- Definite Shape as rigid structure

Supramolecule

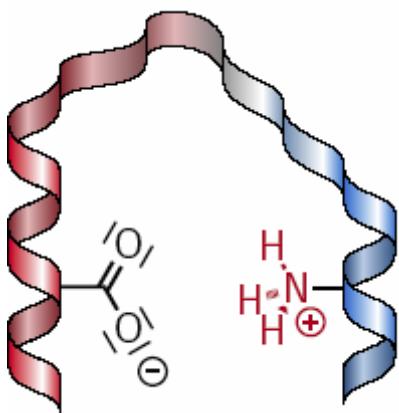
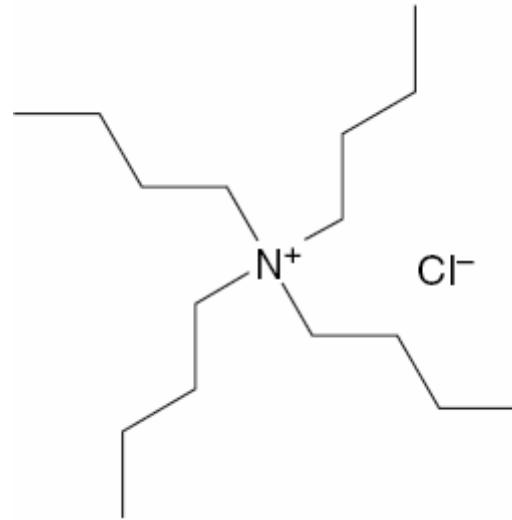
- polymolecular entities from spontaneous, but defined association of many molecules
- the equivalent of high molecular weight polymers and macromolecules
- supramolecular self-assembly
- Non covalent bonded
- Self Catalysed Molecule

• Different types of non covalent interaction

• Ion-Ion Interactions:

- Having Strong energy (200-300 KJ/mol)
- It is non-directional in nature, meaning that the interaction can occur in any orientation.

Tetrabutylammonium chloride (TBAC) has interaction between N+ & Cl-

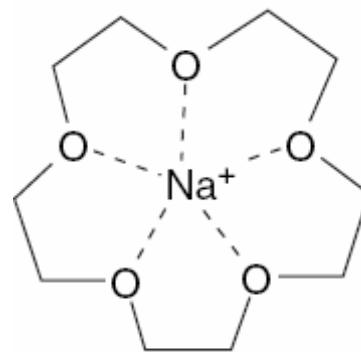


For example: Acid-base pairs in particular in proteins

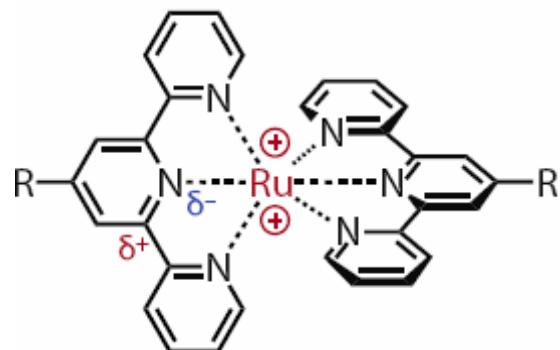
- **Ion-Dipole Interactions:**

- Having Moderately strong (50-200 KJ/mol);
- Stronger when partially covalent (100-400 KJ/mol)

Interaction between
Na⁺ion & O- pole in sodium
complex of crown-5



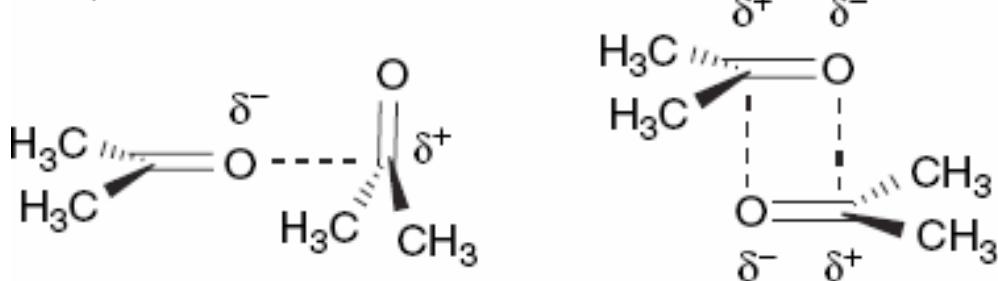
Cation binding hosts



metal complexes (partially covalent)

• Dipole-Dipole Interactions

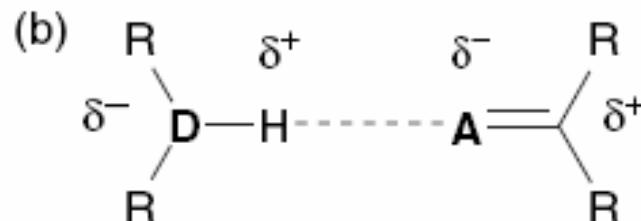
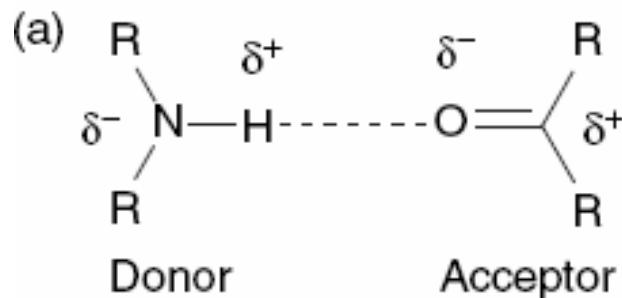
- Having Relatively weak (5-50 KJ/mol)
- Despite being the weakest directional interaction, dipole–dipole interactions are useful for bringing species into alignment, as the interaction requires a specific orientation of both entities.



dipole–dipole interactions occurs in acetone; dipole moment 2.91D

- **Hydrogen bonding (I)**

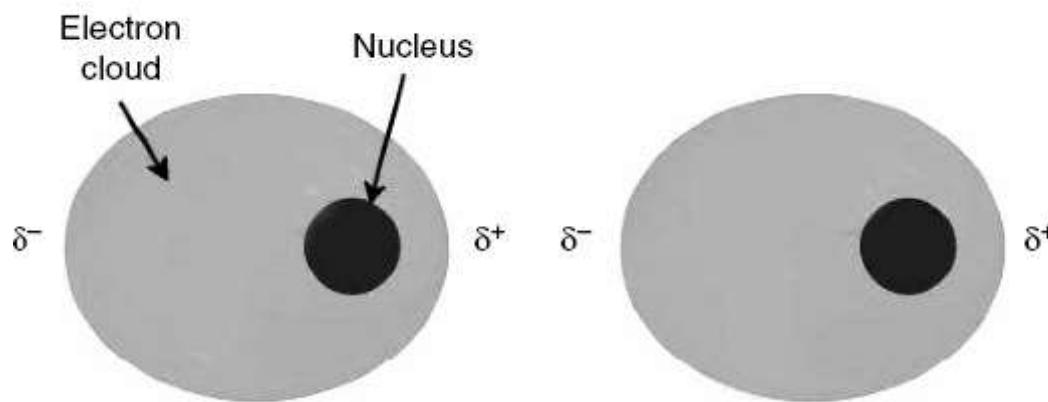
- Hydrogen bond donors are groups with a **hydrogen atom** attached to an **electronegative** atom (such as nitrogen or oxygen), therefore forming a dipole with the hydrogen atom carrying a small positive charge.
- Hydrogen bond acceptors are dipoles with **electron-withdrawing** atoms by which the positively charge hydrogen atom can interact, for example, carbonyl moieties.



A carbonyl accepting a hydrogen bond from a secondary amine donor (a) and (b) the standard way of expressing donor and acceptor atoms (D, donor atom; A, acceptor atom).

- **van der Waals interactions
(mutually induced dipoles)**

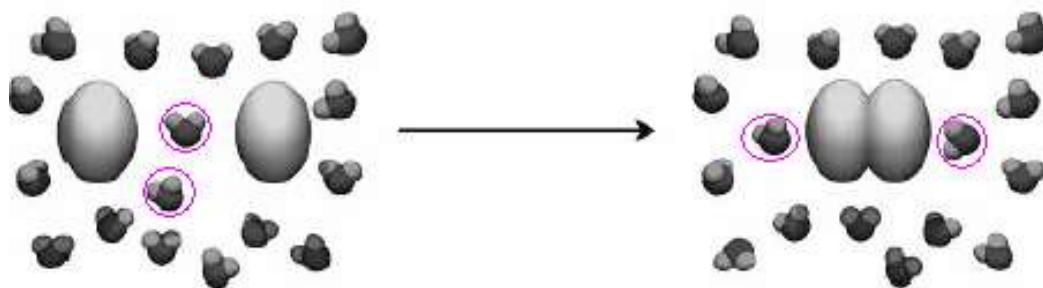
- Weak (2-20 KJ/mol)
- Dispersion effects: London interaction and the exchange and repulsion interaction
- van der Waals interactions arise from fluctuations of the electron distribution between species that are in close proximity to one another.



A London interaction between two argon atoms. The shift of the electron cloud around the nucleus produces instantaneous dipoles that attract each other

- **Hydrophobic effects**

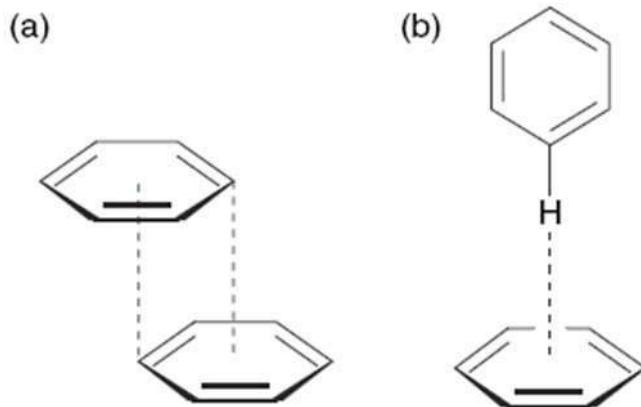
- Hydrophobic effects arise from the exclusion of non-polar groups or molecules from aqueous solution. This situation is more energetically favourable because water molecules interact with themselves or with other polar groups or molecules preferentially.



Two organic molecules creating a hole within an aqueous phase, giving rise to the **entropic hydrophobic effect** – one hole is more stable than two.

and (ii) $\pi-\pi$
interactions

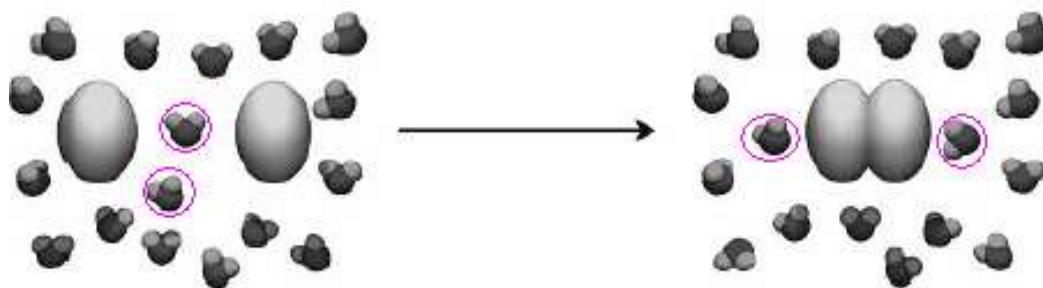
Weak (5-50 KJ/mol)



The two types of – interactions:
(a) face-to-face; (b) edge-to-face.

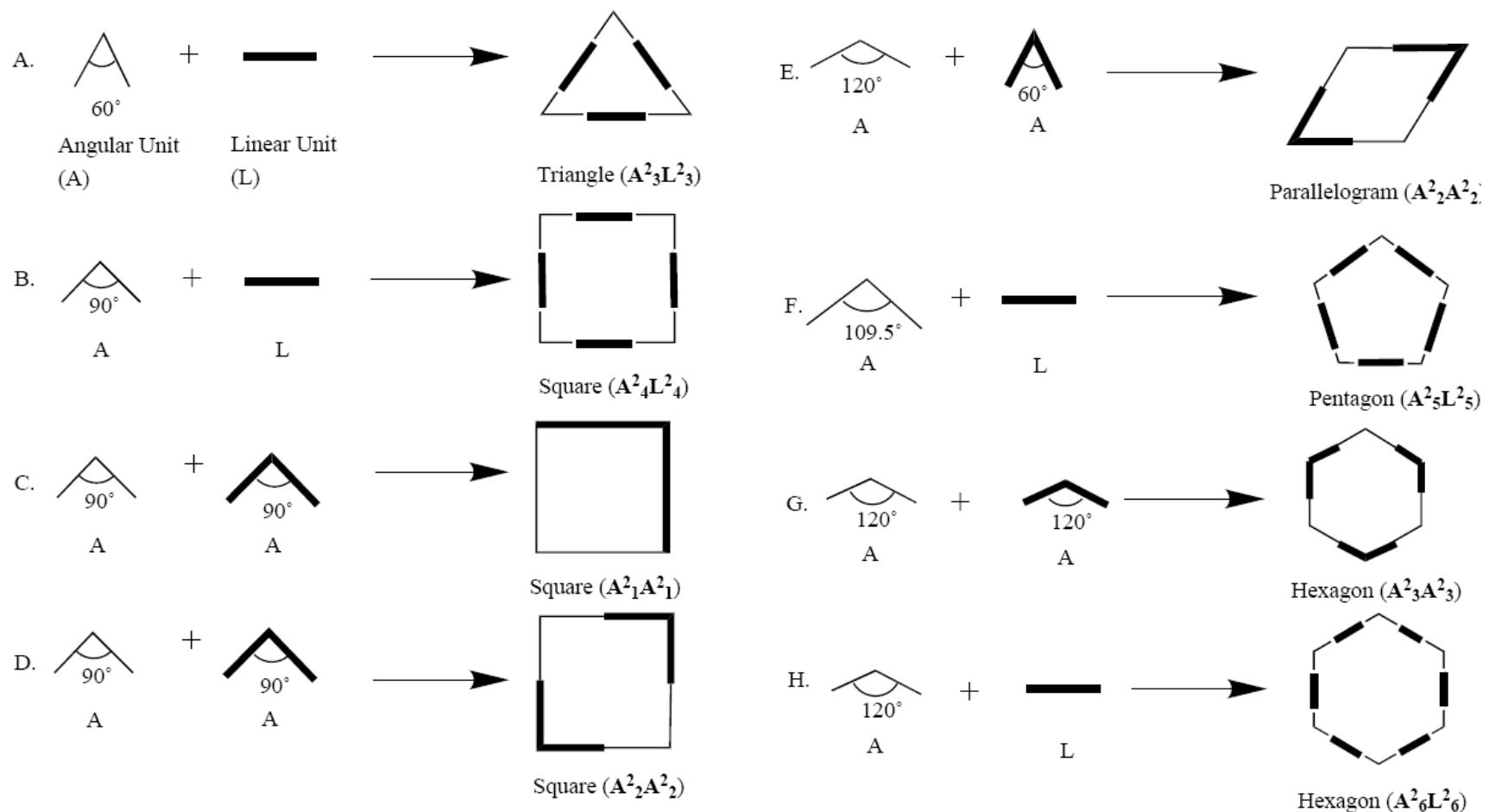
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Assembled by metal-ligand



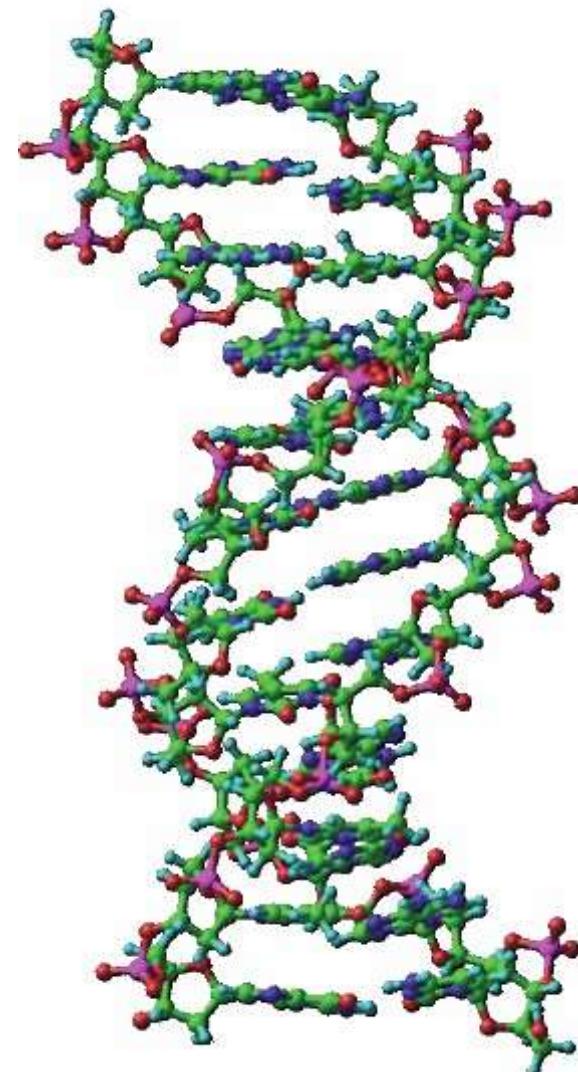
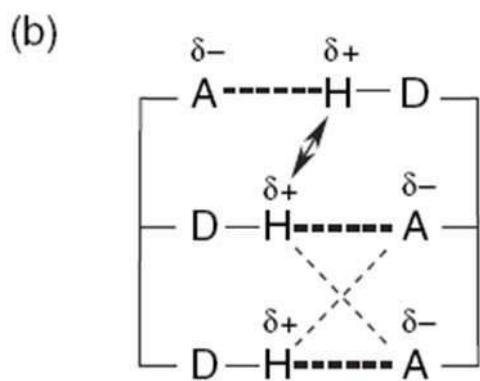
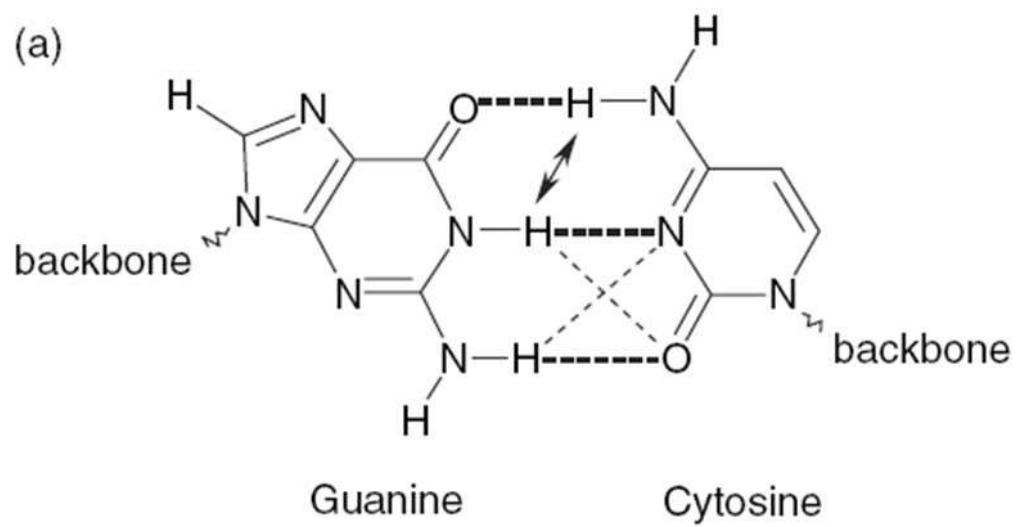
Molecular Self Assembly

This is main characteristics of supramolecule in which there is construction of larger structure of a system without guidance or management from an outside source. The molecules are directed to assemble through non-covalent interaction. It may be divided into intermolecular or intramolecular self assembly (folding)

Perhaps the best known intermolecular self-assembling structure in biological systems is naturally occurring DNA, which exists in a double helical form. The two single strands are held together by a number of hydrogen bonds, involving acidic hydrogen atoms (hydrogen bonding donor), oxygen (hydrogen bonding acceptor), and nitrogen atoms (hydrogen bonding acceptor) of the purine and pyrimidine bases in order to maintain the double helical structure **(Figure-1a)** In this double helix guanine (G) forms triple hydrogen bonds with cytosine (C) and adenine (A) forms double hydrogen bonds with thymine (T).

Multiple Hydrogen-Bonding Sites in DNA Base Pairs

- complementary arrangements of hydrogen-bond acceptors/donors for selective binding
- mutually enforcing donors and acceptors



- (a) Primary and secondary hydrogen bond interactions between guanine and cytosine base-pairs in DNA
- (b) And a schematic representation.

Molecular Recognition

Molecular recognition is the specific binding of a guest molecule to a complementary host molecule to form a host- guest complex. Often, the definition of which species is the "host" and which is the "guest" is arbitrary. The molecules are able to identify each other using non-covalent interactions.

The specific interaction between host and guest molecules occurs through non-covalent bonding such as hydrogen bonding, metal coordination, hydrophobic forces, van der Waals forces, π - π interactions, halogen bonding, electrostatic and/or electromagnetic effects. In addition to these *direct* interactions as well solvent can play a dominant *in direct* role in driving molecular recognition in solution. It is used to preparation of sensor

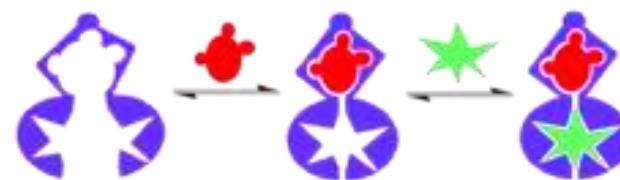
Static recognition between a single guest and a single host binding site.

Static:

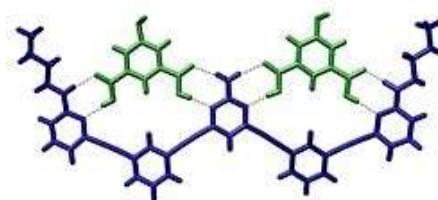


In dynamic recognition binding the first guest at the first binding site induces a conformation change that affects the association constant of the second guest at the second binding site.

Dynamic:



Two isophthalic acid bound to host molecule through H-bond.



Molecular reorganization has been used to serve as synthetic antibodies for optical protein reorganization, sensing tool, biological target etc.

Self Catalytic Properties

A major application of supramolecular chemistry is the design and understanding of catalysts and catalysis. Non-covalent interactions are extremely important in catalysis, binding reactants into conformations suitable for reaction and lowering the transition state energy of reaction. Template-directed synthesis is a special case of supramolecular catalysis.

Encapsulation systems such as micelles and dendrimers are also used in catalysis to create microenvironments suitable for reactions (or steps in reactions) to progress that is not possible to use on a macroscopic scale. Supramolecular host bind to a guest molecule in such a way that guest's labile group is positioned close to the reactive group of the host. The proximity of the two group enhances the probability of a reaction & hence rate of reaction is increased. Due to molecular reorganization & encapsulation within the cavity (intramolecular reaction), the effective local concentration is increased & hence rate of reaction is accelerated

