

Advanced Supramolecular Chemistry: Introduction and Application

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ABSTRACT

Supramolecular molecular is a big ply of interdisciplinary field of science covering physics and biology along with chemistry. It plays a major role in progressive elaboration of a science of informed, organized, evaluative matter. It has vast application in various fields like material technology, catalytic medicine, data storage and processing, and many more. Supramolecular chemistry refers to area of the chemistry beyond the molecule or chemistry of non-covalent bond. In traditional chemistry, we use to see that atoms bind with atoms with covalent bond, but in Supramolecular chemistry molecules bind with molecules with non-covalent bond interactions. Non-covalent interactions may be electrostatic, hydrogen bonding, pi-pi stacking interactions, Van der Waals forces, hydrophobic or cation-pi interaction.

Molecular self-assembly, molecular, recognition template directed synthesis, mechanically interlocking molecular architecture; biomimetics are the important features of supramolecular chemistry. Molecular self-assembly is the construction of systems without guidance or management from source.

The ideas of supramolecular chemistry can be a very vast way of expressing and advancing molecular logic and computation. Supramolecular chemistry has been used to demonstrate computation functions on a molecular scale.

Supramolecular are formed by interaction of molecular of intermolecular bonds using receptor and substrate.

Supramolecular chemistry includes molecular Recognition, transformation molecular self assembly, self-organization priding host-guest chemistry mechanically interlocked molecular architecture.

There are two approaches of Super molecules

1. **Top-Down(current technology)**

- Continued reduction in size of bulk semiconductor devices
- Optical, ultra-violet, ion-beam, electron-beam lithography

2. **Bottom-Up (molecular scale electronics)**

- Design of molecules with specific electronic function
- Design of molecules for self-assembly into Supramolecular structures
- Connecting molecules to the macroscopic world
- Man-made synthesis (e.g. carbon nanotubes)

Finally a degree of technical expertise can lead to functioning devices ready for application of real world.

Keywords

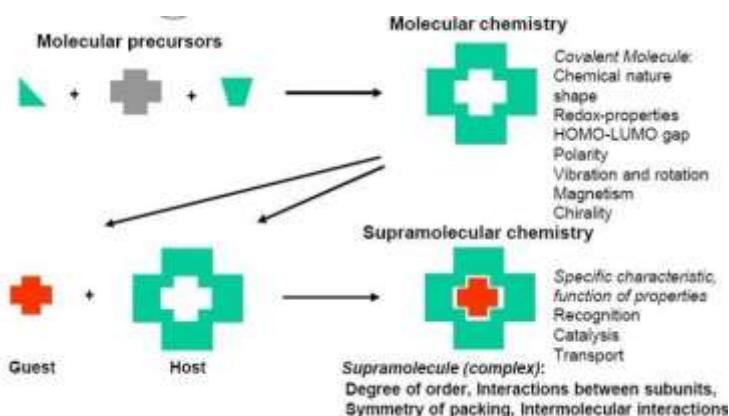
Supramolecular, pi-pi stacking, self-assembly.

Introduction

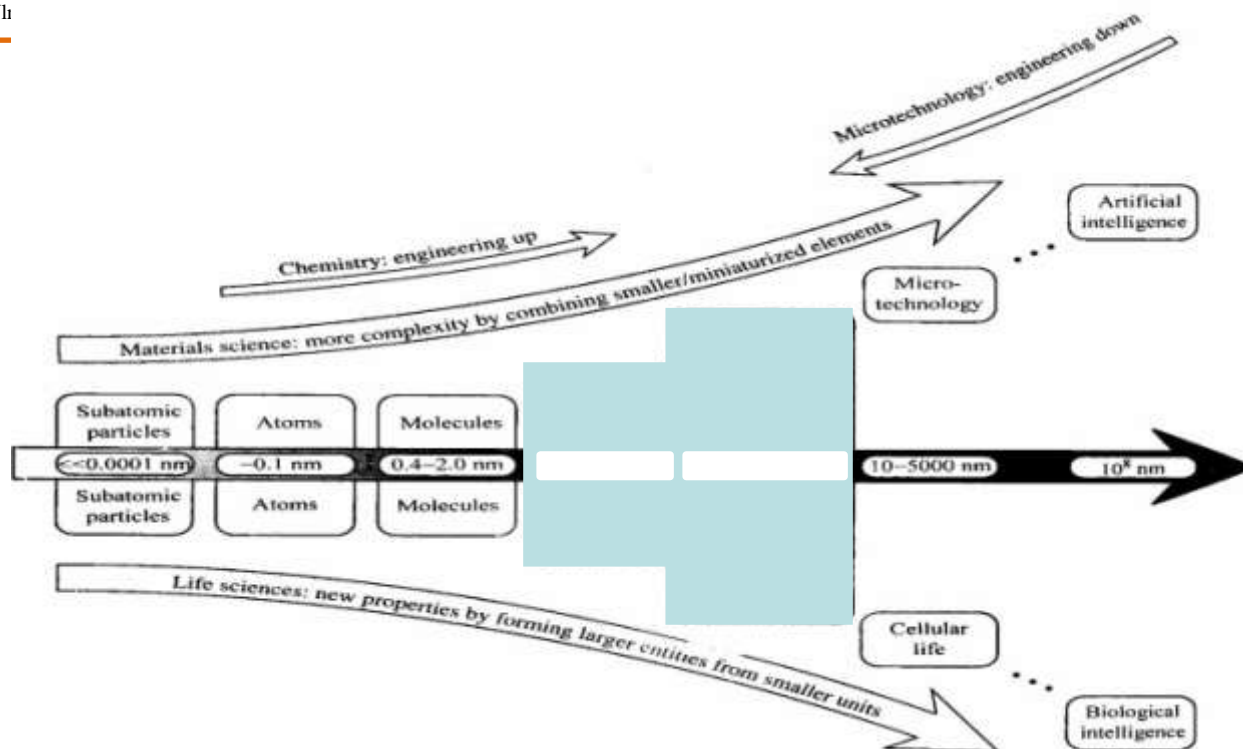
Supramolecular chemistry refers to the study of supramolecular assemblies. It is one of the most popular and rapid growing areas of chemistry which emphasizes going “beyond” molecular chemistry or “chemistry of molecular assemblies and of the intermolecular bond”. Traditional chemistry generally focuses on the covalent bonding but supramolecular chemistry monitored by weak interaction of non-covalent bonds; exists extensively in numerous vital biological processes.

Atoms $\xrightarrow{\text{Covalent Interaction}}$ Molecules

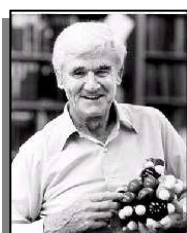
Molecules $\xrightarrow{\text{Non-Covalent Interaction}}$ Supermolecules



The living biological systems seem to be the origin of supramolecular chemistry. Supramolecular chemistry studies the phenomena such as molecular self-assembly, protein folding, molecular recognition host- guest chemistry, mechanically- interlocked molecular architectures and dynamic covalent chemistry. It is a highly interdisciplinary field of science covering physics and biology branches along with chemistry branch.



In 1987 **Donald J. Cram**, USA, **Jean-Marie Lehn**, France and **Charles J. Pedersen**, USA were jointly awarded the Nobel Prize of chemistry for their development and application of molecules with highly selective structure specific interaction, i.e. molecules that can “recognize” each other and choose with which other molecules will form complexes.



Donald J. Cram



Jean-Marie Lehn



Charles J. Pedersen

The laureates’ research has been of great importance for developments within coordination chemistry, organic synthesis, analytical chemistry and bioorganic and bioinorganic chemistry, and has thus laid the foundation for the active interdisciplinary area of research within chemistry that has now come to be termed host-guest chemistry or supramolecular chemistry.

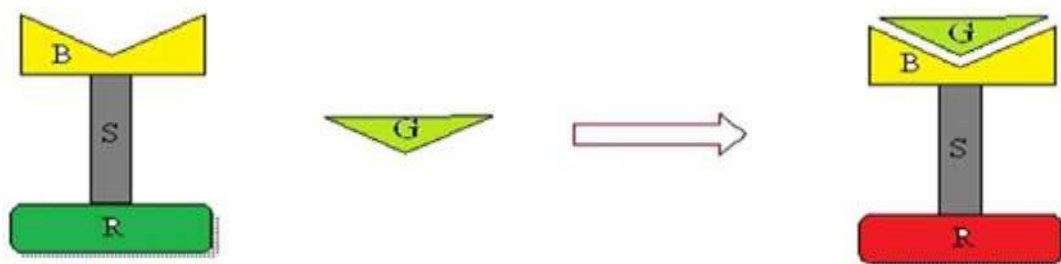


Figure:Design Principle.

Here R= Reporter group, fluorogenic, Chromogenic or Redox active
B= Bindingsite
S= Spacer- separates bindingsiteandReporter group,
G= Guest molecule.

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

A “host” molecule binds a “guest” molecule to produce “Host-Guest” complex or supramolecule. Non covalent interaction plays most crucial role in binding processes. Generally, the host is a large molecule of aggregates possessing a sizable central hole or cavity and also possessing convergent binding site. The guest may be cation or anion or molecules and possesses divergent binding site. The binding sites must be spaced out on the host in such a way to make it possible for the host to interact with guest molecule.

Supramolecular hostdesign

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

- > -Complementarity
- > -Hostpreorganisation

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 anion the following have to be taken into consideration: charge, size, pH dependence, 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.

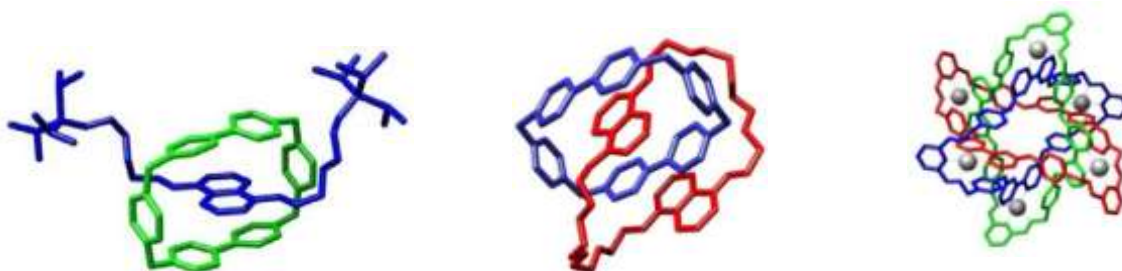
- Neutral species: In order to bind neutral guests, the design of the host has to use non-covalent interactions other than electrostatic. Usually, the design relies on H-bonding, stacking and the hydrophobic effect.

In the 1990's, supramolecular chemistry became even more sophisticated with researches such as James Fraser Stoddart developing molecular machinery and highly complex self-assembled structures and methods of electronic and biological interfacing. He works in the area of supramolecular chemistry and nanotechnology. Stoddart has developed highly efficient syntheses of mechanically-interlocked molecular architectures such as molecular Borromean rings, catenanes (structures of two interlocked molecular rings) and rotaxanes utilizing molecular recognition and molecular self-assembly processes. He has demonstrated that these topologies can be employed as molecular switches. His group has even applied these structures in the fabrication of nanoelectronic devices and nanoelectromechanical systems (NEMS). During this period electrochemical and photochemical motifs integrated into supramolecular systems in order to increase functional research into synthetic self-replicating systems began and work on molecular information processing devices.



James Fraser Stoddart Jean-Pierre Sauvage Ben Feringa

He shared the Nobel Prize in Chemistry together with Ben Feringa and Jean-Pierre Sauvage in 2016 for the design and synthesis of molecular machines.



(Rotaxane)catenane molecular Borromean rings

Rotaxanes: Mechanically-interlocked molecules

Catenanes: Catenanes are a hinge waiting for a nanomechanism to work in or mechanically-interlocked molecular architecture consisting of two or more interlocked macrocycles, i.e. a molecule containing two or more intertwined rings.

Molecular Borromean rings: mechanically-interlocked molecular architecture in which three macrocycles are interlocked in such a way that breaking any macrocycle allows the others to disassociate.

E.g. Borromean rings are made up of three interpenetrated macrocycles formed from the reaction between 2,6-diformylpyridine and diamine compounds, complexed with zinc. This compound was synthesized from two building blocks: 2,6-diformylpyridine (a pyridine with two aldehyde groups) and a diamine containing a 2,2'-bipyridine group. Zinc acetate is added as the template for the reaction, resulting in one zinc atom in each of a total of 6 pentacoordinate complexation sites. Trifluoroacetic acid (TFA) is added to catalyze the imine bond-forming reactions. The preparation of the tri-ring Borromean involves a total of 18 precursor molecules and is only possible because the building blocks self-assemble through 12 aromatic pi-pi interactions and 30 zinc to nitrogen dative bonds. Because of these interactions, the Borromean is thermodynamically the most stable reaction product out of potentially many others. As a consequence of all the reactions taking place being equilibria, the Borromean is the predominant reaction product.

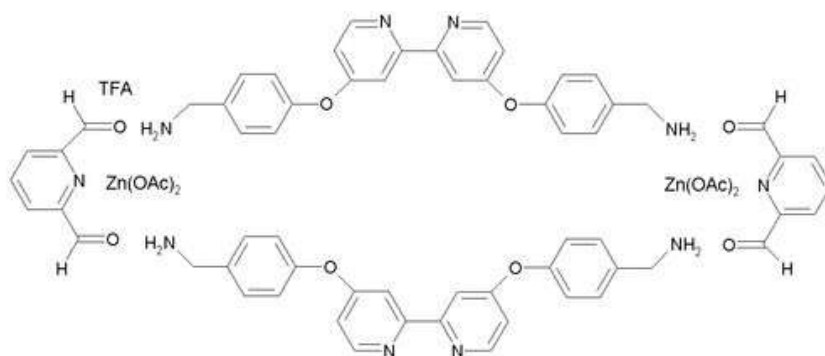
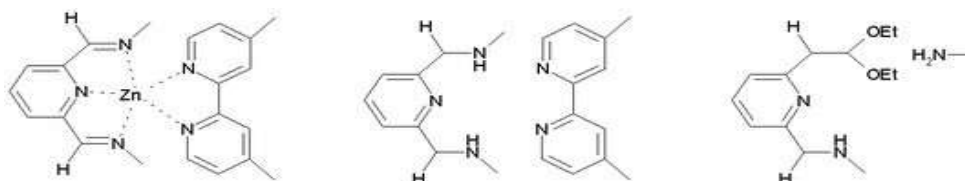


Fig: Synthesis of one ring in Borromean ring system from 2,6-diformylpyridine and a diamine in presence of zinc acetate and TFA. The ring-system consists of three such interlocked rings

Reduction with sodium borohydride in ethanol affords the neutral **Borromean**.^[2] True to a Borromean system, cleavage of just one imine bond (to an amine and an acetal) in this

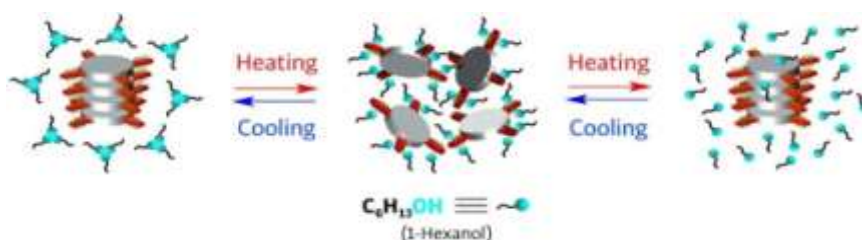
structure breaks the mechanical bond between the three constituent macrocycles, releasing the other two individual rings.



From left to right: Zinc complex with pyridine group and orthogonalbipyridine groups in Borromeate. Reduction to Borromeand with removal of zinc coordination and Bond cleavage of imine to acetal by action of ethanol.

Effect of temperature and strain rate on the compressive behavior of supramolecular

Supramolecular polymers, a newly-developing group of materials, can be loosely defined as those in which the monomers are held together by noncovalent interactions. Therefore, a reversible network can be formed, which is sensitive to temperature, and can be destroyed and reconstructed easily during processing and post-processing. This provides those materials with unique thermoresponsive and thermoreversible properties, thereby delivering dramatic viscosity changes over well-defined and tunable temperature ranges: at room temperature they behave like elastomers, but at elevated temperature these are low viscosity liquids. These characteristics offer huge advantages in processing and also provide unique properties, which are highly desirable in both bulk commodity and valued-added applications.



In other words we can say that supramolecular chemistry deals with subtle interactions and consequently control over the processes involved can require great precision. In particular, non-covalent bonds have low energies and often no activation energy for formation. As demonstrated by the Arrhenius equation, this means that unlike in covalent bond forming chemistry, the role of bond formation is not increased at higher temperatures. In fact, chemical equilibrium equations show that the low bond energy results in a shift towards the breaking of supramolecular complexes at high temperatures.

However, low temperature can also be problematic to supramolecular processes. Supramolecular chemistry can require molecules to distort into thermodynamically disfavored conformations (for example, during the “slipping” synthesis of rotaxanes) and

may include some covalent chemistry that goes along with the supramolecular. In addition the dynamic nature of supramolecular chemistry is utilized in many systems and cooling the system would slow these processes.

Thus, thermodynamics is an important tool to design, control and study supramolecular chemistry. Perhaps the most striking example is that of warm-blooded biological systems, which cease to operate entirely outside a very narrow temperature range.

Environment

The molecular environment around a supramolecular system is also of prime importance to its operation and stability. Many solvents have strong hydrogen bonding, electrostatics, and charge transfer capabilities, and are therefore able to become involved with the system, even breaking complexes completely. For this reason, the choice of solvent can be critical.

Host	Guest	Interaction	Class	Example
Crown ether	Metal cation	Ion - dipole	Complex (Cavitate)	[K ⁺ · [18]crown-6]
Spherand	Alkyl ammonium cation	Hydrogen bonding	Complex (Cavitate)	Spherand (CH ₃ NH ₃ ⁺)
Cyclodextrin	Organic molecule	Hydrophobic/van der Waals	Cavitate	(α -cyclodextrin) (<i>p</i> -hydroxybenzoic acid)
Water	Organic molecule, halogen, etc.	Van der Waals/crystal packing	Clathrate	(H ₂ O) ₆ · (CH ₄)
Calixarene	Organic molecule	Van der Waals/crystal packing	Cavitate	(<i>p</i> - <i>t</i> -butylcalix[4]-arene)(toluene)
Cyclotrimer-triene (CTV)	Organic molecule	Van der Waals/crystal packing	Clathrate	(CTV) · 0.5(acetone)

Classification of Host-Guest Compounds

Nature of Supramolecular Interactions

Covalent bond energies:

C-O bond	340kJ / mol	1.43Å
C-C bond	360kJ / mol	1.53Å
C-H bond	430kJ / mol	1.11Å
C=C bond	600kJ / mol	1.33Å
C=O bond	690kJ / mol	1.21Å

Compared to most non-covalent interactions these are:

- Very high energies
- Very short distances
- Highly dependent on orientation
- Driving Forces for the Formation of Supramolecular Structures ➡ hydrophobic interaction < 40kJ/mol

NATURE OF SUPRAMOLECULAR INTERACTIONS

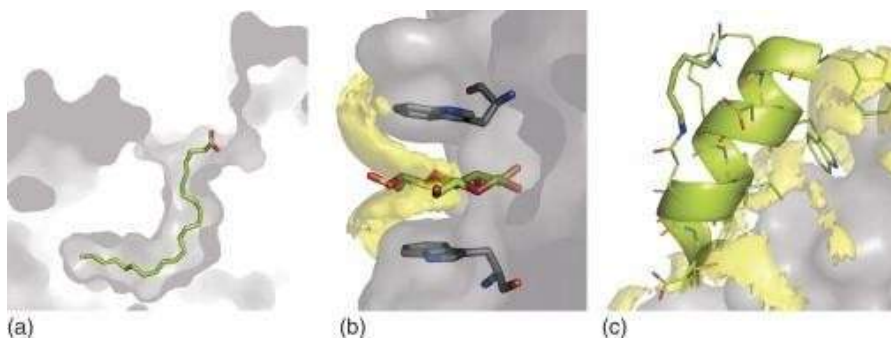
1. Hydrophobic Interaction
2. Electrostatic interaction ~20kJ/mol
3. hydrogen bond interaction 12-30kJ/mol
4. Vander Waals interaction 0.4-4kJ/mol
5. cation- π interaction 5-80kJ/mol
6. π - π stacking interaction 0-50kJ/mol

The total inter-molecular force acting between two molecules is the sum of all the forces they exert on each other.

1. Hydrophobic Interaction

The hydrophobic effect is that nonpolar molecules tend to self-associate in the presence of aqueous solution. This short-range attractive interaction is due to both enthalpic and entropic effects. It describes the energetic preference of nonpolar molecular surfaces to interact with other nonpolar molecular surfaces, and thereby to displace water molecules from the interacting surfaces. When a nonpolar molecule is surrounded by water, stronger than normal water-water interactions are formed around the solute molecule to compensate for the weaker interactions between solute and water. This results in an increasingly ordered arrangement of water molecules around the solute and thus negative entropy of dissolution. The decrease in entropy is roughly proportional to the nonpolar surface area of the molecule. The association of two such nonpolar molecules in water reduces the total nonpolar surface area exposed to the solvent, thus reducing the amount of structured water, and therefore providing favorable entropy of association. The enthalpic contribution to hydrophobic interactions is due to the water molecules occupying lipophilic binding sites, which are consequently unable to form hydrogen bonds with the receptor. Their release from the hydrophobic pocket lets them form strong hydrogen bonds with the bulk water.

- Responsible for:
- aggregation of amphiphiles to micelles and liposomes
 - folding of proteins
 - protein-ligand and protein-protein interactions
 - solubilization of non-polar substances by surfactant aggregates
 - supramolecular complexation of guests with non-polar parts



- (a) Proposed fatty acid ligand C₂₃H₄₈O₂ in the active site of cholesterol esterase (PDB code 1LLF). The long alkyl chain of the ligand makes interactions with the hydrophobic environment of the gorge below the reactive site of the enzyme.
- (b) Two tryptophan residues (grey sticks), in the carbohydrate-binding module of xylanase 10A, provide planar hydrophobic stacking interactions for a glucose disaccharide (green sticks) (PDB code 1I82). Yellow patches indicate favorable regions for the DRY probe as calculated with GRID.
- (c) Structure of a cross-linked helical peptide, C14linkmid, bound to IQN17, a soluble peptide that contains the HIV-1 gp41 hydrophobic pocket (surface representation) (PDB code 1GZL). Yellow patches indicate favorable regions for the DRY probe as calculated with GRID.

(2) **Electrostatic interactions [Ion-ion, Ion-dipole, Dipole-dipole]**

Ion-ion- Ionic bonding which is similar in strength to covalent bonding (i.e. 100-350 KJ/mol). It can be an attractive or a repulsive force and Non-directional force. It is highly dependent on the dielectric constant of the medium.

$$V_{\text{ion-ion}} = \frac{k \cdot z_1 \cdot z_2 \cdot e^2}{r_{12} \cdot \epsilon}$$

$k = 1 / 4\pi\epsilon_0 = \text{Coulomb constant} = 9 \cdot 10^9 \text{ Nm}^2/\text{C}^2$

$e = \text{elementary charge} = 1.6 \cdot 10^{-19}$

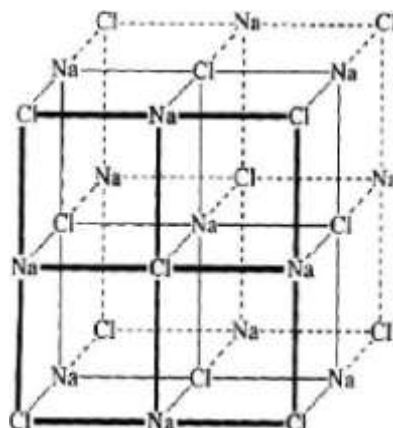
$\epsilon = \text{dielectric constant}$

$r_{12} = \text{meters between the objects}$

The energy of an ion-ion interaction only falls off at a rate proportional to $1/r$. Therefore these are very long range forces.

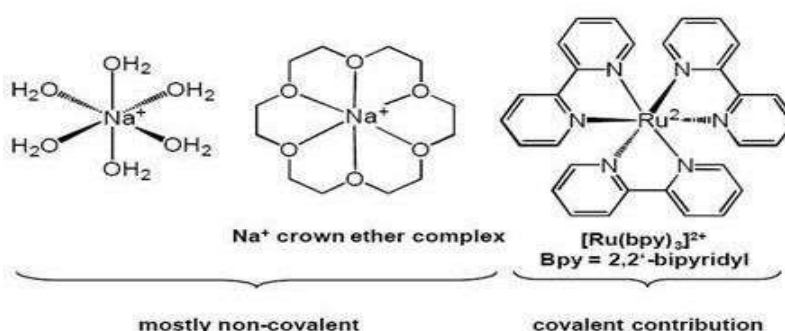
In its simplest form an NaCl lattice but more importantly the interaction of a lone cation with an anion.

Ex. - NaCl ionic lattice



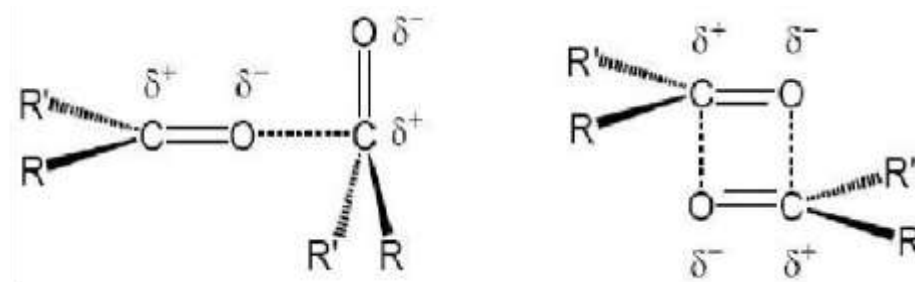
a. Ion-dipole interaction (50-200KJ/mol)

Bonding of an ion to a polar molecule (could be called a coordinate bond). For example Na^+ is bound to six water molecule when NaCl is dissolved in water. It can also be bound to oxygen demurs form a crown ether ligand.



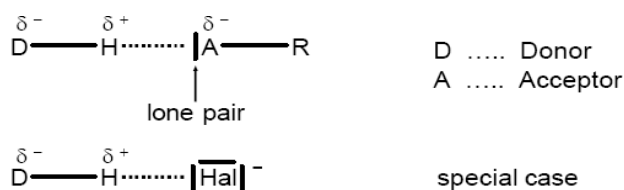
b. Dipole-dipole interaction:

Significant attraction can result from alignment of one or more dipoles on adjacent molecules. These are directional forces and can be attractive or repulsive. These interactions are medium range i.e. directly proportional to $1/r$ These interactions are significantly weaker than ion-ion interactions Ketones are good example of this type of interaction but the low boiling points show that the interactions are relatively weak.



(d) Hydrogenbonding:

These are related to dipole-dipole interactions. It is regarded as one of the most important interactions in supramolecular chemistry because it is strong and directional.



- special kind of dipole – dipole interaction
- strong H-bonds are
3-center-4-electron bonds
- highly directional in nature

Protein shapes/ DNA double helix are classical examples of compounds held together by multiple hydrogen bonds. The directional nature of hydrogen bonds, combined with the precision with which the individual components can build into molecular systems has made them especially attractive to molecular designers. This has facilitated the construction of complex architectures.

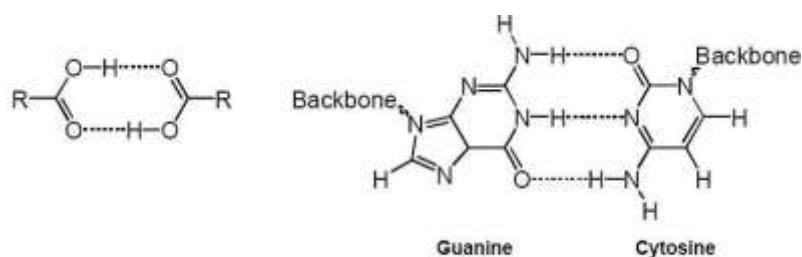


Fig. 1.15. Hydrogen bonded carboxylic acid dimers and base pairing in DNA by hydrogen bonding.

ideally linear arrangement



Table 1.3 Properties of hydrogen interactions

	Strong	Moderate	Weak
D? H-----B interaction	Mainly covalent	Mainly covalent	Electrostatic
Bond energy (kJ/mol)	60 – 120	16 – 60	< 12
Bond lengths (Å)			
H Bond angles	1,2 - 1,5	1.5 - 2.2	2.2 - 3,2
D -----A	2.2 - 2.5	2.5 - 3.2	3.2 - 4.0
Bond angles (°)	175 – 180	130 – 180	90 - 150
Relative IR Vibration (stretching symmetrical mode, cm ⁻¹)	25 %	10 – 25 %	< 10 %
¹ H NMR chemical shift downfield (ppm)	14 – 22	< 14	?
Examples	Gas phase dimers with strong acids/ bases Proton sponge HF complexes	Acids Alcohols Biological molecules	Minor components of bifurcated bonds C—H hydrogen bonds O—H ^{δ+} ...π hydrogen bonds

4. Vanderwaalsinteraction

Polarizations of the electron cloud by proximity an adjacent nucleus generally create of this type of forces. These Vanderwaals forces are believed to provide additionalenthalpic stabilization to the coordination of a hydrophobic guestintoahydrophobiccavity.Strengthofinteractionis essentially a function of the surface area of contact. The larger the surface area the stronger the interaction willbe. These forces are non-directional and hence have limited scope for design.Ex- X- ray crystal structure of the Vander Waal inclusion complex P-tert-butylcalix[4]arenetoluene.

Polarization of an electron cloud by the proximity of an adjacent nucleus

→ weak electrostatic forces

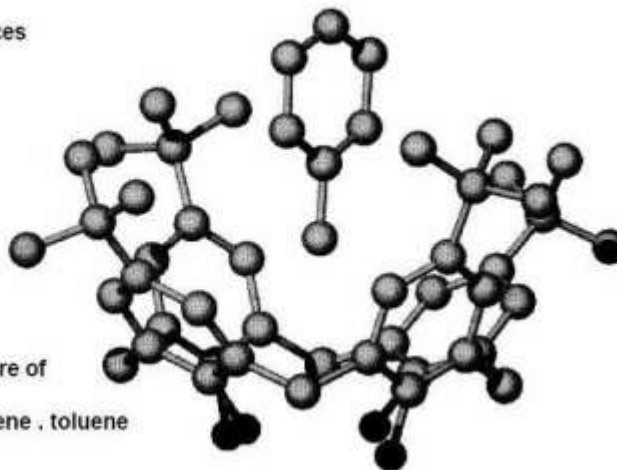


Fig. 1.24 X-ray crystal structure of the van der Waal inclusion complex *p*-tert-butylcalix[4]arene . toluene

5. Cation- π interaction

The cation $-\pi$ interaction is seen

- in transition metal complexes such as ferrocene [$\text{Fe}(\text{C}_5\text{H}_5)_2$]:
covalent bonds → d - Orbitals
- However: no covalent „weak“ interaction of e.g. alkaline or alkaline earth metal cations with π -bonds (C=C double bonds)

Gas phase interactions

$\text{K}^+ \dots \dots$ benzene 80 kJ/mol
 $\text{K}^+ \dots \dots$ H_2O (one molecule) 75 kJ/mol



* see also ion-dipole interactions

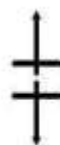


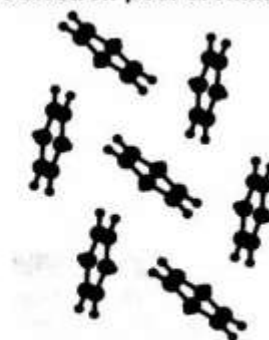
Fig. 1.18. Schematic drawing of the cation- π interaction showing the contact between the two. The quadrupole moment of benzene, along with its representation as two opposing dipoles is also shown.

However, we do not observe covalent weak interaction of alkaline or alkaline earth metal cations with π -bonds (c=c double bonds)

6. $\pi - \pi$ Stacking interactions

$\pi - \pi$ Stacking interactions occurs between aromatic rings often dependent on one being more electron rich and the other electron poor. Two types of stacking are possible, one face to face and another end to face.

especially favorable: one electron rich and one electron poor aromatic



face to face: Graphite, DNA

edge to edge: herring bone packing of benzene in the solid state

Some very elegant receptors have been synthesized employing $\pi - \pi$ interactions, including a receptor for benzoquinone.

Approaches

There are two types of approaches of supramolecule chemistry

1. Top-Down(currenttechnology).

- Continued reduction in size of bulk semiconductor devices
- optical, ultra-violet, ion-beam, electron-beam lithography

2. Bottom-Up (molecularscaleelectronics).

- Design of molecules with specific electronic function

Design of molecules for self-assembly into supramolecular structures

- Connecting molecules to the macroscopic world
- Man-made synthesis (e.g. carbon nanotubes)

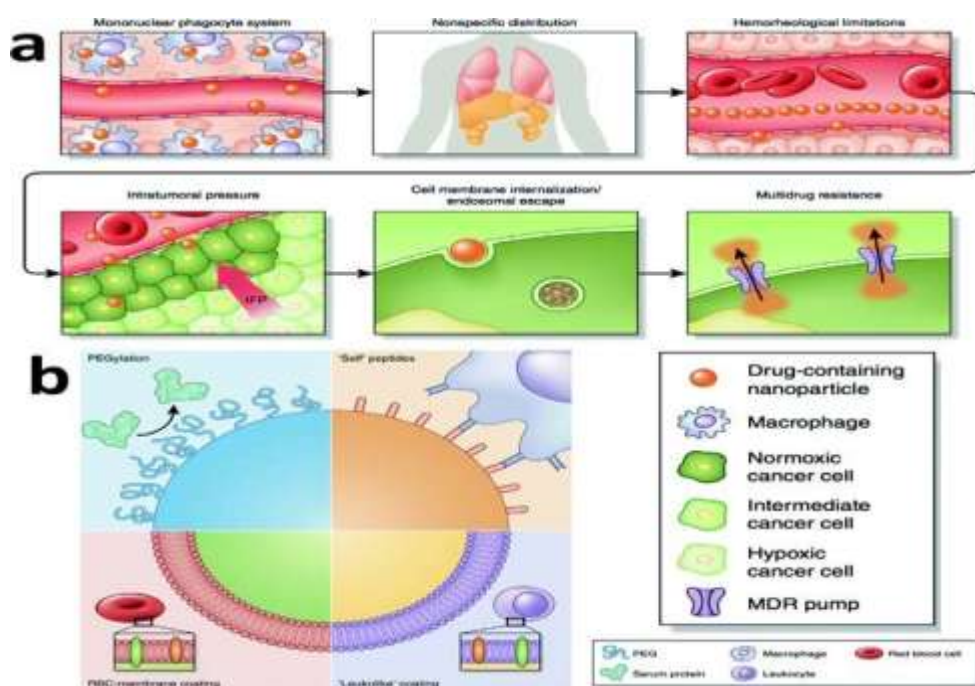
Application of Supramolecular Chemistry

a. Intransportprocess

Ion recognition, extraction and transport through membrane plays vital role in many biological processes. Large quantity of sodium, potassium, magnesium and calcium ions, in particular, is all critical to life. The design and synthesis of host molecules have made a range of compounds that may become carriers and receptors. For example- Hemoglobin, playing vital role in uptake and transport of oxygen, are the iron complex supramolecule of porphyrin ring.

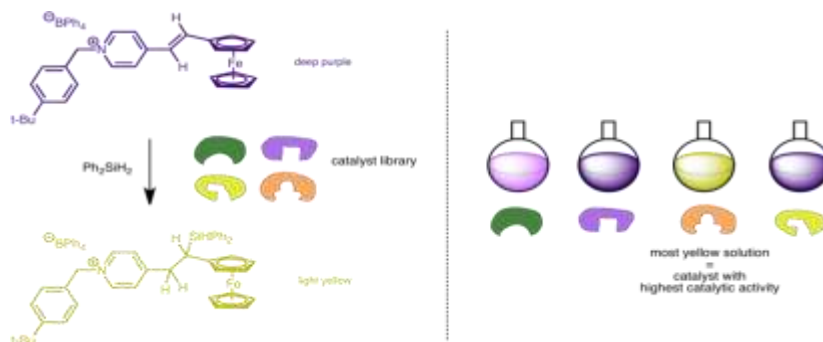
b. In Medicines

Supramolecular chemistry can help to understand better how to make effective drugs. Supramolecular drug are formed by two or more molecules through non-covalent bonds. Binding of small molecules to complex proteins that are complementary in shape and charge to the bimolecular target with which they interact and therefore will bind to it forms the basis of modern drug design. Supramolecular drugs playing important roles in many medicinal needs such as antitumor, antibacterial, antifungal, antiviral, antiepileptic, cardiovascular agents and magnetic resonance imaging agentsetc.



c. In Supramolecular Catalysis

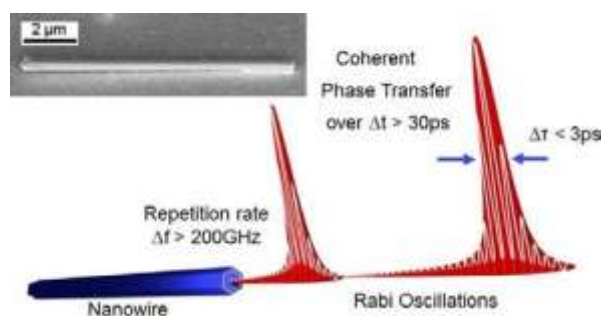
The beginnings of supramolecular chemistry may be traced back to Fisher's lock and key model of enzymatic catalysis. Enzyme catalysis shows the preferential complexation and stabilization of the transition states over the corresponding starting materials and products. Binding occurs by three-dimensional contacts between enzyme and substrate by intermolecular interaction. Supramolecular chemistry has therefore been to utilize these supramolecular interactions for the development of highly efficient catalysts for organic transformations.



The above diagram depicting a use of catalytic activity screening approach to screen a catalyst

a. In nanotechnology&moleculardevices

The bottom-up approach to miniaturization, which starts from molecules to build up nanostructures, enables the extension of the macroscopic concepts of a device and a machine to molecular level. Molecular-level devices and machines operate via electronic and/or nuclear rearrangements and, like macroscopic devices and machines, need energy to operate and signals to communicate with the operator. Examples of molecular-level photonic wires, plug/socket systems, light-harvesting antennas, artificial muscles, molecular lifts, and light-powered linear and rotary motors are illustrated. The extension of the concepts of a device and a machine to the molecular level is of interest not only for basic research, but also for the growth of nanoscience and the development of nanotechnology.



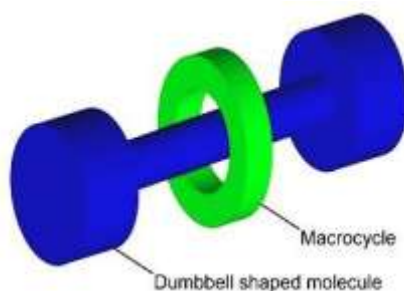
Nanowire lasers for ultrafast transmission of information in light pulses

Conclusion

The selective binding of a substrate by a molecular receptor to form a supramolecular species involves molecular recognition which rests on the molecular information stored in the interacting species. The functions of Supramolecules cover recognition, as well as catalysis and transport. In combination with polymolecular organization, they open ways towards molecular and supramolecular devices for information processing and signal generation. The

development of such devices requires the design of molecular components performing a given function (e.g., photoactive, electroactive, ionoactive, thermoactive, or chemoactive) and suitable for assembly into an organized array.

Light conversion devices and charge separation centers have been realized with photoactive cryptates formed by receptors containing photosensitive groups. Electroactive and ionoactive devices are required for carrying information via electronic and ionic signals. Redox-active polyolefinic chains, like the "caroviologens", represent molecular wires for electron transfer through membranes. Push pull polyolefins possess marked nonlinear optical properties. Tubular mesophases, formed by organized stacking of suitable macro-cyclic components, as well as "chundle" type structures, based on bundles of chains grafted onto a macrocyclic support, represent approaches to ion channels. Lipophilic macro cyclic units form Langmuir Blodgett films that may display molecular recognition at the air water interface. Supramolecular



Graphical representation of a rotaxane, useful as a molecular switch

chemistry has relied on more or less preorganized molecular receptors for effecting molecular recognition, catalysis, and transport processes. A step beyond preorganization consists in the design of systems undergoing self organization, that is, systems capable of spontaneously generating a well defined supramolecular architecture by self assembling from their components under a given set of conditions.

Several approaches to self assembling systems have been pursued: the formation of helical metal complexes, the double stranded helicates, which result from the spontaneous organization of two linear polybipyridine ligands into a double helix by binding of specific metal ions; the generation of mesophases and liquid crystalline polymers of supramolecular nature from complementary components, amounting to macroscopic expression of molecular recognition; the molecular recognition directed formation of ordered solid state structures.

Endowing photo, electro, and ionoactive components with recognition elements opens perspectives towards the design of programmed molecular and supramolecular systems

capable of self assembly into organized and functional supramolecular devices. Such systems may be able to perform highly selective operations of recognition, reaction, transfer, and structure generation for signal and information processing at the molecular and supramolecular levels. Supramolecular chemistry has discovered great possibilities in nearfuture.

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