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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; biomimetic are the important features of supramolecular chemistry. Molecular self-assembly is the construction of systems without guidance or management fromsource.

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 andsubstrate.

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 (currenttechnology)**
   - Continued reduction in size of bulk semiconductordevices
   - Optical, ultra-violet, ion-beam, electron-beamlithography
2. **Bottom-Up (molecular scaleelectronics)**
   - Design of molecules with specific electronicfunction
   - Design of molecules for self-assembly into Supramolecularstructures
   - Connecting molecules to the macroscopic world
   - Man-made synthesis (e.g. carbonnanotubes)

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

Keywords; Supramolecular, pi-pi stacking, self- assembly.

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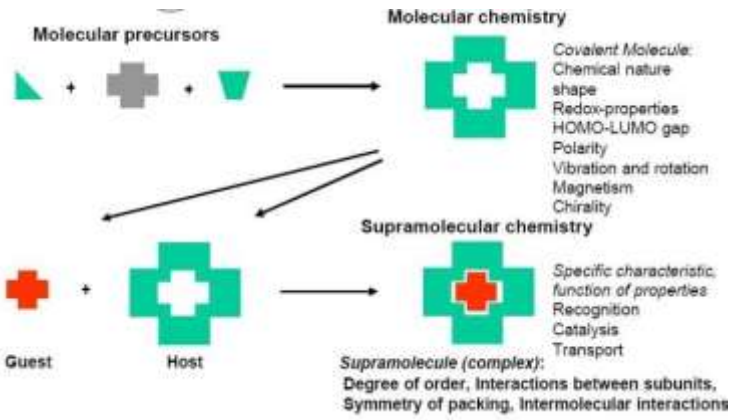
Introduction

Supramolecular chemistry refers to the study of supramolecular assemblies. It is one of the most popular and rapid growing areas of chemistry which emphases 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; exits extensively in numerous vital biological processes.

Atoms CovaletInteraction Molecules

Molecules Non-CovalentInteraction 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 chemistrybranch.

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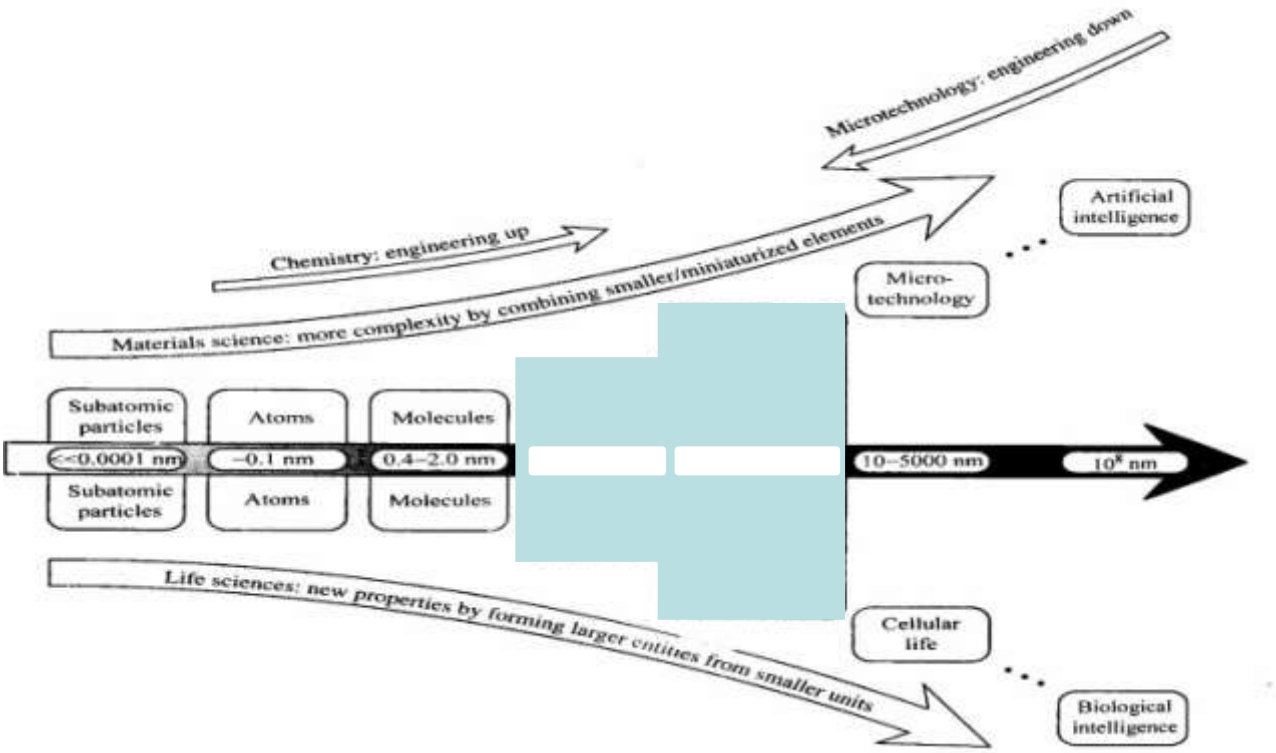
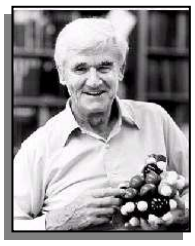


In 1987**Donald J. Cram**, USA, **Jean-Marie Lehn**, France and **Charles J. Pedersen**, USA were jointly awarded the Nobel Prize of chemistry for their development andapplication of molecules with highly selective structure specific interaction, i.e. molecules that can "recognize" each other and choose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


DonaldJ.Cram


Jean-MarieLehn


CharlesJ.Pedersen

The laureates" research has been of great importance for developments within coordination chemistry, organic synthesis, analytical chemistry and bioorganic and bioinorganic chemistry, and hasthus 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.

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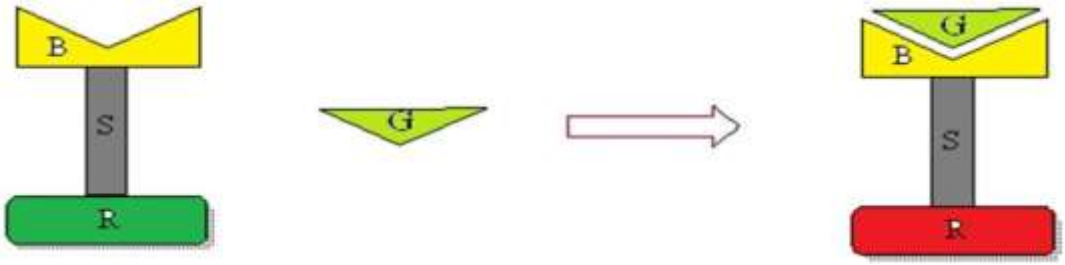

Figure:Design Principle.

Here R= Reporter group, flourorganic, 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 host design

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

- -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 alsobe used to enhancetheinteractions.
- Anionic: In comparison to cation binding, the design of hosts for anionic guests is

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a relatively new area. Todesignahostforanionsthefollowinghavetobe taken into consideration: charge, size, pH dependence, solvation and geometry.

- Simultaneous cationic and anionic binding: This type of recognition (known as ditopic) is particularlychallenging since two different receptor sites have to be designed within thesamehost.

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

In the 1990"s, supramolecular chemistry become 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 supramolecularchemistry and nanotechnology. Stoddart has developed highly efficient syntheses of mechanically-interlocked molecular architectures such as molecular Borromean rings,catenae's(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 system in order to increase functionally research into synthetic self-replicating system began and work on molecular information processing devices.

irFraserStoddart Jean-PierreSauvage 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.

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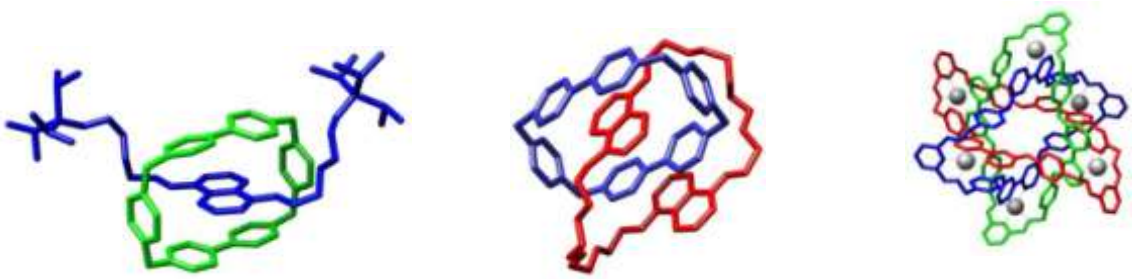

(Rotaxane)catenanemolecular Borromean rings

Rotaxanes: Mechanically-interlocked molecules

Catenanes: Catenanes are a hinge waiting for a Nanomechanism to work in or mechanically-interlockedmolecular architecture consisting of two or more interlockedmacrocycles, i.e. a molecule containing two or more intertwinedings.

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

E.g. Borromeate is made upof threeinterpenetratedmacrocycles formed from the reaction between2,6-diformylpyridine and diamine compounds, complexedwithzinc.This compound was synthesized from two buildingblocks: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 pentacoordinatecomplexation sites. Trifluoroacetic acid (TFA) is added to catalyze the imine bond-forming reactions. The preparation of the tri-ring **Borromeate**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 Borromeate is thermodynamically the most stable reaction product out of potentially many others. As a consequence of all the reactions taking place being equilibria, the Borromeate is the predominant reactionproduct.

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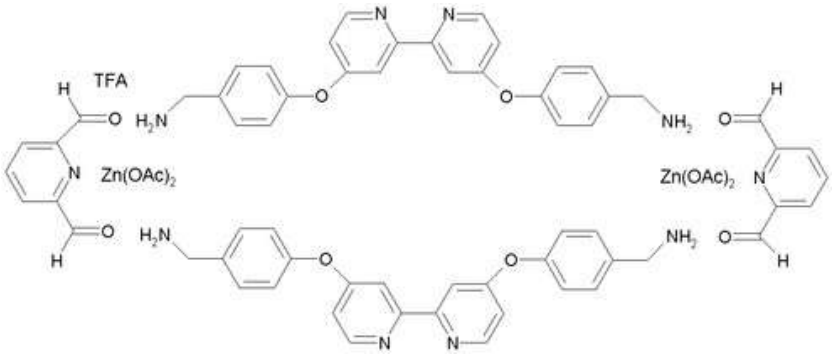
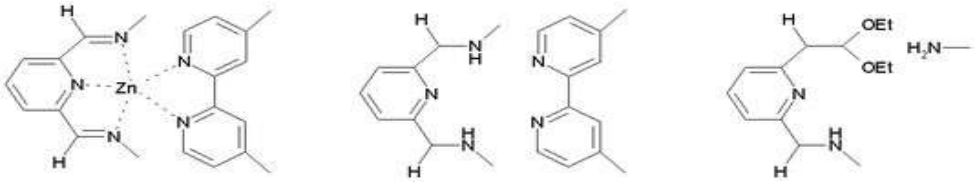


Fig: Synthesis of one ring in Borromean ring system from 2, 6-diformylpyridine and a diamine in presence of zinc acetate and TFA. The ring-system consists of three such interlocked rings

Reduction with sodium borohydride in ethanol affords the neutral **Borromeand**.[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 compressivebehaviour of supramolecular

Supramolecular polymers, a newly-developing group of materials, can be loosely defined as those inwhich 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 processingand post-processing. This provides those materials with unique thermos responsive and thermos reversibleproperties, 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.

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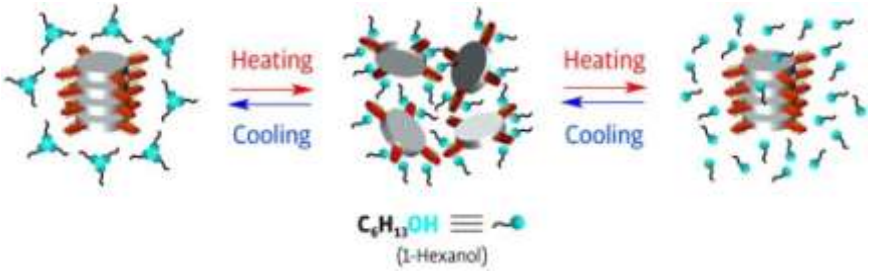

In other words we can say that supramolecular chemistry deals with subtle interactions and consequently control over theprocessesinvolvedcanrequiregreatprecision.In particular, non- covalent bonds have low energies and often no activation energy for formation. As demonstrated by the Arrhenius equation, 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 highertemperatures.

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 canbecritical.

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Host	Guest	Interaction	Class	Example
Crown ether	Metal cation	Ion - dipol	Complex (Cavitate)	[K⊂ [18]crown-6]
Spherand	Alkyl ammonium cation	Hydrogen bonding	Complex (Cavitate)	Spherand ($CH_3NH_3^+$)
Cyclodextrin	Organic molecule	Hydrophobic/van der Waals	Cavitate	(α-cyclodextrin) (*p*-hydroxy-benzoic acid)
Water	Organic molecule, halogen, etc.	Van der Waals/crystal packing	Clathrate	$(H_20)_6 \cdot (CH_4)$
Calixarene	Organic molecule	Van der Waals/crystal packing	Cavitate	(*p*-*t*-butylcalix[4]-arene)(toluene)
Cyclotrivera-trylene (CVT)	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 highenergies
- Very shortdistances
- Highly dependent onorientation
- Driving Forces for the Formation ofSupramolecularStructures ➡ hydrophobicinteraction<40kJ/mol

NATURE OF SUPRAMOLECULARINTERACTIONS

1. HydrophobicInteraction
2. Electrostaticinteraction ~20kJ/mol
3. Hydrogenbondinteraction12-30kJ/mol
4. VanderWaalsinteraction 0.4-4kJ/mol
5. cation–πinteraction 5-80kJ/mol
6. π-πstackinginteraction0-50kJ/mol

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

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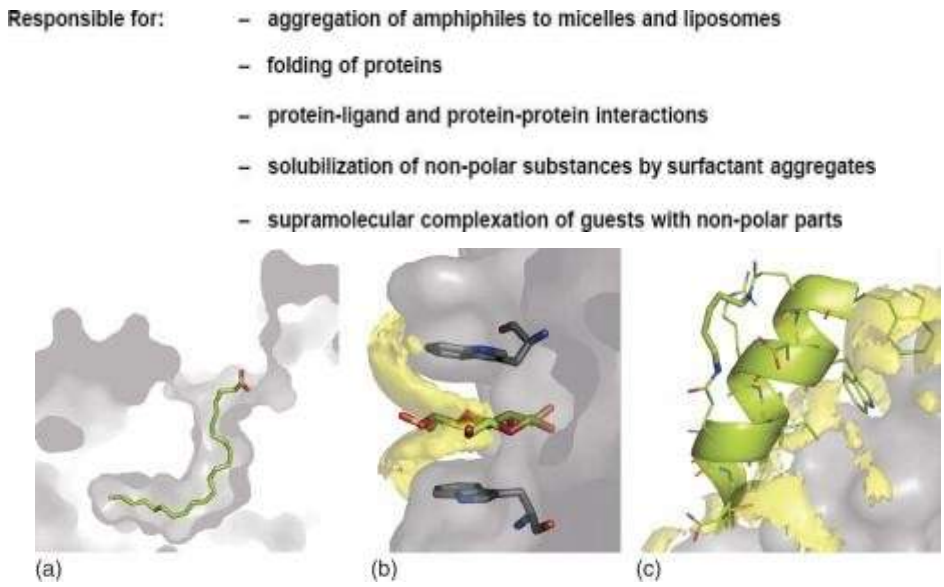
1. **HydrophobicInteraction**

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 enthalpy 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 soluteandthusnegativeentropy 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 enthalpy 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 bulkwater.



(a) Proposed fatty acid ligand $C_{23}H_{48}O_2$ 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 theenzyme.

(b) Two tryptophan residues (grey sticks), in the carbohydrate-binding module of xylanase 10A, provide planar hydrophobic stacking interactions for a glucose disaccharide (green

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sticks) (PDB code 1I82). Yellow patches indicate favorable regions for the DRY probe as calculated withGRID.

(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 withGRID.

(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 repulsiveforce and Non-directionalforce. It is highly dependent on the dielectric constant ofthemedium.

$$\text{Ion–Ion InteractionsEnergy} = (k * z_1 * z_2 * e^2)/(r_{12})$$

$k = 1 / 4\pi e_o$ = Coulomb constant = $9*10^9$ Nm /C^2

e = elementary charge = $1.6*10^{-19}$

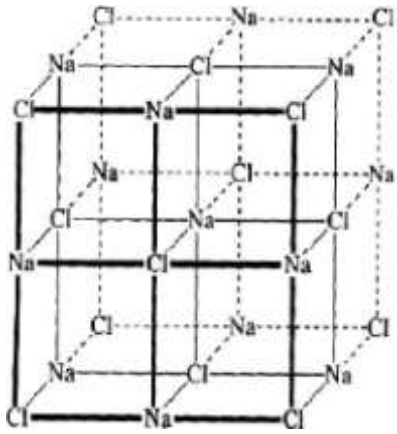
e = dielectric constant

r_{12} = meters between the objects

The energy of an ion-ion interaction only falls of 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 ananion.

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.

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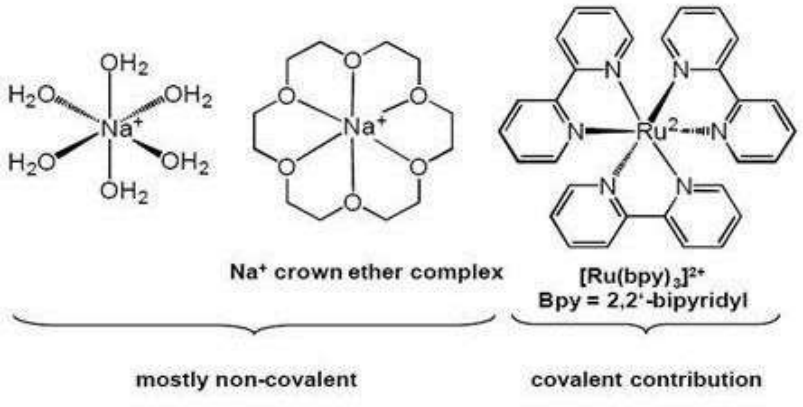
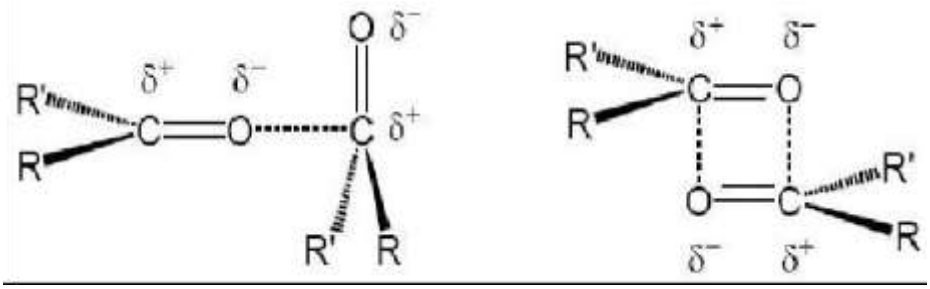


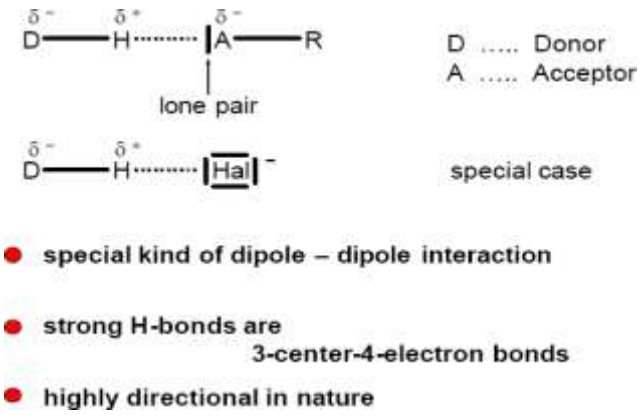
b. Dipole-dipoleinteraction:

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 Theseinteractions are significantly weaker than ion-ion interactionsKetones are good example of this type of interaction but the low boiling points show that the interactions are relatively weak.



(d) Hydrogen bonding:

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.



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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.

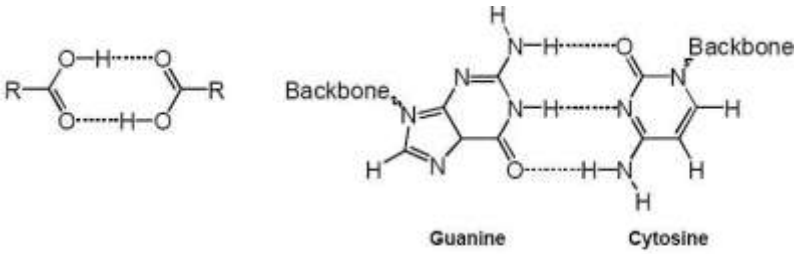

Fig. 1.15. Hydrogen bonded carboxylic acid dimers and base pairing in DNA by hydrogen bonding.

ideally linear arrangement

D—H····· A (angle 180°)

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 %
^1H NMR chemical shift downfield (ppm)	14 – 22	< 14	?
Examples	Gas phase dimers with strong acids/ bases	Acids	Minor components of bifurcated bonds
			C—H hydrogen bonds
	Proton sponge	Alcohols	O—H π hydrogen bonds
	HF complexes	Biological molecules	

4. Vander Waalsinteraction

Polarizations of the electron cloud by proximity an adjacent nucleus generally create of this type of forces. These Vander Waals forces are believed to provide additionallenthalpic stabilization to the coordination of a hydrophobic guestintoa hydrophobic cavity.Strengthofinteractionis essentially a function of the surface area of contact. The larger the surface area the stronger the interaction willbe. These forces are

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non-directional and hence have limited scope for design.Ex- X- ray crystal structure of the Vander Waal inclusion complex P-tert-butylcalix [4]areNE toluene.

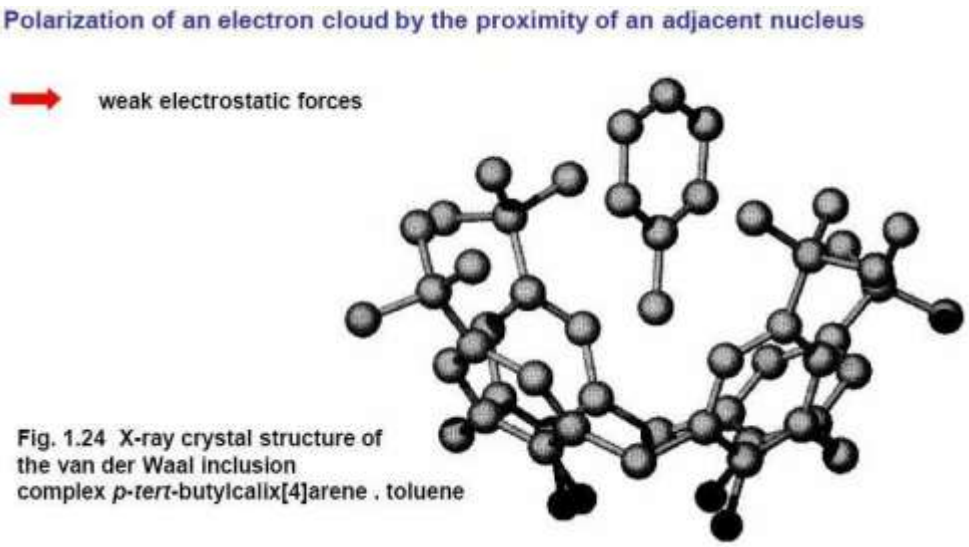

Fig. 1.24 X-ray crystal structure of the van der Waal inclusion complex *p-tert*-butylcalix[4]arene . toluene

5. Cation-πinteraction

The cation –π interaction is seen

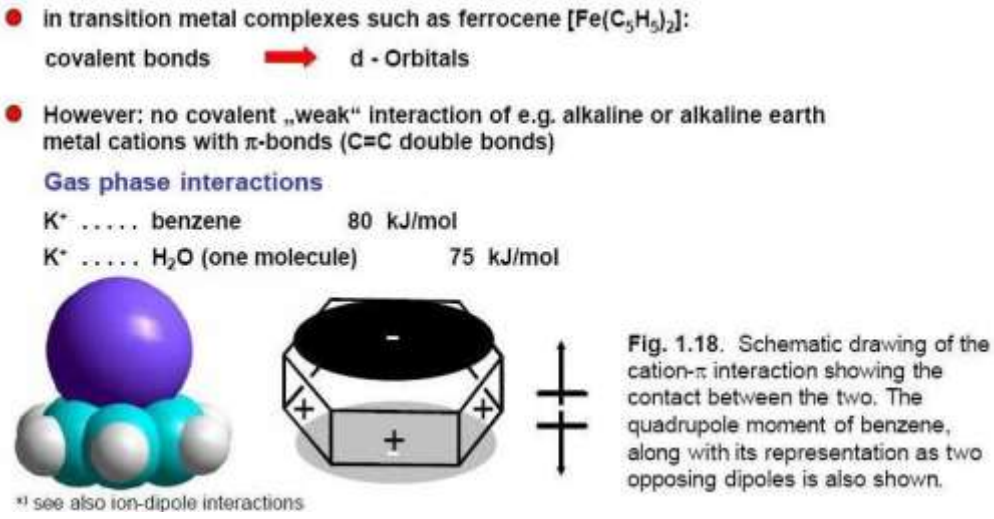

Fig. 1.18. Schematic drawing of the cation-π interaction showing the contact between the two. The quadrupole moment of benzene, along with its representation as two opposing dipoles is also shown.

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

6.π – π Stackinginteractions

π – π Stacking interactions occurs between aromatic tings 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.

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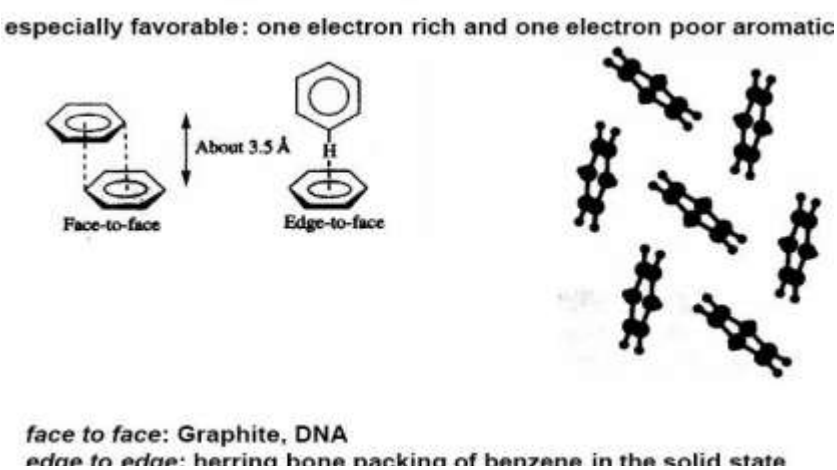

Some very elegant receptors have been synthesized employing π – π interactions, including a receptor for benzoquinone.

Approaches

There are two types of approaches of supramolecular chemistry

1. **Top-Down (current technology).**
   - Continued reduction in size of bulk semiconductordevices
   - optical, ultra-violet, ion-beam, electron- beamlithography
2. **Bottom-Up (molecular scaleelectronics).**
   - Design of molecules with specificelectronicfunction

     Design of molecules for self-assembly into supramolecularstructures
   - Connecting molecules to themacroscopicworld
   - Man-made synthesis (e.g. CarbonNanotubes)

Application of Supramolecular Chemistry

a. In transportprocess

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, isallcritical 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 supramolecular of porphyrin ring.

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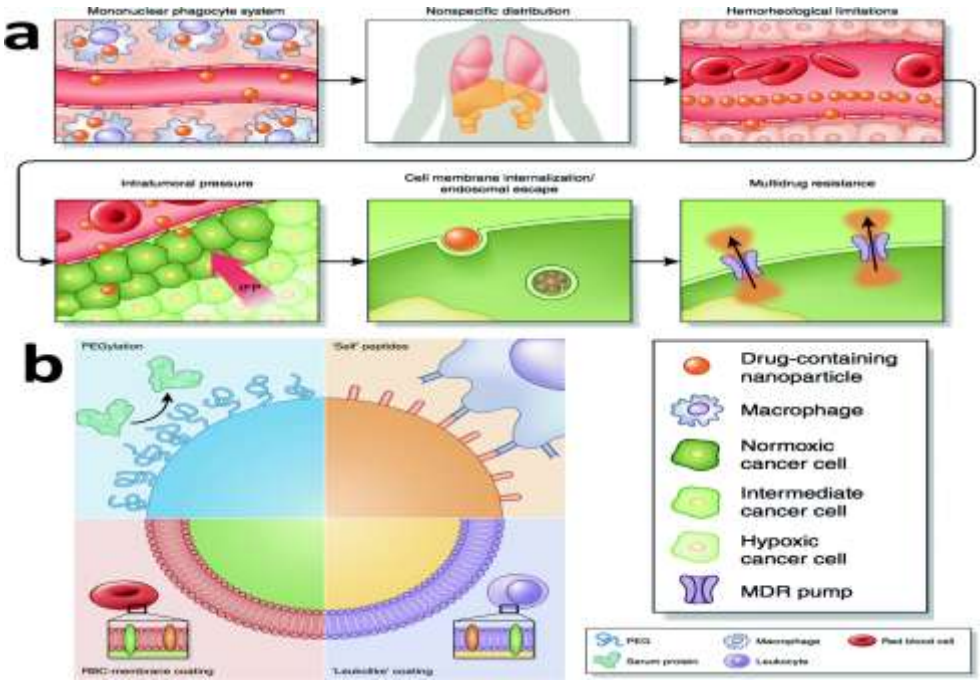
b. InMedicines

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 agents etc.



c. In SupramolecularCatalysis

The beginnings of supramolecular chemistry may be traced back to Fisher's lock and key model of enzymatic catalysis. Enzyme catalysis shows the preferential compel xationands 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 fororganictransformations.

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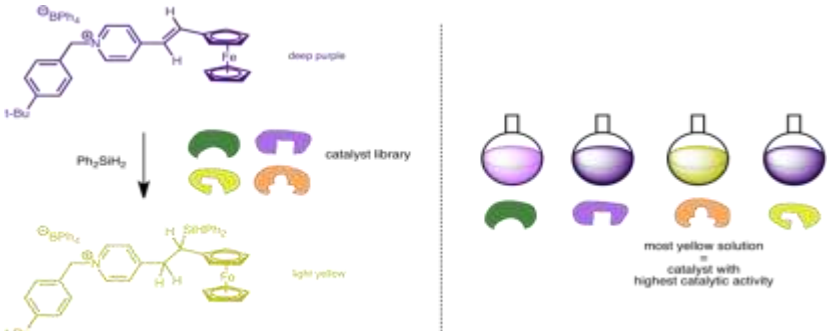
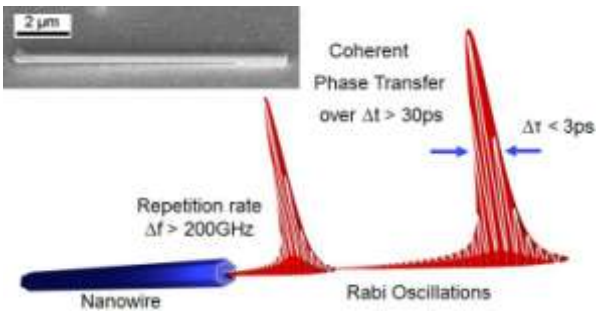


The above diagram depicting a use of catalytic activity screening approach to screen a catalyst

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 rearrangementsand,like macroscopicdevicesandmachines, 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. Theextension 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 inlightpulses

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 Super molecules cover recognition, as well as catalysis

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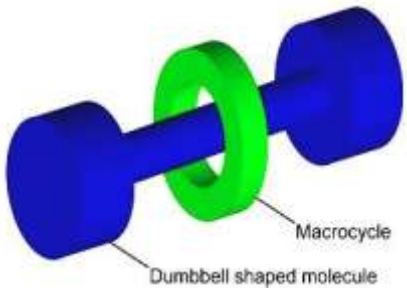
and transport. In combination with polymolecular organization, they open ways towards molecular and supramolecular devices for information processing and signal generation. The development of such devices requires the design of molecular components performing a given function (e.g., photoactive, electroactive, ionactive, thermos active, or chemoactive) and suitable for assembly into an organizedray.

Light conversion devices and charge separation centers have been realized with photoactivecrepitates formed by receptors containing photosensitive groups. Electroactive and inactive devices are required for carrying information via electronic and ionic signals. Redox- active polyolefin chains, like the "caroviologens", represent molecular wires for electron transfer through membranes. Push pull Polyolefin 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 rotenone, useful as a molecularswitch

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 helicases, 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 ionactive 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.

Reference

1. H Dugas,Bioorganic Chemistry: A chemical Approach to Enzyme Action,3rdedition Springer private limited India, 2007.
2. C J Pedersen, Cyclic Polyethers and Their Complexes With Metal Salts,J.Am. Chem. Soc., Vol.89, No.26, pp.7017– 7036, 1967
3. D J Cram, T Kaneda, R C Helgeson, G M Lein, Spherands – Ligands WhoseBinding of Cations Relieves Enforced Electron-electron Repulsions,J.Am.Chem. Soc., Vol.101, No.22, pp.6752–6754,1979.
4. B Dietrich, J M Lehn, J P Sauvage, Cryptates-XI Complexes Macrobi-cycliques, Formation, Structure, Properties,Tetrahedron, Vol.29, No.11,pp.1647–1658,1973,
5. E V Anslyn, D A Dougherty,Modern Physical Organic Chemistry, UniversityScience Books, California,2006.
6. L K S Krbek, C A Schalley, P Thordarson, Assessing Cooperativity inSupramolecularSystems,Chem. Soc. Rev., Vol.46, No.9, pp.2622–2637,2017.
7. J Li, D Yim, W-O Jang, J Yoon, Recent Progress in the Design and Appli-cations of Fluorescence Probes Containing Crown Ethers,Chem. Soc. Rev.,Vol.46, No.9, pp.2437–2458, 2017.
8. A P de Silva, S A de Silva, Fluorescent Signalling Crown Ethers; „SwitchingOn" of Fluorescence by Alkali Metal Ion Recognition and Bindinginsitu,J.Chem. Soc. Chem. Commun., Vol.0, No.23, pp.1709–1710,1986.
9. J Mei, N L C Leung, R T K Kwok, J W Y Lam, B Z Tang, Aggregation-Induced Emission: Together We Shine, United We Soar,Chem. Rev., Vol.115,No.21, pp.11718–11940, 2015.
10. S Kassem, T Leeuwen, A S Lubbe, M R Wilson, B L Feringa, D A Leigh,Artificial Molecular Motors,Chem.Soc.Rev., Vol.46, No.9, pp.2592.[11] E A Neal, S M Goldup, Chemical Consequences of Mechanical Bonding inCatenanes and Rotaxanes: Isomerism, Modification, Catalysis and MolecularMachines for Synthesis,Chem. Commun., Vol.50, No.40, pp.5128–5142,2014.

Websites:

11. https://www.sciencedirect.com
12. http://www.newworldencyclopedia.org
13. https://www.researchgate.net
14. https://www.frontiersin.org
15. https://www.nature.com/subjects/supramolecular-chemistry
16. https://www.internetchemistry.com