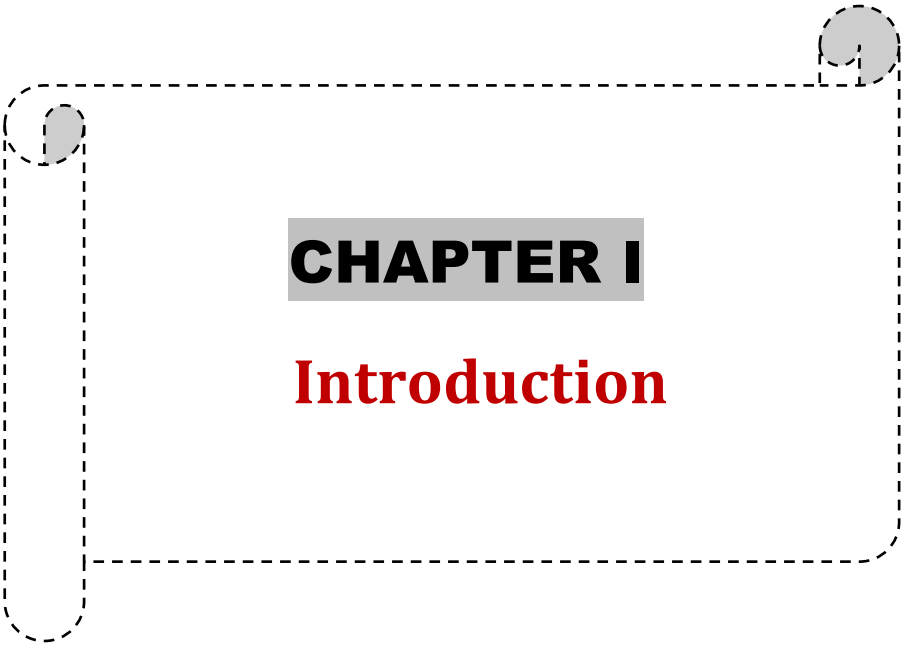


CHAPTER I

Introduction

1.1 INTRODUCTION

1.1.0 Symmetry

Where there is matter, there is geometry wherein *symmetry* begins as the first property of an ordered geometry. Symmetry is a result of a balancing act and connotes harmony of proportions. Hence usefulness, function and aesthetic appeal are the artifacts of symmetry in the fields of technology and art.[1] Symmetry is a phenomenon of *natural* world, as well as the world of *human* invention as observed from our circumambient.

Symmetry is omnipresent in the nature from subatomic level to the planets and the universe. In living organisms from a plant shoot to flowers and fruits or in animals, there exists radial or bilateral symmetry, and flowers with a symmetrical shape have greater chances of pollination. Birds during their flight in the sky follow some rules of symmetry in the fashion of Pascal's triangle. The aesthetically appealing 'Golden ratio number' is found in plants and in many human architectures for example while tracing the seeds of sunflower from the center outwards. The majority of animals are bilaterally symmetric (Figure 1).

Figure 1 ***Symmetry in Nature***

Many manmade magnificent architectural structures attract attention due to symmetry present in them. The Taj Mahal and Lotus temple situated in India while Hungarian parliament, Budapest and the famous structure by Buckminster Fuller at Missouri

Botanical Garden located in St. Louis of United States are some of the examples of the same (Figure 2).

Figure 2 ***Man-made symmetrical architectures***

Platonic solids are three dimensional shapes made out of basic geometric figures having high degree of symmetry embedded in them (Figure 3). They are named so after the great Greek philosopher Plato who conceptualized these structures.

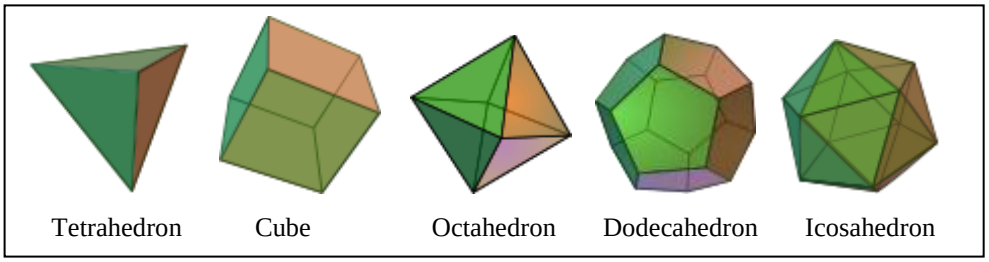


Figure 3 ***Platonic solids***

Symmetry in **Molecules**[1]

Molecular symmetry is a fundamental concept in chemistry. It can explain many of the molecular properties such as dipole moment, spectroscopic transitions, optical property and crystal packing. Arrangement of atoms or group of atoms in molecules is reflected in

symmetry they possess. Symmetry arises because of atoms or groups repeated in a regular rhythmic form of pattern. Different *symmetry operations* reflect the extent of symmetry present in molecules. Different symmetry operations lead to symmetry characteristics in molecules which are reflected in symmetry elements or group symmetry they possess. Symmetry element is a geometrical entity such as a line or a plane or a point about which an operation of rotation, reflection or inversion is carried out. There are five types of symmetry elements as listed below.

1. Rotational Axis of symmetry, $\boldsymbol{C_n}$
2. Plane of symmetry, $\boldsymbol{\sigma}$
3. Improper Rotational Axis of symmetry, $\boldsymbol{S_n}$
4. Inversion centre or Center of symmetry, **i**

In organic molecules symmetry is originated from the characteristic shapes the orbitals of carbon attain due to hybridization it undergoes. Some simple or basic organic molecules with different symmetry elements are shown in Figure 4.

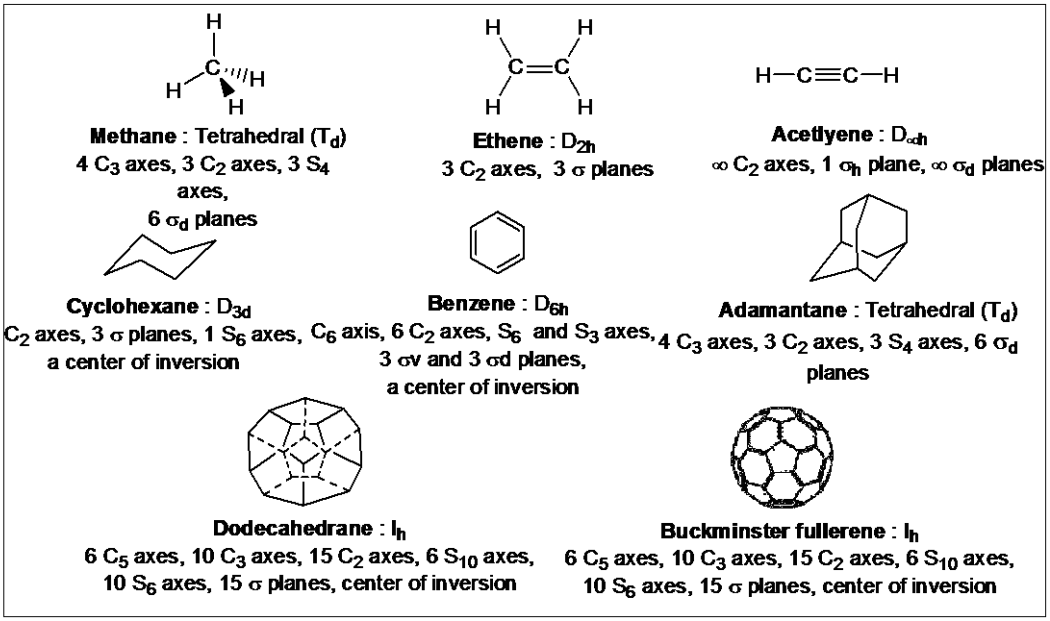


Figure 4 ***Molecules with inherent symmetry***

Molecules with higher order of symmetry are symbol of the harmony of proportions. Beauty is induced in them due to symmetry they posses – as is induced in nature, art,

architecture and geometry, for example symmetry in dodecahedrane and in fullerenes. Symmetry may be advantageous in synthesis design,[2] in supramolecular self assembly[3] and for chemical selectivity.[4]

C_3 symmetric molecules have attracted much attention of synthetic organic chemists in recent past[5]. C_3 symmetric molecules must have threefold rotational axis of symmetry as a basic requirement.[6] Chemistry of such molecules involves their synthesis and characterization, and deals with their utility in the fields of catalysis, materials science, supramolecular chemistry and nano science.

Different topologies may exist in C_3 symmetric molecules; there can be cyclic C_3 symmetric compounds or acyclic C_3 symmetric compounds. Cyclic C_3 symmetric compounds may form macrocyclic structures. The acyclic C_3 symmetric compounds may have more possible coordination modes due to their flexible arms which allow them to adopt different conformations according to the geometric requirements of different guests, both non-ionic and ionic.

C_3 symmetric compounds may have a variety of applications depending upon the structural features they possess. Some of the important applications are discussed in the following sections.

1.1.1 C_3 symmetric compounds in catalysis

There are a number of reports describing the application of C_3 symmetric compounds as catalysts. The advantage of C_3 symmetric compounds over mono or di equivalents have been well demonstrated in many studies. C_3 symmetric compounds are preferred ligands for many metal complexed catalysts as it results in reduction in the number of possible diastereomeric intermediates or transition states.[5a,7] They are known as efficient chirality transfer agents as they form octahedral complexes and hence widely applied in the field of asymmetric catalysis.

The enantiopure C_3 symmetric ligand **1** when employed as a catalyst in alkylation of carbonyl compounds leads to high enantiomeric excess of the corresponding alcohols **2**[8] (Figure 5).

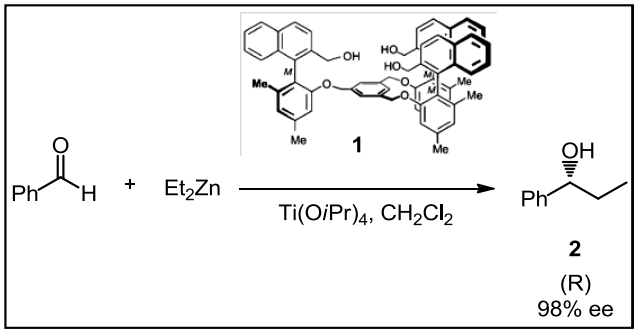


Figure 5 ***Axially chiral C_3 symmetric ligand***

The tris-(β–hydroxy amide) ligand **3** when employed as a chiral catalyst for alkynlation of aldehydes resulted in high % ee of the corresponding alkynyl alcohols **4** in comparison to its bis or mono analog[9] (Figure 6, Table 1).

Table 1

Sr. No.	Type of L	Yield [%]	*ee* [%]
1	Tris	85	92
2	Bis	86	51
3	Mono	82	62

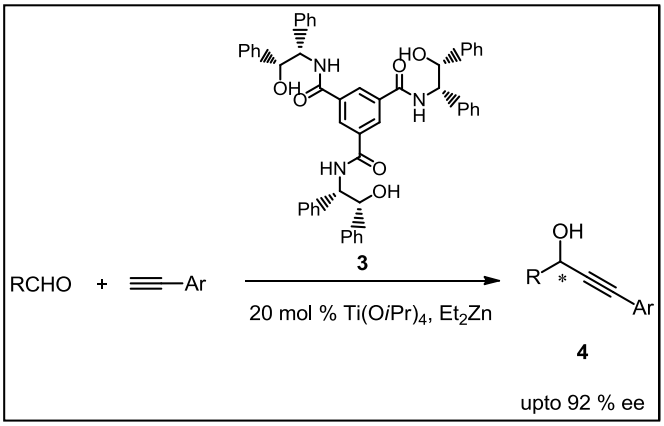


Figure 6 ***Chiral tris-amido catalyst***

The role of C_3 symmetric compounds in asymmetric synthesis has not been limited to their applications as ligands but they have also been used as chiral organocatalysts.

The proline derived C_3 symmetric organocatalyst **5** was found effective in enantioselective Michael addition reactions. The transition state shown is clearly indicating the advantage of tri-podand catalyst over mono or bis-podand catalyst[10] (Figure, Table 2).

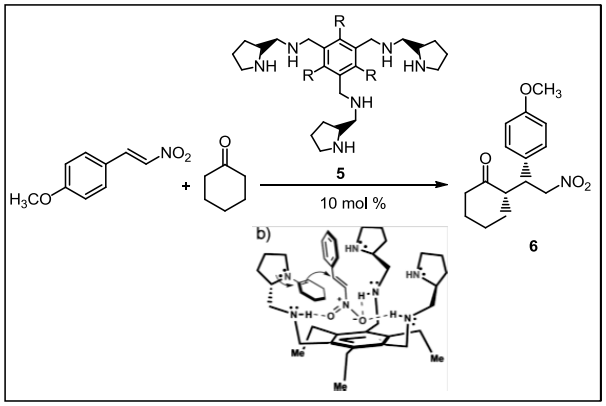


Figure 7 ***Tris-proline as organo catalyst***

Table 2

Sr. No.	Catalyst type	yield [%]	*dr* [%]	ee [%]
1.	Tris R = Me	82	95:5	86
2.	Tris R = Et	88	98:2	98
3.	Bis R = Et	88	96:4	90
4.	Mono R = Et	45	96:4	78

The tripodal tris-ureas **7a** and **7b** have been demonstrated to act as versatile and efficient catalysts for Michael addition reactions with various substrates[11] (Figure 8).

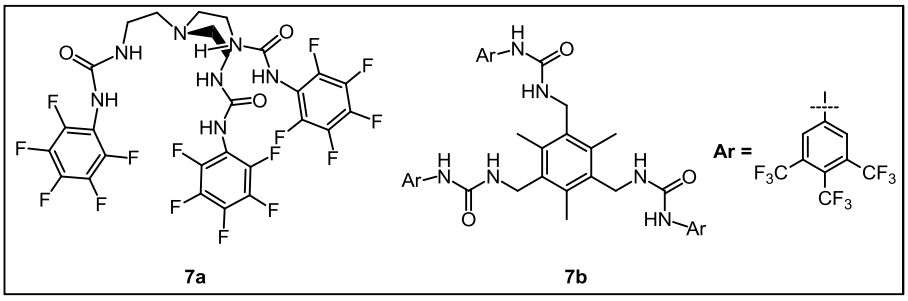


Figure 8 ***C_3 symmetric tris-urea derivatives as catalysts***

Enantioselective bromolactonization of alkenoic acids by C_3 symmetric chiral tris(imidazoline) **8** has been demonstrated in the figure 9.[12]

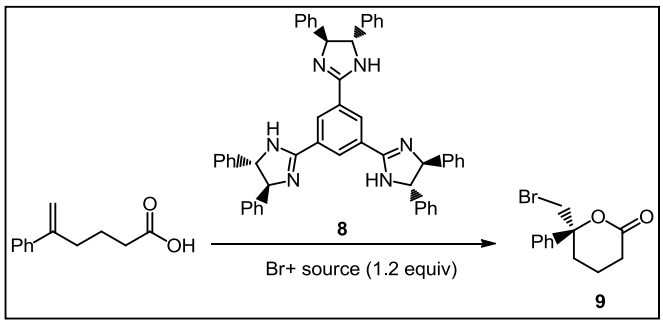


Figure 9 ***Tris-imidazoline chiral catalyst***

Table 3

Sr. No.	Type of Catalyst	Yield [%]	ee [%]
1	Tris	95	69
2	Bis	99	28
3	Mono	92	6

The same catalyst **8** was also used for enantioselective Michael addition reaction to give **10**[13] (Figure 10).

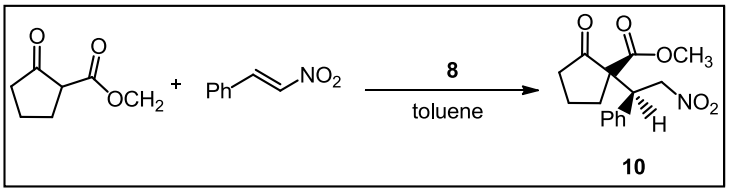


Figure 10 ***Enantioselective Michael addition reaction***

Table 4

Sr. No.	Type of Catalyst	Yield [%, *dr*]	ee [%]
1.	Tris	94 (18:1)	89
2.	Bis	91 (18:1)	61
3.	Mono	29 (5:1)	1

There is a significant decrease in enantiomeric excess when bis and mono variants of the imidazoline catalysts were employed (Table 3 and 4).

The C_3 symmetric tris-(benzyltriazolylmethyl) amine (TBTA) **11** was shown to be a powerful stabilizing ligand for Cu^I while enhancing its catalytic activity in triazole formation from azide-alkyne cycloaddition reaction[14] (Figure 11).

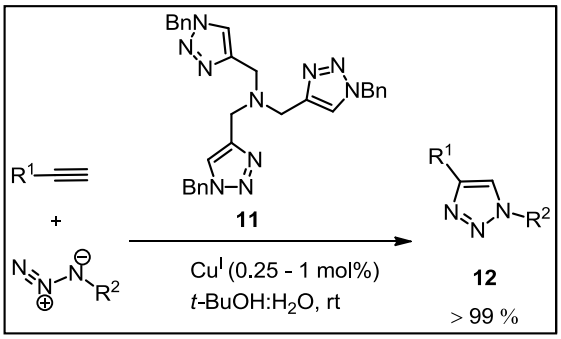


Figure 11 ***Tripodal TBTA catalyst***

Similarly n-butylcarboxylate pendant derivative of C_3 symmetric tris-benzimidazole ligand **13** was also found to be an efficient catalyst for the azide-alkyne copper catalyzed cycloaddition reaction[15] (Figure 12).

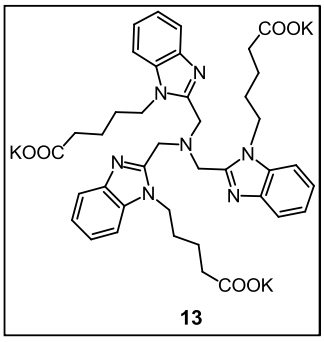


Figure 12 ***Tris-benzimidazole ligand***

1.1.2 C_3 symmetric compounds and Supramolecular chemistry

Supramolecular chemistry[16] in general involves non-covalent interactions which include electrostatic interactions– ion-ion interaction, ion-dipole interaction, dipole-dipole interaction, hydrogen bonding, π–π and cation–π interactions and solvophobic effects which may result in supramolecular self assemblies. Supramolecular chemistry includes the study of host-guest chemistry which deals with the study of large molecules called '*hosts*' which are capable of holding smaller chemical entities called '*guests'* having both non-ionic and ionic non-covalent interactions. The sites where the non covalent interactions take place are called binding sites. Biological systems extensively depend on such non-covalent and host-guest interactions where enzymes are hosts and the substrates are guests to form an enzyme-substrate complex, as due to best fit also known as lock and key model (Figure 13).

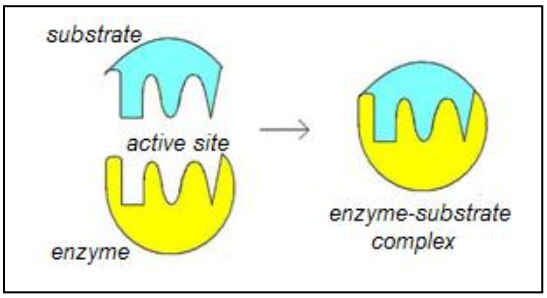


Figure 13 ***Enzyme-substrate selectivity model***

Binding induced modification is a consequence of many biological 'trigger' processes, such as muscle contraction or synaptic response. In general, in order to achieve a strong and selective binding, the binding sites of both host and guest must be chemically complementary as well as host needs to be complementary to shape and size of guest. The stability of the host-guest complex can be enhanced when the host has multiple interaction sites that are covalently bonded such an effect is termed as *Chelate effect.* The stability of the host-guest complex can further be improved from the pre-organized type of host molecule. A pre-organized host is one that has a series of binding sites in a well defined and complementary geometry within its structure and does not undergo a significant conformational change in order to bind to guest entity. Such characteristics are found in rigid hosts called macrocycles and the above mentioned effect is termed as macrocyclic effect. Unlike macrocycles, other class of host is ***podands***. Podands can be

defined as acyclic or chain–like or branching host with two or more binding sites that are situated at the length of the molecule or about a common spacer. Podands have high degree of flexibility owing to several movable bonds, thus going through conformational changes upon binding to a guest to produce a host–guest complex. Host flexibility plays a key role, especially in biological systems, where the recognition of a substrate results in a conformational change which is of a significant importance, for example in a protein's biochemical role. Hence, formation of host-guest complexes or chemistry of supramolecular self assembly is driven by various interactions which are non-covalent in nature and of prime importance in supramolecular chemistry.

The stability of the host-guest complex is associated with a definite value termed as *Binding constant* or *Association constant* $\mathbf{K_a}$ or **K** which can be determined by titration method using UV-Vis, fluorescence or/and NMR spectroscopic techniques.[16,17] The changes observed during the titration is correlated to the concentration of the host-guest complex at equilibrium which is used to determine $\mathbf{K_a}$. The equation for 1:1 host-guest complex is as shown below.

$$\text{Host} + \text{Guest} \rightleftharpoons \text{Host} \cdot \text{Guest}$$

$$\text{Ka} = \frac{[\text{H} \cdot \text{G}]}{[\text{H}][\text{G}]}$$

Prior to the determination of $\mathbf{K_a}$ values, stoichiometry of the host-guest complex is determined using various methods, one of which is *Mole Ratio* method. In this method, solution sets of varied concentration of either host or guest and keeping the other's concentration constant are prepared including all possible equivalence of host:guest and then recording their absorbance. The experimental data thus obtained are processed by plotting the absorbance value against the species whose concentration was varied and such a plot is termed as Job's plot. The equation for 1:1 stoichiometry of host-guest complex is as shown below:

$$\Delta A_{obs} = \in_{\Delta HG}([HG])$$

UV–Vis spectroscopic technique is a common technique used for the determination of binding constant as well as stoichiometry of the host-guest complex. The region of

interest to observe the change in absorbance should be such that there is a strong absorbance for the complex and zero absorbance for guest and host.

Fluorescence spectroscopic technique is used when either free host or host-guest complex is fluorescent and shows fluorescence ON (enhancing) or OFF (quenching) upon host-guest complexation. The equation for the calculation of binding constant is as shown below:

$$\Delta F_{obs} = k_{\Delta HG}([HG])$$

This technique is very sensitive and one of the efficient way to determine the binding constant.

NMR Spectroscopic technique is most sophisticated and one of the modernized ways to calculate binding constant. This technique is highly sensitive and works at equally low concentration with respect to the rest of techniques. Data analysis for 1:1 stoichiometric complex for fast exchange region assumes that the resonance δ of interest is weighed average of the free host and the complex. While for the slow exchange region of NMR integration of relative ratios of the free and bound host will give binding constant value directly.

1.1.3 C_3 Symmetric host molecules

C_3 Symmetric tripodal *N*-donor heterocyclic receptors having pyrazole **14**[18] and oxazoline **15**[19] heterocyclic binding ligands have been found efficient in the recognition of biologically important NH_4^+/K^- ions with very good binding constants compared to commercially available Nonactin[20] (Figure 14).

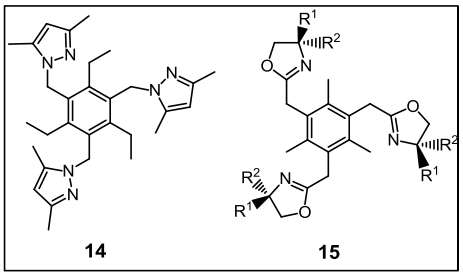


Figure 14 ***Artificial receptors for NH_4^+/K^- ions***

C_3 Symmetric tripodal oxazoline derivative **16** was designed as a chiral receptor for the enantiomeric recognition of phenylethylammonium ion through hydrogen bonding and π–π supramolecular interaction as observed in the X-ray crystal structure of host-guest inclusion complex.[21]

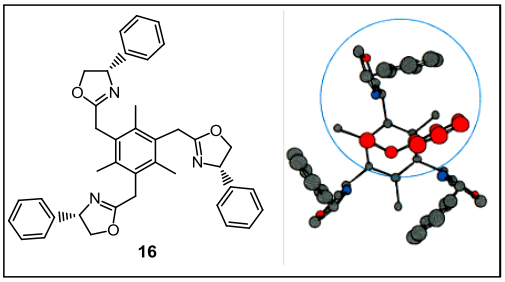


Figure 15 ***Chiral tripodal host for recognition of phenylethylammonium ions***

Tripodal receptor having guanidinium arms **17** was selectively binding to citrate and trimesic acid tricarboxylate ions and was termed as *'molecular flytrap'* with high association constants of $K_{assoc} > 10^5\ M^{-1}$ in water.[22] (Figure 16) Since such molecules demonstrate the importance of the flexibility provided by the C_3 symmetric molecules.

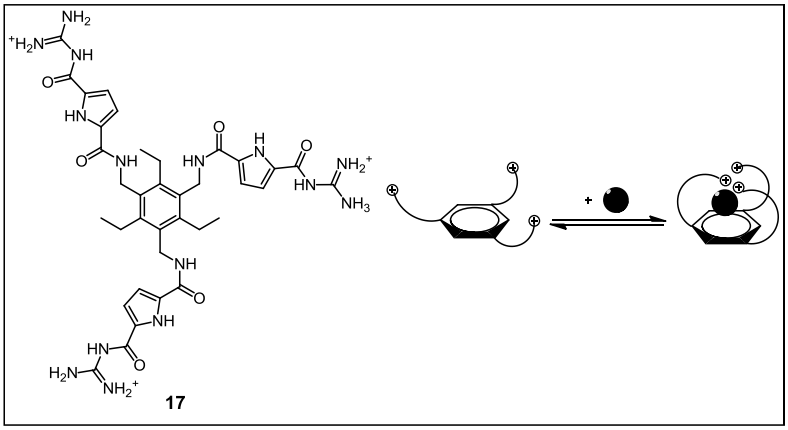


Figure 16 ***C_3 symmetric tri-guanidinium armed receptor***

The concentration of anticoagulant oligosaccharide heparin needs to be monitored during surgery and post operative therapy to prevent hemorrhage. A fluorescent C_3 symmetric artificial receptor **18** for heparin **19** was developed[23] (Figure 17).

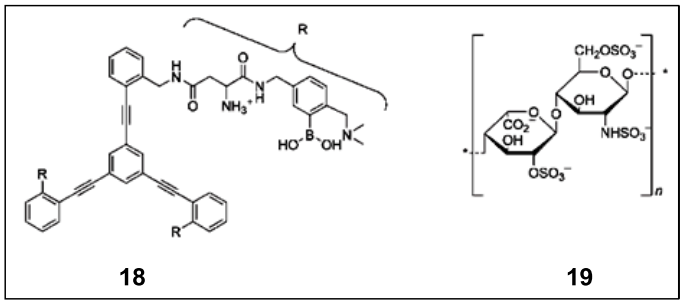


Figure 17 ***Tripodal fluorescent receptor for heparin***

Heparin **19** interacts with multiple binding sites present in a kind of macroreceptor **18**.

Singh and co workers designed a novel tripodal fluorescent receptor **20** possessing benzimidazole rings with nitrogen atoms as binding sites was found to be selectively binding with iodide anion resulting the quenching of fluorescence[24] (Figure 18).

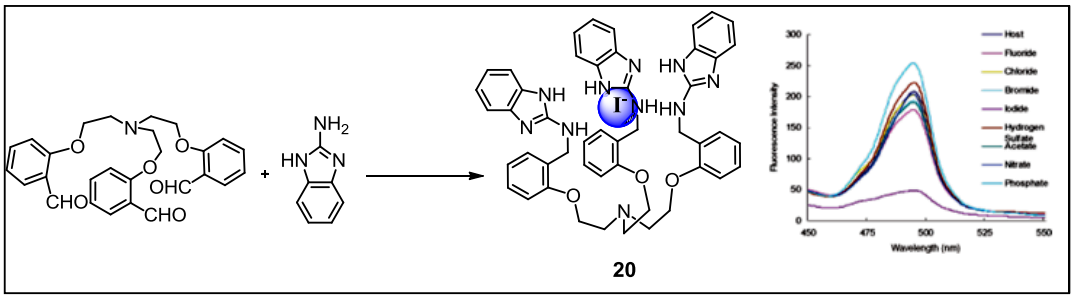


Figure 18 ***Tris-benzimidazole host***

A C_3 symmetric receptor **21** with triphenylene core having triazole heterocycle was found to be selectively binding the biologically important Cu^{2+} and CN^- ions[25] (Figure 19).

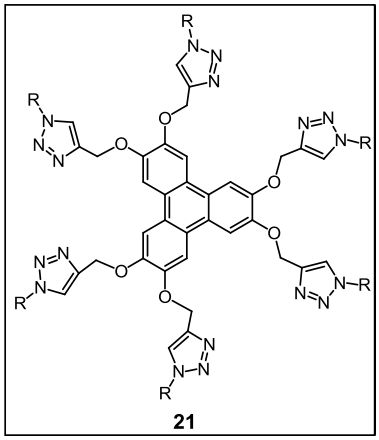


Figure 19 ***Triphenylene based tripodal triazole receptor***

A C_3 symmetric tripodal cationic imidazolium receptors were studied for recognition of various anions using NMR titrations. The nitro substituted imidazolium receptor **22** was having greatest affinity for chloride ions giving the corresponding complex as shown in figure 20.[26]

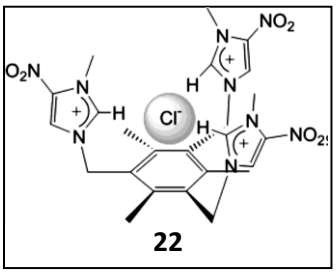


Figure 20 ***Tripodal cationic imidazolium receptor***

Tripodal esters **23** carrying electron deficient aromatic rings were found to have affinity for the halide anions as was observed through NMR titrations[27] (Figure 21).

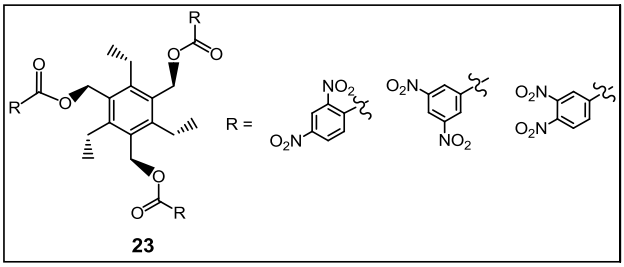


Figure 21 ***C_3 symmetric tri-esters as artificial receptors***

Guanidine and pyridine-2-carboxaldehyde derived C_3 symmetric tris-hydrazone receptor **24** recognize Zn^{2+} ion with switch ON fluorescence[28] (Figure 22).

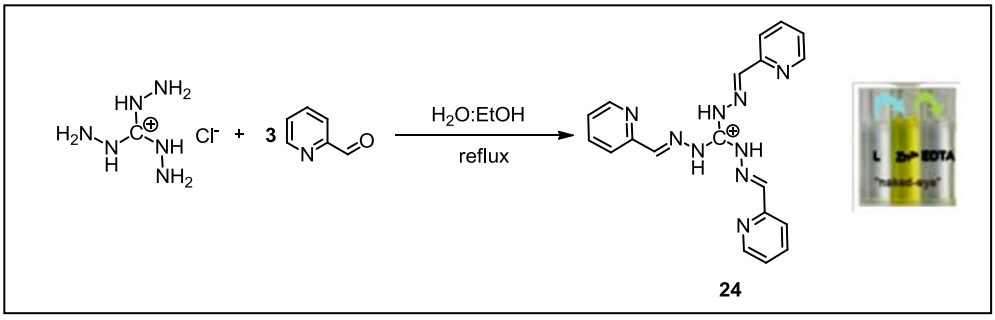


Figure 22 ***Fluorescent tripodal tris-hydrazone sensor***

TREN derived C_3 symmetric salen receptor **25** was found to be sensing Zn^{2+}, Fe^{2+} and Cu^{2+} ions using fluorescence and colorimetric techniques[29] (Figure 23).

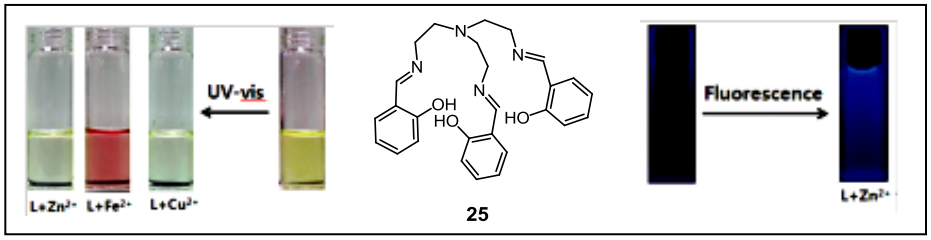


Figure 23 ***TREN derived tris-salen host***

A tripodal artificial receptor **26** having strong affinity for Fe^{3+} ion was designed[30] mimicking Enterobactin **27**, a natural C_3 symmetric receptor[31] (Figure 24).

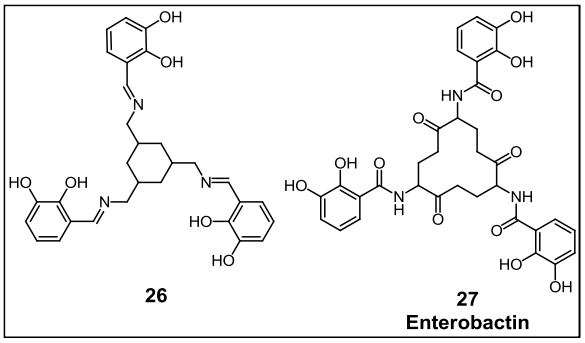


Figure 24 ***Tripodal host, mimicking enterobactin***

A C_3 symmetric tripodal receptor **28** (Figure 25) was prepared with salen binding sites near termini, which selectively recognize Ag^+ ion with enhancement in fluorescence.[32]

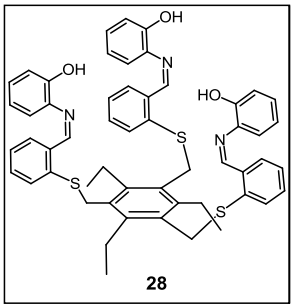


Figure 25 ***Tripodal host for Ag^+ recognition***

Similar tripodal receptor **29** with nitro substituted salen was found to selectively sense Cu^{2+} with switch off fluorescence[33] (Figure 26).

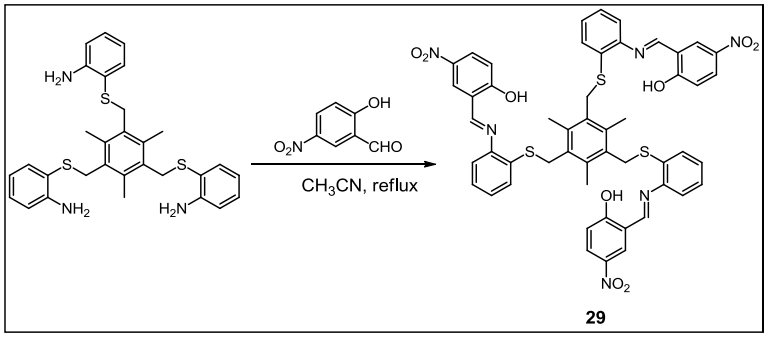


Figure 26 ***C_3 symmetric fluorescent host for Cu^{2+} recognition***

A C_3 symmetric compound **30** with guanidinium end groups was reported to recognize inositol-triphosphate (IP_3) through ionic interactions[34] (Figure 27).

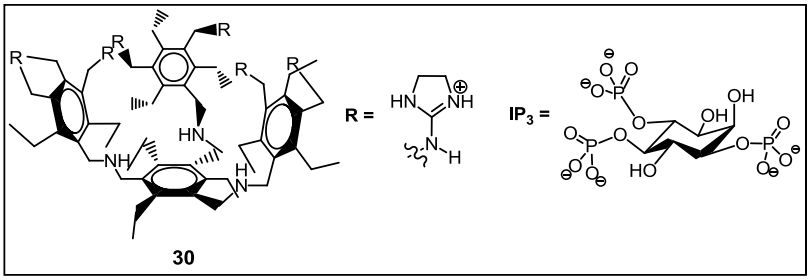


Figure 27 ***Tripodal tris-substituted amine as hosts***

A tripodal host molecule **31** with oxygen atoms as electron donor binding sites comparable with crown ethers accommodate Na^+ through ion-dipole type of interactions[35] (Figure 28).

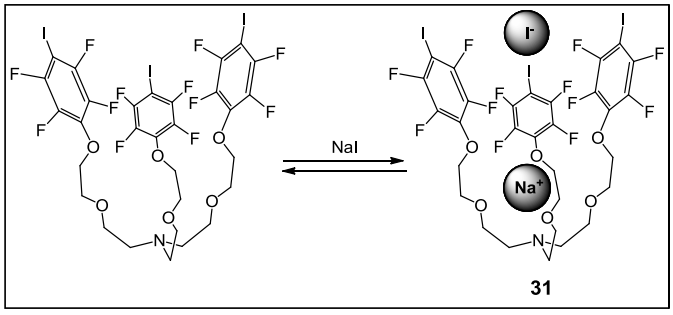


Figure 28 ***Tripodal artificial receptor***

1.1.4 *C_3* Symmetry and Materials Science

C_3 Symmetric molecules have been widely studied in the field of materials science with a wide range of properties and applications. Many C_3 symmetric compounds have been prepared are liquid crystalline because of specific structural features embedded in them.

Tris-aryl oxadiazoly aromatic compounds **32** with alkyloxy end groups exhibit columnar discotic liquid crystalline property were reported[36] (Figure 29).

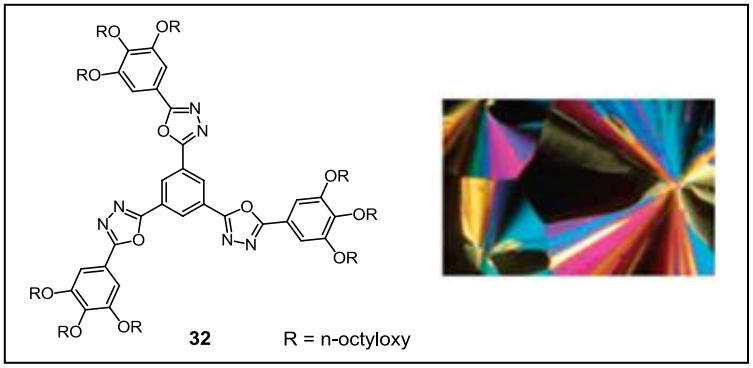


Figure 29 ***Tris-aryl oxadiazolyl molecules having LC property***

A C_3 symmetric molecule **33** having oxadizole heterocycle directly attached to the alkoxy chain and also connected to the central ring via phenylacetylene spacer exhibits discotic nematic liquid crystalline property as reported[37] (Figure 30).

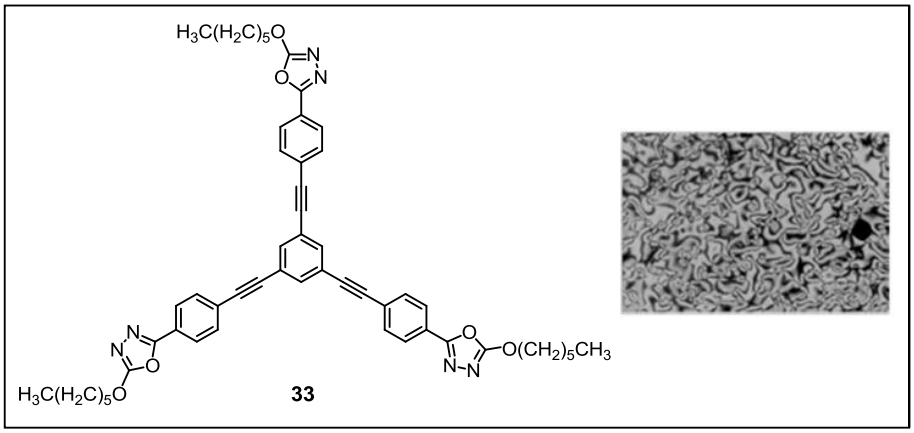


Figure 30 ***Tripodal tris-oxadiazole compound with LC property***

A highly luminescent discotic columnar compound **34** having tris-triazolyl triazine core group was synthesized via a click reaction.[38] The discotic columnar liquid crystalline property was observed in them at room temperature (Figure 31).

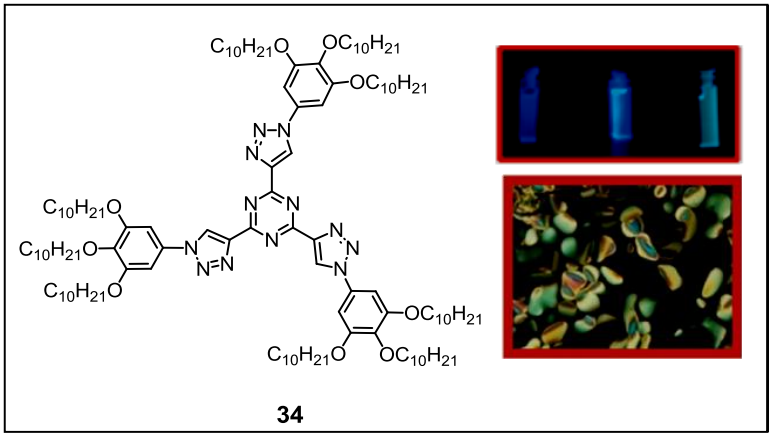


Figure 31 ***C_3 symmetric fluorescent compound with LC property***

Novel C_3 symmetric deep blue OLED emitters **35** were constructed by the Suzuki coupling of 1,3,5-trianthracenyl benzene with mono, di or tri-(dialkylfluorenes)[39] (Figure 32).

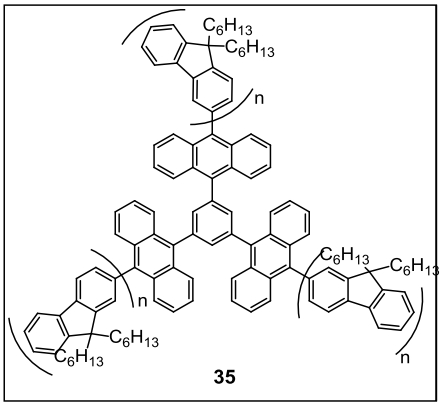


Figure 32 ***Highly fluorescent tripodal OLED emitters***

C_3 Symmetric tris-alkyltriazolyl benzene **36** prepared by the azide-acetylene click reaction on mixing with tri-octlyoxy benzoic acid in a 1:3 stoichiometry exhibited thermotropic columnar discotic liquid crystalline phase. The LC property resulted from threefold supramolecluar hydrogen bonding interactions between the alkoxy acid and the tris-alkylated triazoles providing conformational rigidity. The study was supported by the theoretical and spectroscopic data[40] (Figure 33).

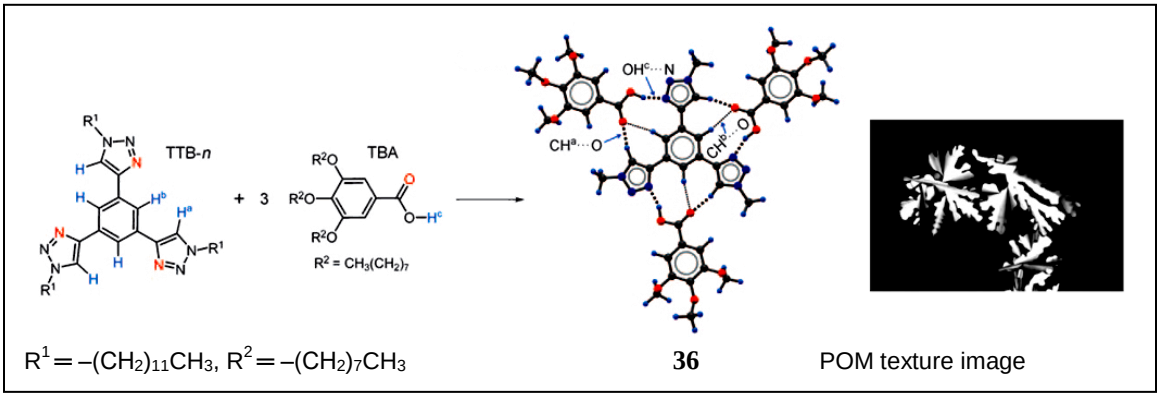


Figure 33 T*ripodal LC compounds having 1,2,3-triazoles*

C_3 symmetric molecules exhibit various other properties due to supramolecular interactions either among themselves or with solvent molecules or due to host-guest complexation or combination of all of these. Some representative examples of this kind have been presented in the following section.

1.1.5 C_3 Symmetry and Self-assemblies

The synthesis and self assembling properties of C_3 symmetric donor-acceptor molecule **37** containing 1,3,4-oxazdiazole and bisthiophene moieties near the core, functionalized with alkyl substituted phenylacetlyene units at the periphery are reported to form gels in both aliphatic and aromatic solvents giving different textures[41] as shown in figure 34.

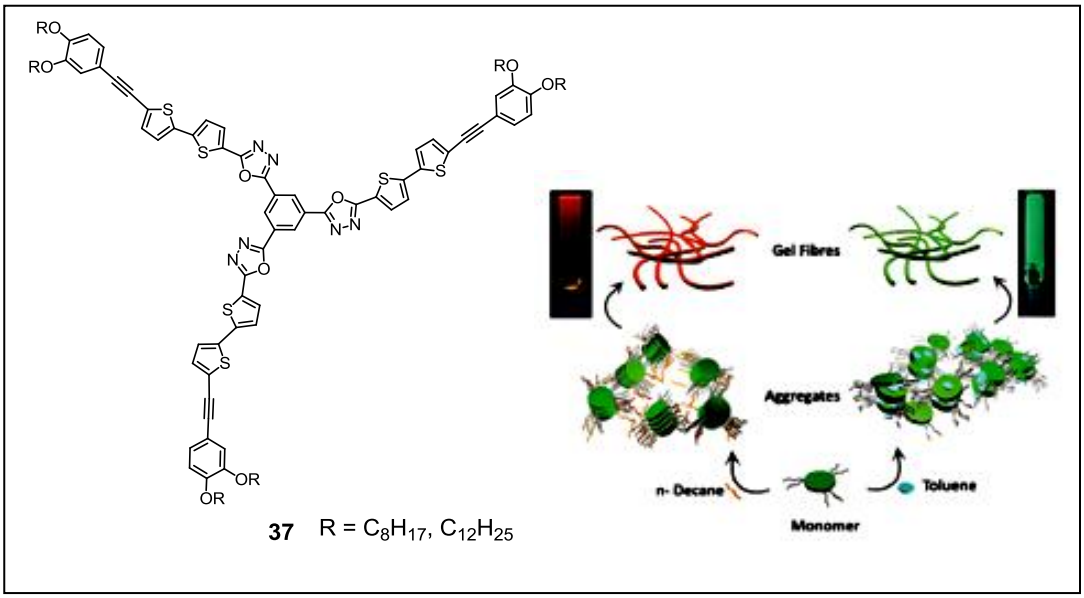


Figure 34 *Tripodal tris-oxadiazole-bis-thiophenes as organogel*

A pyridine based tripodal ligand **38** form metallogels in the presence of Pd(II) giving fibrous network and spherical assemblies as visualized under SEM.[42] Due to palladium π–π interaction and hydrogen bonding provide auxiliary forces to stabilize the gel (Figure 35).

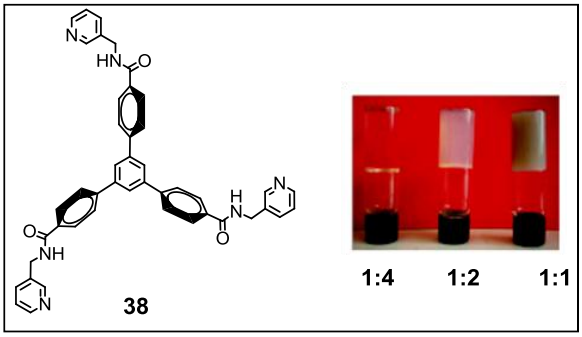
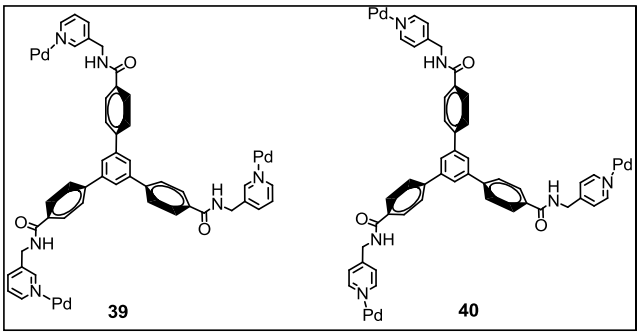


Figure 35 ***C_3 symmetric ligand as metallogel***

C_3 Symmetric tris-amides **39** and **40** prepared from trimesic acid chloride and 3-amino methylpyridines in the presence of Pd(II) ions resulted in a high symmetry nanosized octahedral cages with truncated octahedral geometry[43] as shown in figure 36.



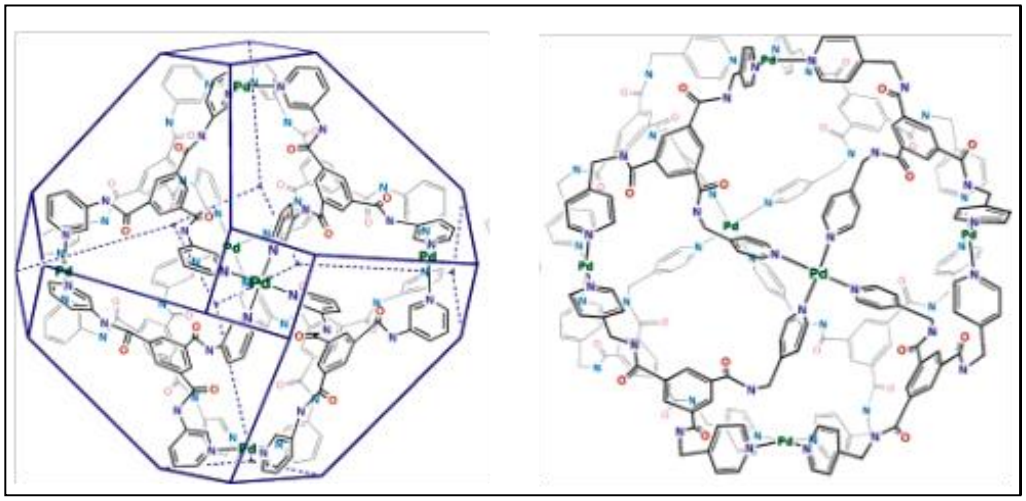


Figure 36 ***Octahedral nanocages from C_3 symmetric ligands***

C_3 Symmetric compounds are frequently used in the preparation of dendritic molecules.[44] One such 4th generation dendrimer **41** with tetrathiafulvelene incorporated as the end groups was found to bind with twelve molecules of Buckminster fullerene via non covalent interactions [45] (Figure 37).

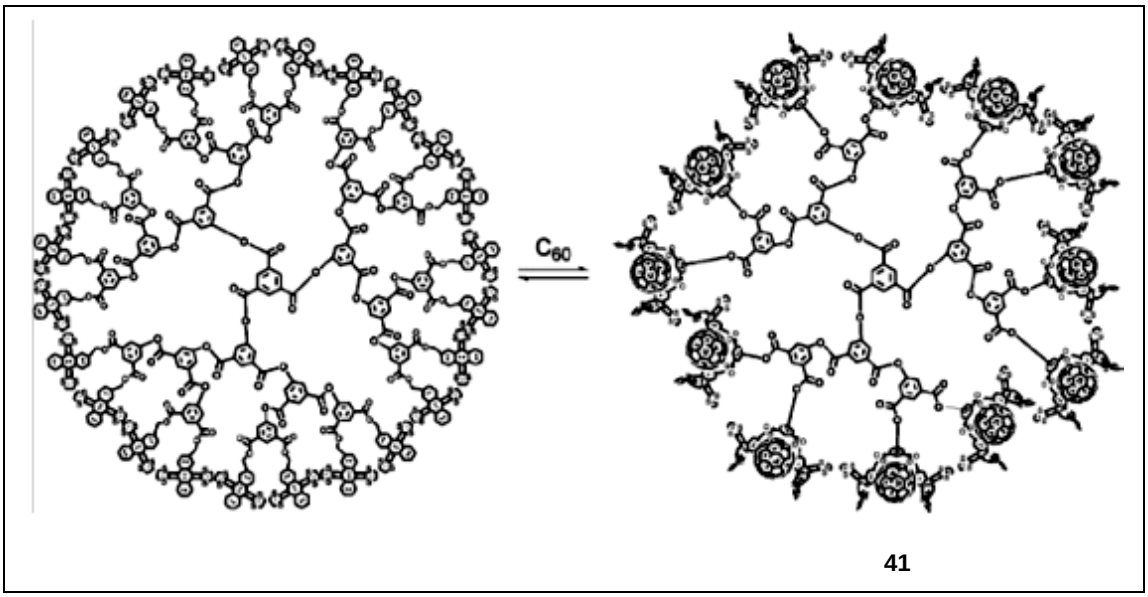


Figure 37 ***C_3 symmetric dendritic molecule with fullerene end groups***

1.1.6 Importance of Heterocyclic Compounds

Presence or introduction of a covalently bonded atom other than carbon or hydrogen in carbon compounds induces specific characteristics and properties in the resulting molecules. When this atom is part of a cyclic structure it is called a heterocycle and the compound containing such heterocycle is called heterocyclic compound. Heterocylces are classified according to their size and heteroatoms they posses (Figure 38). Five and six member heterocycles are more common than three or four member or higher member heterocycles. The most common heteroatoms which can have covalent bonding are nitrogen, oxygen and sulfur.

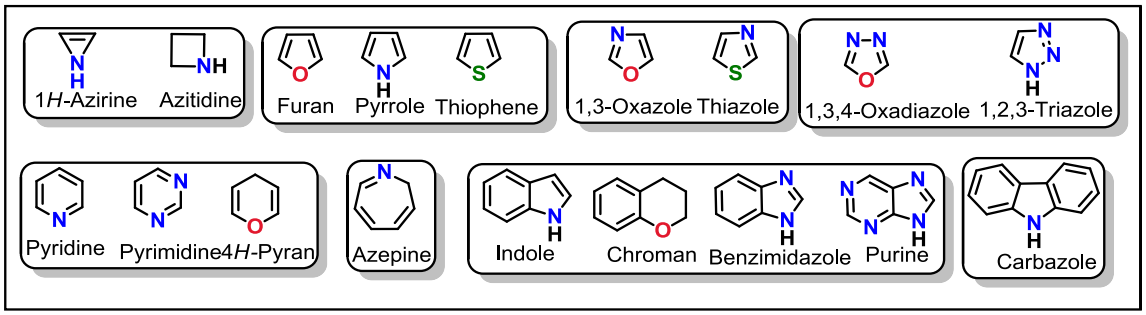


Figure 38 ***Some common heterocyclic compounds***

Most of the biomolecules have one or more heterocycles as part of their structures and their enzymatic or biochemical processes are greatly influenced by their presence. The double helix structure and functions of RNA and DNA are governed by the presence of heterocyclic bases and due to the supramolecular interactions present in their structure (Figure 39).

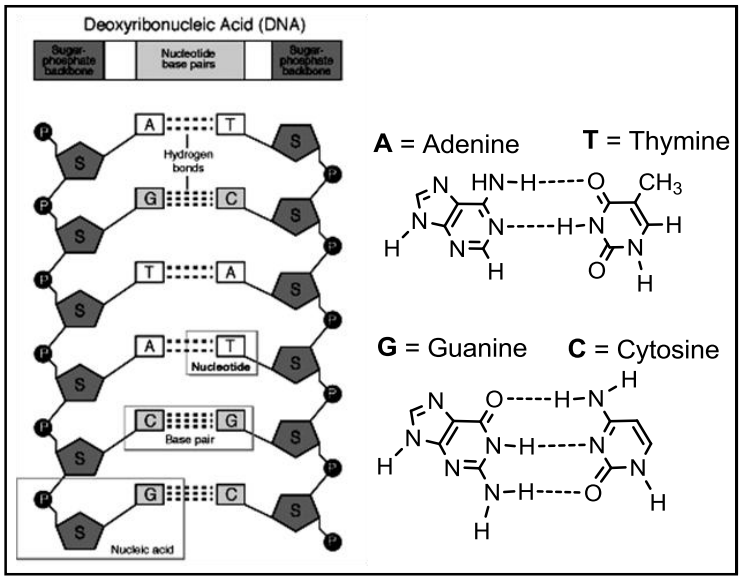


Figure 39 ***Single strand DNA structure***

Most of the medicinal compounds and drugs have one or more heterocycles as a part of their structure (Figure 40). This is attributed to the ability of heteroatoms in drug moleclules to coordinate with the biomolecules via non covalent interactions.

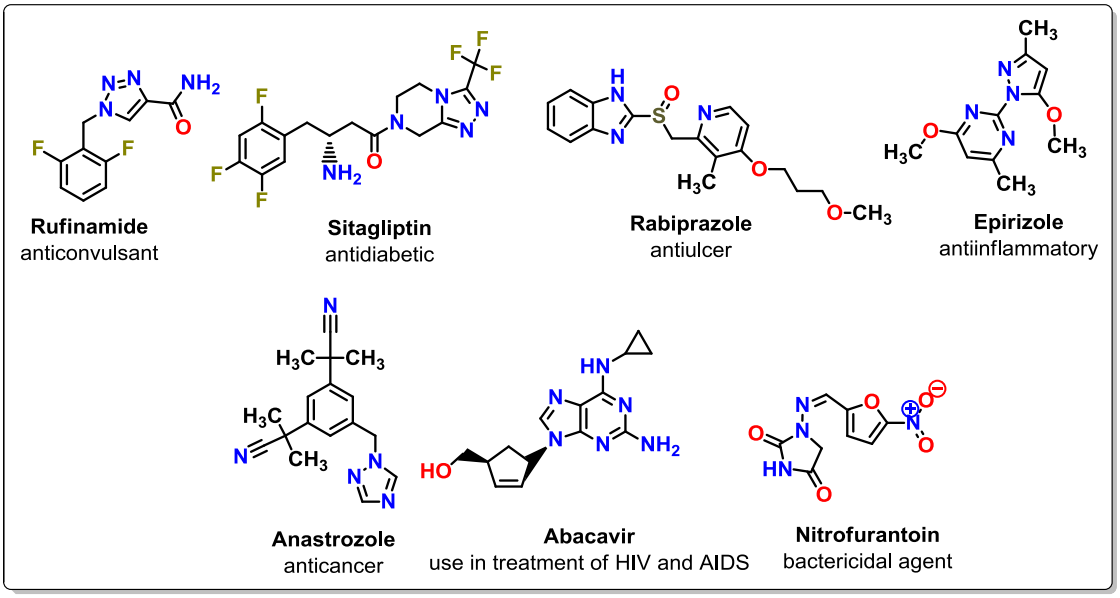


Figure 40 ***Some heterocyclic drug molecules***

Thus the non covalent interactions are heart of all the biochemical processes and of the supramolecular chemistry – the chemistry of non covalent bonds- taking place even outside the living systems are due to heteroatoms present in form of functional groups or as heterocycles.

The chemistry of C_3 symmetric compounds being a part of supramolecluar chemistry must also inculcate heteroatom or heterocycle as podand groups or linkers as an essential part of their structures. The design of C_3 symmetric compounds in the present study essentially involves the construction of podand groups having heteroatoms and/or heterocycles. A major part of it deals with the synthesis of such podands by assembling or introducing five member heterocycles in a single step threefold reaction strategy.

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