1.1 INTRODUCTION

Over the past few decades, significant progress has been made towards the design and synthesis of discrete molecular architectures via metal-directed self-assembly process.\(^1\) There are many reports available in literature for the construction of metallasupramolecular architectures like molecular triangles, molecular squares, molecular rectangles, prisms and other polyhedra.\(^{2-4}\) These molecular architectures have useful applications in molecular recognition, catalysis, selective guest inclusion and gas storage and electrochemical sensing.\(^5\) Among all supramolecular systems, the construction of metallasupramolecular systems with flexible ditopic ligands and rigid azine ligands are of current interest.\(^6\) Incorporation of flexible ligands into the metallasupramolecular systems, result in the formation of unusual novel products. Such macrocyclic host systems were found to change their cavity size depending upon the size and shape of the guest molecules. The ability of the host systems to change the cavity size and shape can be attributed to the flexibility of the bridging ligands.\(^7\) Molecular squares assembled from metallacorners and linear bridging ligands have highly ordered structures of discrete size and shape and were found to have enormous applications in the field of molecular sensors and molecular magnets.\(^8\)

1.2 Self-assembly

Self assembly is the fundamental principle which generates structural organization on all scales from molecules to galaxies.\(^9\) It is defined as reversible processes in which pre-existing parts or disordered components of a pre-existing system form structures of patterns. Self-assemblies can be classified as either static or dynamic.\(^10\) Static self-assembly is when the ordered state occurs when the system is in equilibrium and does not dissipate energy.\(^11\) Dynamic self-assembly is when the ordered state requires dissipation
of energy.\textsuperscript{12} Examples of self-assembling system include solar systems, histogenesis and self-assembled monolayers. The most well-studied subfield of self-assembly is molecular self-assembly.

1.3 Molecular self-assembly

Molecular self-assembly is the self organizing phenomenon from fundamentally distinct molecular entities using no external driving force to offer highly ordered macromolecular architectures. There are two types of molecular self-assembly, intramolecular and intermolecular. Intramolecular self-assembly is often achieved by the complex polymers with the ability to assemble from random coil conformation into a well-defined stable structure (secondary and tertiary structure)\textsuperscript{13} such as protein folding. Intermolecular self-assembly is the ability of molecules to form supramolecular ensembles (quaternary structure).\textsuperscript{14}

1.4 Supramolecular Interactions

Ever since the van der Waals interactions were brought in to focus, the weak non-covalent interactions have played a constitutive role in biological or biomimetic systems as well as in designing the synthetic supramolecular structures. Non-covalent interactions were leading to the formation of molecular clusters whereas the covalent interactions were dominating in classical molecules. Non-covalent interactions are weak interactions enough to bind different kinds of building blocks together into supramolecular entities.\textsuperscript{15} A covalent bond requires overlapping of partially occupied orbitals of interacting atoms, which share a pair of electrons. In non-covalent interactions, irrespective of overlapping, the attraction comes from the electrical properties of building blocks. Covalent bonds are generally stronger and shorter than 2 Å, while non-covalent interactions function within range of several angstroms. van der Waals interactions are classified by the nature of
interaction, based on the categorical strengths and bond energies.\textsuperscript{16} The non-covalent interactions or van der Waals forces involved in supramolecular entities may be a combination of several interactions, \textit{e.g.} ion-pairing, hydrogen bonding, cation–π and π–π interactions etc.\textsuperscript{17}

1.5 \textbf{Metal-directed self-assembly of discrete cyclic nanostructures}

1.5.1 \textbf{Molecular triangles}

Molecular triangle is one of the simplest and interesting lower nuclear basic macrocyclic systems. It strictly adheres to the directional bonding methodology. Molecular triangle requires three linear building blocks and three angular ones which are assembled in a cyclic manner. Self-assembled triangles involve building blocks with acceptor sides and donor corners. The design of triangles requires three angular and three linear components to be assembled in a cyclic manner. The design of such entities can be accomplished in two different ways. By using \(180^\circ\) connecting linear linking units in combination with \(60^\circ\) angular building blocks or by using distorted angular components with angles higher than \(60^\circ\) in combination with distorted linear linking units.

Stang and co-workers have reported a novel, self-assembled supramolecular triangle formed from the stoichiometric reaction of ditopic platinum acceptor unit and ditopic pyrazine donor unit in nitromethane. This assembly was monitored by multinuclear NMR spectroscopy and the structure was confirmed using single crystal X-ray analysis (Scheme 1.1)\textsuperscript{18}.
Puddephatt *et al.* have reported on the reaction of cis-blocked palladium(II) / platinum(II) precursors with amide functionalized angular or flexible bis(pyridyl) ligands that self-assembled to form molecular triangles. They have emphasized on the predictability of nature of the hydrogen bonded superstructure due to the presence of amide functionality in the molecular triangles (Scheme 1.2).
Scheme 1.2  Formation of \[ [(\text{bu}_2\text{bipy})\text{Pt}(\text{t-NC}_5\text{H}_4\text{-CONH-4-C}_5\text{H}_4\text{N})]_3 \] $6^+$(CF$_3$SO$_3$)
1.5.2 Molecular squares

Molecular squares are termed for discrete cyclic assemblies that possess per definition 90° turns in the assembly. Transition metals with square planar coordination geometries, in which the four coordination sites are separated by about 90° from the adjacent one are most suitable as metal corner building blocks for the square formation. Cis-metal corner units with 90° angle may be easily derived from such metal species by blocking two adjacent coordination sites with strong chelating reagents, but keeping the other two sites accessible for further coordinative interactions. Indeed, the readily available cis-protected Pd(II) and Pt(II) corners have proven to be versatile metal building blocks for molecular squares (Scheme 1.3).²⁰

Scheme 1.3 Formation of [(en)Pd(μ-bpy)]₄ 8(NO₃)
Stang et al. have designed and synthesized acetylene moiety incorporated platinum-based molecular squares wherein the acetylene moiety showed a range of metal-binding ability. The molecular squares upon reacting with silver triflate gave a host-guest complex wherein, silver was $\pi$ bonded through the acetylene moiety, which on further treatment with pyrazine, phenazine or 4,4’-dipyridyl ketone in acetone resulted in formation of corresponding ternary complexes (Scheme 1.4).$^{21}$

![Scheme 1.4 Formation of $\{[\text{cis-Pt(dppp)}(4\text{-ethynylpyridine})_2][\text{cis-Pt(dppp)}]_2\}4(\text{CF}_3\text{SO}_3)$](image)

1.5.3 Molecular rectangles

Molecular rectangles (tetranuclear metallacyclopahnes constructed with two different lengths of bridging ligands) can be synthesized through a stepwise synthesis.

Lu and co-workers have synthesized a series of neutral luminescent molecular rectangles $\{[\text{Re(CO)}_3(\mu-\text{bpy})\text{Br}]\{\text{Re(CO)}_3(\mu-\text{L})\text{Br}\}\}_2$ having $\text{fac-Re(CO)}_3\text{Br}$ as corners
and 4,4'-bipyridine (bpy) as the bridging ligand on one side and other bipyridyl ligands of varying length (L) on the other side. These molecular rectangles were characterized by a variety of analytical techniques such as IR, NMR and FAB-MS (Scheme 1.5).\textsuperscript{22}

\textbf{Scheme 1.5 Formation of [\{Re(CO)\textsubscript{3}(\mu-bpy)Br\}\{Re(CO)\textsubscript{3}(\mu-L)Br\}\]\textsubscript{2}}

Hupp and co-workers have reported on the synthesis of rhenium based neutral molecular rectangle, since a rectangular cavity was expected to offer enhanced binding and selectivity for planar guests. The molecular rectangle was constructed using M(CO)\textsubscript{3}Br (M = Mn, Re), bis-benzimidazole and 4,4'-bipyridine. This new class of molecular rectangles offer significant advantages over earlier metal-based rectangular host systems including overall charge neutrality, which facilitates solid state applications since potentially cavity-filling counterions are absent and luminescence, which provide a tag for sensory applications (Scheme 1.6).\textsuperscript{23}
Scheme 1.6 Formation of \{[M_2(CO)_6(\mu-BiBzIm)]_2(\mu-bpy)_2}\}

1.5.4 Molecular rhomboids

Han and co-workers have used conformationally flexible ligands like 1,2-bis(3-pyridyl)ethyne and 1,2-bis(3-pyridyl)-1,3-butadiyne in combination with chelated bis-phosphine platinum complex to synthesize metallasupramolecular rhomboids. In both the cases the chair conformers formed preferentially over their boat conformers due to the close imminence of the chelated bis-phosphine platinum groups. The photophysical properties of the rhomboids were studied using spectroscopic experiments and quantum chemistry calculations (Scheme 1.7). \(^{24}\)
Scheme 1.7 Formation of [(Et₂P)₂Pt(μ-L)]₂ 4(CF₃SO₃)

Chen et al. have synthesized a copper based molecular rhomboid by hydrothermal method. The molecular rhomboid was prepared from Cu(NO₃)₂, 1,10-phenanthroline (phen) and biphenyl-4,4′-dicarboxylic acid (H₂bpa). In the rhomboid, each [Cu(phen)]²⁺ acted as four corners that were bridged by four bpa²⁻. Solid state structure of the rhomboid evidenced the interpenetration of the molecules via supramolecular interactions to form a polyrotaxane (Scheme 1.8).²⁵
1.6 Synthetic strategy for the design of dinuclear metallacyclophanes

Dinuclear metallamacrocycles containing transition metal atoms in the backbone have been made by the directional bonding approach. The favourable conditions to prepare dinuclear metallacyclophanes are (i) ligands must be bidentate, (ii) ligands must be flexible, (iii) metal centers preferably have open coordination sites at 90°.
1.7 Synthesis of dinuclear metallacyclophanes

1.7.1 Synthesis of palladium based dinuclear metallacyclophanes

Hori et al. have reported the reaction of [Pd(en)(NO$_3$)$_2$] with 4,4'-bis(4-pyridylmethyl)-biphenyl in deuterated methanol to afford the palladium based dinuclear metallacyclophanes (Scheme 1.9).$^{26}$
1.7.2 Synthesis of dinuclear silver(I) metallacyclophanes

Wan and co-workers have reported the stepwise synthesis of silver(I) dinuclear metallacyclophanes. Imidazolinium precursor of 9,10-bis(N-ethylimidazoliummethyl)anthracene hexafluorophosphate was formed by treating 9,10 dichloromethylnaphthacene with N-ethylimidazole in a 1:2 molar ratio. The carbene precursor was further treated with silver oxide in acetonitrile medium to yield dinuclear metallacyclophane (Scheme 1.10). 27

Scheme 1.10 Formation of \([\text{Ag}(\mu-L)]_2 \text{PF}_6\)
1.7.3 Synthesis of Rhenuim(V) dinuclear metallacyclophanes

Gancheff et al. have reported on the synthesis of rhenium(V) based dinuclear metallacyclophane by the reaction of $[\text{ReOCl}_3(\text{PPh}_3)]$ with 1,2-bis(2,3-dimercaptobenzamido)ethane in the presence of sodium carbonate (Scheme 1.11).^{28}

![Scheme 1.11 Formation of (PPh₄)₂[ReO(μ-L)]₂](image)

1.7.4 Synthesis nickel dinuclear metallacyclophanes

Huynh and co-workers have prepared a nickel based dinuclear metallacyclophane from 1,2-bis(2,3-dimercapto phenyl)ethane (bdmpe) and nickel chloride in methanol medium in the presence of sodium methoxide as a base at room temperature (Scheme 1.12).^{29}
1.7.5 Synthesis of cyclic binuclear ytterbium metallacyclophanes

Zhao and co-workers have reported the preparation of \([\mu_2-p-(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4\text{YbCl(THF)}_2]_2\) from \(\text{N,N}'-\text{di(trimethylsilyl)p-benzene diamine, n-butyl lithium and anhydrous ytterbium chloride. \text{Ytterbium metallacyclophanes}}\)

Scheme 1.12 Formation of \(\text{Na}_4[\text{Ni}_2(\mu\text{-bdmpe})_2]\)

Scheme 1.13 Formation of \([\mu_2-p-(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4\text{YbCl(THF)}_2]_2\)
1.8 Synthetic strategy for the design of tetranuclear molecular squares

The favourable conditions to prepare tetranuclear metallacyclophanes are (i) ligands must be bidentate, (ii) ligands must be rigid and linear, (iii) metal centers must have open coordination sites at 90°.

1.9 Synthesis of tetranuclear molecular squares

Leadbeater et al. have reported on the photochemically generated molybdenum and chromium containing heterometallic molecular squares. In the first step, the metellacorner [Mo(CO)\(_3\)(4,4′-bpy)] was formed by the photolysis of Mo(CO)\(_6\) and 4,4′-bipyridine in the ratio of 1:2. Further photolysis of Cr(CO)\(_6\) with the metellacorner Mo(CO)\(_6\) in 1:1 ratio lead to the formation of heterometallic molecular squares (Scheme 1.14). \(^{31}\)
1.9.1 **Synthesis of transition metal based cationic molecular squares.**

Stang and co-workers have reported a systematic design approach for the synthesis of molecular squares that relied heavily on lipophilic phosphine substituted as well as chelated bis-phosphine platinum and palladium complexes. Reaction of the chelated complexes with equimolar amounts of 4,4'-bipyridine in dichloromethane at room temperature resulted in the formation of the molecular squares (Scheme 1.15). Characterization of these novel complexes were based on multinuclear NMR, physical properties and single-crystal X-ray diffraction studies.\(^{32}\)
1.9.2 Self-assembly of dicyano based molecular squares

Stang and co-workers have reported highly fluxional cyano-based macrocycles in solution by the reaction of bis(triflate) complexes with equimolar amounts of 1,4-dicyanobenzene and 4,4'-dicyanobiphenyl in CH$_2$Cl$_2$ at room temperature that gave the corresponding macrocyclic molecular squares (Scheme 1.16).\textsuperscript{33}

Scheme 1.15 Formation of [(dpppM)$_4$(µ-bpy)$_4$] 8(CF$_3$SO$_3$)

\begin{equation}
\text{Scheme 1.16 Formation of [(dpppM)$_4$(µ-dcb)$_4$] 8(CF$_3$SO$_3$)}
\end{equation}
1.9.3 Synthesis of ferrocene containing molecular squares

When the diaqua complexes of the ferrocenyl palladium and platinum complexes were treated with 2,7-diazapyrene, the desired heterobimetallic assemblies were isolated in excellent yields (Scheme 1.17). These molecular squares are an interesting combination of several redox-active ferrocenyl centers with highly conjugated aromatic linker units. The compounds are intensely colored both in solution and solid state and have interesting absorption spectra and electrochemical properties.\(^{34}\)

![Scheme 1.17 Formation of [Pd(dppf)(2,7-diazapyrene)]_4[CF_3SO_3]_8](image-url)
1.10 Host-guest chemistry of metallacyclophanes

Host-guest chemistry is also known as molecular recognition chemistry and it has been an emerging and fascinating research field, since J. M. Lehn pioneered on cryptands in which certain molecules unusually bind with other molecules. Molecular recognition deals with the selective binding approach of a specific substrate or analyte to a receptor molecule. This concept imitates biological interactions like antigen-antibody association or enzymatic reactions. Host-guest chemistry encompasses the idea of molecular recognition and interactions through noncovalent bonding. In discrete supramolecular systems, CH–π, π–π and hydrogen bonding interactions have been widely utilized to synthesize many host-guest complexes. Encapsulation of guest molecules in this type of metallasupramolecular assemblies is of great interest and the subject of many studies. These supramolecular compounds have many potential applications, ranging from drug delivery systems to molecular reaction chambers for catalysis and stabilization of reactive intermediates. The supramolecular architectures are very versatile and have been used to generate confined environments that encapsulate compounds, protect and stabilize an otherwise unstable molecule, inhibit certain enzymatic activity, recognize and trap specific guest molecules, or even act as microreactors for specific reactions.

1.11 Two-dimensional neutral dinuclear host-guest systems

Stang et al. have reported the reaction of flexible 1,3-bis(4-pyridyl)propane (1,3-bpyp) ligand and the neutral [Mn(hfac)₂(H₂O)₃] (hfac. 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate) acceptor complex to result into a metallacyclophane [{Mn(hfac)₂(1,3-bpyp)}₂](C₆H₆) (Scheme 1.18).
Scheme 1.18 Formation of [{Mn(hfac)$_2$(1,3-bpy)}$_2$](C$_6$H$_6$)

1.12 Two-dimensional neutral tetranuclear host-guest systems

Lu and co-workers have demonstrated the self-assembly of rhenium-based rectangular boxes with a large inner cavity via a simple one-step synthetic route and these molecules selectively recognize planar aromatic molecules. Rectangular box compound $[[{(CO)_3}Re(\mu\text{-CA})Re(CO)_3]_2(\mu\text{-bpy})_2]\text{mesitylene}$ was synthesized by reacting Re$_2$(CO)$_{10}$, 4,4′-bipyridine (bpy) and chloranilic acid (H$_2$CA) in a single step. The dianion of chloranilic acid (CA$^{2-}$) chelates to the two rhenium(I) atoms through the four oxygen atoms, acting as a tetradentate ligand. One mesitylene guest resides inside the cavity and interacts with the rectangular box with weak $\pi\cdots\pi$ and C–H–$\pi$ interactions (scheme 1.19).

45
\[2 \text{Re}_2(\text{CO})_{10} + 2 \text{H}_2\text{L}^1 + 2 \text{L}^2 \rightarrow \{(\text{CO})_3\text{Re}(\mu-\text{L}^1)\text{Re}(\text{CO})_3\}_2(\mu-\text{L}^2)_2\text{L} \]

CA = chloroanilic acid  
\(\text{bpy} = 4,4'\text{-bipyridine}\)  
\(\text{bpe} = 1,2\text{-bis}(4\text{-pyridyl})\text{ethylene}\)

\[\text{G} = \text{Mesitylene}\]

**Scheme 1.19** Formation of \[\{(\text{CO})_3\text{Re}(\mu-\text{L}^1)\text{Re}(\text{CO})_3(\mu-\text{L}^2)\}\]

### 1.13 Significance of Manganese chemistry

Organometallic compounds of manganese deserve particular interest owing to their specific role in chemical biology. Manganese ions are involved in the evolution of dioxygen during photosynthesis in chloroplasts in plants and they are also associated with many oxygen evolving complexes performing some important biological functions such as Mn-polypeptide to protect the reaction centre from redox and radical destruction.\(^{46}\) They have a vital role in halogen-metal exchange reaction and enantioselective catalysis as well.\(^{37}\) High-valent manganese(V)–oxo porphyrin complexes considered as reactive
intermediates in the catalytic oxidation of organic substrates and NHC–manganese(I) complexes are versatile carbene transfer agents.\textsuperscript{48}

On the other hand Mn(CO)\textsubscript{3} complexes play an increasing role in modern organometallic chemistry as [Mn(CO)\textsubscript{3}]\textsuperscript{+} fragment is recognized as a versatile arenophile in design and synthesis of novel supramolecular fabrication.\textsuperscript{49} Favorable properties such as high spin number, long electronic relaxation time, labile water exchange are responsible for the potential use of the manganese(II) compounds as an MRI contrast agent. Also manganese-based oxo clusters can be considered as another sort of contrast agents and prototypical single molecule magnets due to their high spin state and anisotropy.\textsuperscript{50}

Design and synthesis of novel Mn(I)-containing compounds yet remain as an enthusiastic and exciting research area because of the interesting physical properties observed for these materials, such as single-molecule magnetism of multinuclear Mn complexes. Mn(I) ions can be combined with bridging ligands capable of charge transfer in order to construct the molecular magnets.\textsuperscript{51}
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