

Synopsis

Nature has always remained a constant source of inspiration for chemists for synthesizing natural products, mimicking enzymatic reactions or to construct molecular architectures resembling biological assemblies. With the rapid growth of ‘Supramolecular Chemistry’ along with the advancement of the synthetic methodologies, molecular systems with brand new complexities have been synthesized, alongside the efficacy of weak, reversible non-covalent interactions have also been extensively explored. A number of such forces including hydrogen bonding, solvophobic effect, dynamic covalent interactions and metal-ligand coordination have been exploited to assemble the molecular building blocks and stitch them together to construct discrete ‘self-assembled’ architectures integrated with desired functionalities.

Metal-ligand coordination driven self-assembly certainly evolved as one of the most successful approaches for the construction of discrete supramolecular architectures during last two and half decades. The high directionality and reversible nature of certain metal-ligand bonds allow the pre-designing of sophisticated architectures which can be successfully obtained by ‘error corrections’ via a thermodynamically controlled self-assembly process. Numerous aesthetically elegant two dimensional (2D) and three dimensional (3D) metallosupramolecular architectures have been constructed which have been studied for various potential applications including guest encapsulation, catalysis, sensing, optoelectronics, drug delivery, protection of reactive species etc. Construction of such molecular architectures uses symmetric and rigid building blocks which strictly preserves their geometrical coding and thus finally determines the fate of the self-assembly. Pyridyl-based donors have been extensively used due to their well-behaved coordination with transition metal ions. Interestingly, imidazole based donors remained almost unexplored for such purpose mainly due to the rotational flexibility of imidazole moieties owing to the lack of π -electron delocalization with the aromatic backbone, which makes pre-designing an architecture extremely difficult. However, this unpredictability can lead to the formation of unprecedented molecular architectures. Furthermore, the conventional rigid ‘acceptors’ used in the ‘directional bonding approach’ always results in the formation of rigid assemblies, which cannot be utilized for the construction of smart molecular machine based applications. In this context, incorporation of restricted rigidity in the building blocks can be a convenient approach to construct versatile and flexible supramolecular architectures. Although flexible donors are quite common in coordination-driven self-assembly, the use of flexible metal acceptor is scarcely

reported in the literature.

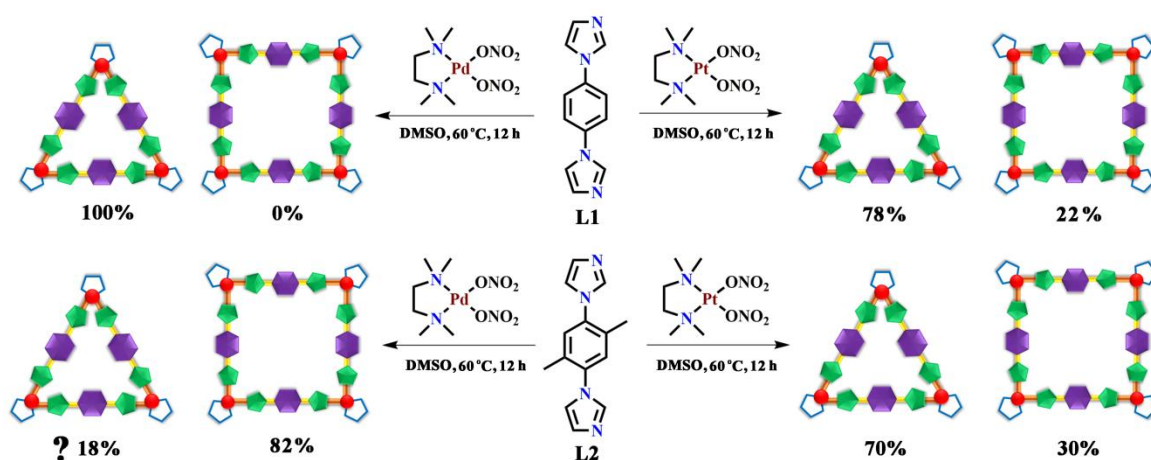
Highly symmetric spherical assemblies of square planar Pd(II) and Pt(II) ions are one of the most extensively studied metallosupramolecular architectures owing to their topological similarity with the spherical virus capsids. Unfortunately, none of the reported molecular spheres are soluble in water which restricts their applications in aqueous media. On the other hand, most of the metallosupramolecular architectures cannot be used for redox based applications as the oxidation state of the associated metal ions must be kept unaltered. Although, assemblies constructed mainly by the ferrocene containing acceptors are shown to be exhibiting redox property, the donor inherited redox active metallosupramolecular systems are extremely rare.

Discrete 3D metallosupramolecular cages have been extensively studied as synthetic hosts where the hydrophobic pockets have been utilized as safe shelter for reactive species, for catalyzing chemical transformations, tuning electronic and optical properties of guest molecules, as delivery vehicle for drug molecules etc. However, a major drawback of many such 3D cages is associated with their closed-shell topology, where the large cavities are accessible through relatively much smaller apertures which prevent larger guest molecules to enter inside. So, an interesting finding in this field would be to construct molecular hosts with larger apertures.

Picric acid (PA) is a strong organic acid and like many other polynitroaromatic compounds, it is a powerful explosive. In addition, it has large scale industrial application for the synthesis of dyes and pharmaceuticals. However, PA has potential health hazards and it is a water pollutant owing to its high aqueous solubility. Thus, the development of selective receptors which can efficiently interact with PA and detect it at very lower concentration is an appealing field of research.

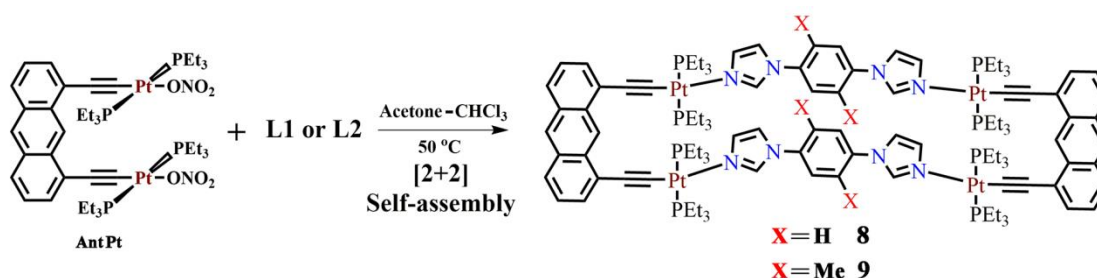
Chapter 1 briefly discusses the history of supramolecular chemistry and the concept of ‘self-assembly’ along with the several synthetic methodologies for the construction of discrete supramolecular architectures. It also includes a brief discussion on the various design approaches to construct 2D and 3D molecular architectures by metal-ligand coordination which is followed by an account on some of the important applications of such metallosupramolecular architectures. At the end, a small introduction on the fluorescence-based detection techniques for PA has also been included.

Chapter 2A accounts for the exploration of two linearly substituted benzene bisimidazole donors **L1** and **L2** for coordination-driven self-assembly. **L1** and **L2** possess different ‘natural’ donor angles as the imidazole moieties in **L2** are twisted heavily with respect to the phenyl plane due to the steric hindrance exerted by the methyl groups. Interestingly, while the self-assembly of **L1** with $[cis-(tmeda)Pd(NO_3)_2]$ (*tmeda* = N,N,N',N'-tetramethylethane-1,2-diamine) exclusively formed a [3+3] molecular triangle, the self-assembly of **L2** yielded a [4+4] molecular square as the major product with the same acceptor. In addition, similar treatment with the analogous Pt(II) acceptor resulted mixtures of [3+3] and [4+4] assemblies in both cases; however, the [3+3] assembly was the major product in case of **L2**. These contradictory product distributions in case of **L2** with analogous Pd(II) and Pt(II) acceptors could be corroborated by the delicate balance between the entropic and enthalpic contributions.



Scheme 1. Self-assembly of **L1/L2** with $[cis-(tmeda)Pd(NO_3)_2]$ and $[cis-(tmeda)Pt(NO_3)_2]$, respectively.

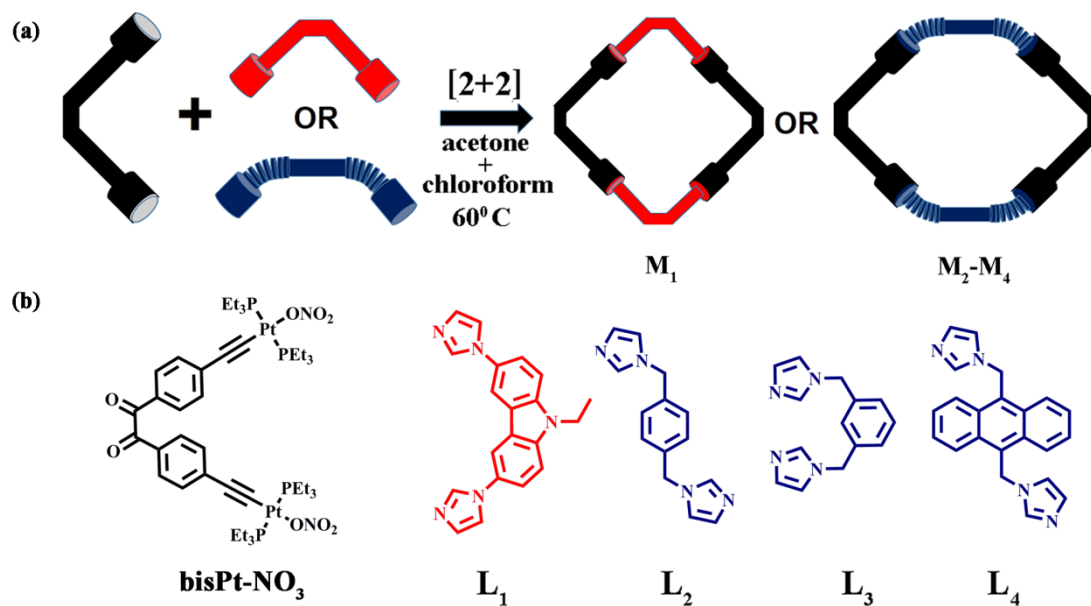
Furthermore, the reactions of **L1** and **L2** with a 0° bisplatinum acceptor, *viz.* **AntPt** yielded the expected [2+2] macrocycles (**8** and **9**), respectively. However, the interesting observations



Scheme 2. Self-assemblies of **L1** and **L2** with the 0° bisplatinum acceptor **AntPt**.

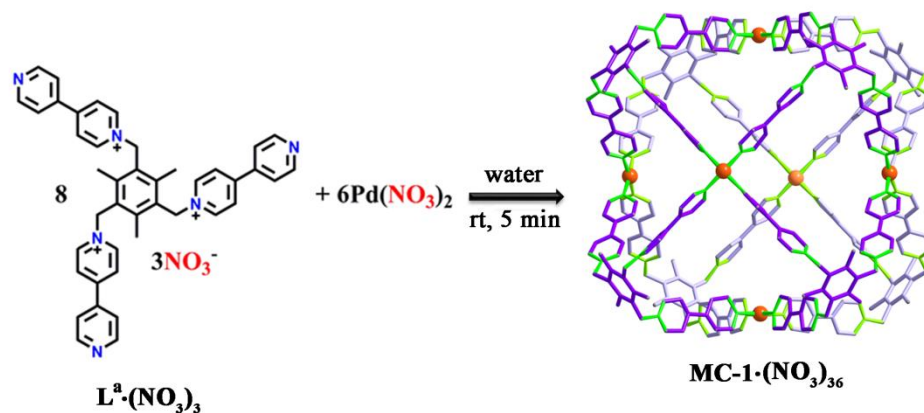
obtained from the variable temperature NMR studies suggested the existence of a mixture of inter-convertible conformational isomeric structures of **9**.

Chapter 2B describes the synthesis of a novel semi-rigid bisplatinum acceptor **bisPt-NO₃** based on benzil backbone for the construction of flexible metallamacrocycles. The benzil group was selected due to its unique rotational flexibility along the benzyl C-C bond which can generate a wide range of bite angles to make it compatible with the variety of donors of diverse shapes and sizes. The acceptor was successfully self-assembled with four different bisimidazole donors (**L1-L4**) to yield corresponding [2+2] metallamacrocycles (**M1-M4**) which were characterized by multinuclear NMR and ESI-MS spectrometry; and their structures were elucidated by semi-empirical geometry optimizations.



Scheme 3. Self-assembly of [2+2] metallamacrocycles **M1-M4** by a semi-rigid bisplatinum acceptor **bisPt-NO₃**.

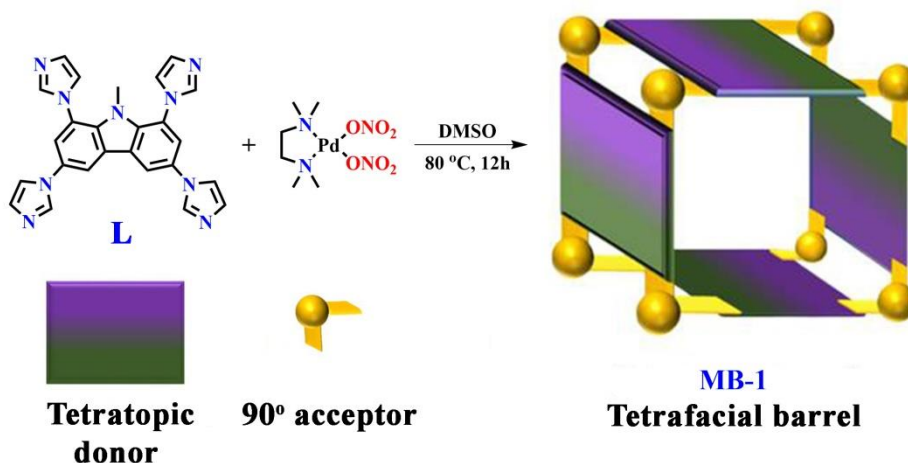
Chapter 3 discusses the synthesis of the very first example of a water soluble molecular sphere **MC-1** by the self-assembly of square planar Pd(II) ions with a flexible cationic tritopic donor **L^a·(NO₃)₃** containing 4,4'-bispyridyl arms. The structural flexibility of **L^a·(NO₃)₃** makes it capable of binding with metal ions in its *syn*- or *anti*-conformations which was also experimentally observed in the structures of the three newly synthesized coordination polymers, *viz.* **Ag-CP**, **Zn-CP** and **Cd-CP** constructed by using **L^a·(NO₃)₃** as (co)ligand. Finally, the 4:3 self-assembly of [**L^a·(NO₃)₃**] and Pd(NO₃)₂ in aqueous media produced the desired M₆L₈ type



Scheme 4. Self-assembly of the water soluble molecular dice **MC-1** from the tricationic tritopic donor $L^a \cdot (NO_3)_3$.

molecular sphere- **MC-1**, which contain 36+ overall charges. The compound could be easily solubilized in water after isolation as solid by simple stirring at room temperature. Single crystal X-ray diffraction analysis (SCXRD) revealed the ‘dice’-shaped architecture of **MC-1** where the eight faces are occupied by the coordinated Pd^{2+} ions and the bispyridyl arms and the vertices are occupied by mesityl moieties. **MC-1** is stable in aqueous media, however disintegrates in DMSO, as observed by variable temperature NMR experiments. In addition, **MC-1** also produced ligand inherited redox signals in cyclic voltammetry experiments.

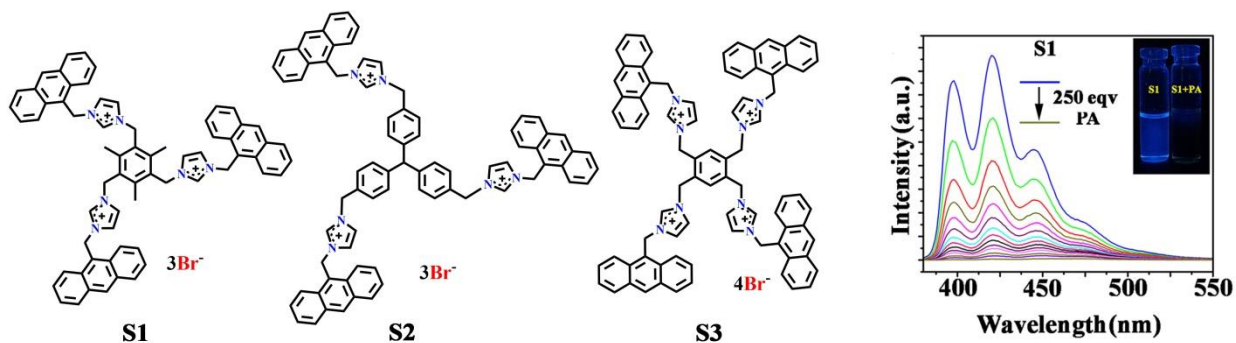
Chapter 4 describes the synthesis of a novel non-symmetric tetraimidazole donor **L** based on carbazole backbone. The complexity of the donor is associated with the allowed free rotation of the imidazole moieties along with the non-symmetric nature of the carbazole backbone which make **L** a very unusual donor for coordination-driven self-assembly. The crystal structure of **L** showed that the presence of the *N*-Me group caused a greater twisting of the nearby imidazole moieties with respect to the other set of imidazole moieties. The self-assembly of **L** with $[cis-(en)Pd(NO_3)_2]$ (*en* = ethane-1,2-diamine) yielded a mixture of M_4L_8 and M_6L_{12} type self-assembled products, as evidenced from the ESI-MS spectrometry. However, the DOSY NMR spectra of the product showed a single diffusion coefficient for all the peaks, indicating that both type of assemblies have similar size and hence suggested the formation of a tetrafacial barrel and a cubic architecture. A similar self-assembly of **L** with $[cis-(tmeda)Pd(NO_3)_2]$ also produced a water soluble product. ESI-MS spectra in this case only confirmed the formation of a M_4L_8 assembly- **MB-1**. SCXRD analysis of the coronene encapsulated complex of **MB-1** gave more insights on the sophisticated non-symmetric tetrafacial barrel architecture of **MB-1** with large



Scheme 5. Construction of the water soluble molecular barrel **MB-1** by the self-assembly of a non-symmetric tetraimidazole donor **L**.

rectangular apertures. The centrosymmetric molecule can encapsulate two aromatic guest molecules inside its hydrophobic cavity and was found to be efficiently encapsulating polyaromatic hydrocarbons (PAHs) in aqueous media. In addition, **MB-1** has been successfully exploited to carry water insoluble perylene molecule inside HeLa cells for fluorescence imaging purpose without showing significant toxicity. **L** also formed a water insoluble tetrafacial barrel (**MB-2**) by self-assembly with $[cis-(dppf)Pd(OTf)]$ (dppf=diphenylphosphino ferrocene) which interestingly has a symmetrical architecture, as evidenced from the SCXRD analysis. The formation of the symmetrical barrel is driven by the steric hindrance between the bulky phenyl groups of the nearby dppf moieties.

Chapter 5 reports the study of interactions between picric acid (PA) with a few newly synthesized fluorescent imidazolium salts (**S1-S3**). The fluorescence titration study of the positively charged receptors with PA showed rapid decrease of the corresponding fluorescence intensities upon gradual addition of PA. The Stern-Volmer plots suggested the involvement of both static and dynamic quenching mechanisms which was further supported by fluorescence lifetime measurements, NMR and UV-Vis spectroscopic analyses. The values of the Stern-Volmer constants (K_{sv}) reflected strong receptor-PA binding. The quenching efficiency calculations in the presence of several other analytes proved that the receptors are highly selective for PA in both aqueous and non-aqueous media. The mode of interactions in solid state was investigated by the crystal structure analysis of the [**S1**-PA] complex. 1H NMR spectra of the same complex indicated strong interaction between the imidazolium moieties of the receptor



Scheme 6. The fluorescent imidazolium salts based receptors **S1-S3** and the fluorescence titration plot for **S1** with PA. Inset: the solutions of **S1** and (**S1**+PA) in DMSO under UV light.

with PA in solution; however, no significant interaction of PA with the anthracene moieties was observed in solution as well as in the solid state. Also the quenching efficiencies and the K_{sv} values were correlated with the positive charge(s) present on the receptors with the help of two newly synthesized mono-positive receptors **S4** and **S5**.