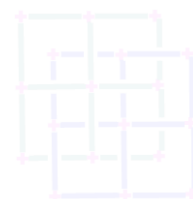
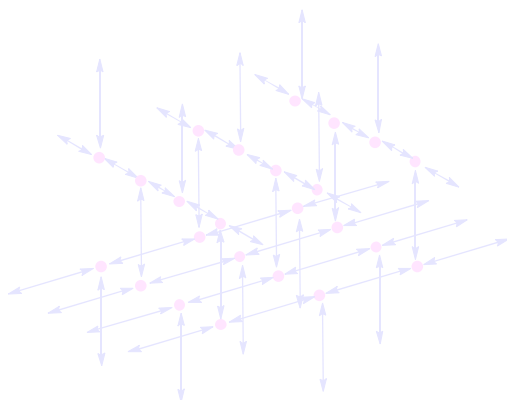




CHAPTER-1

Introduction



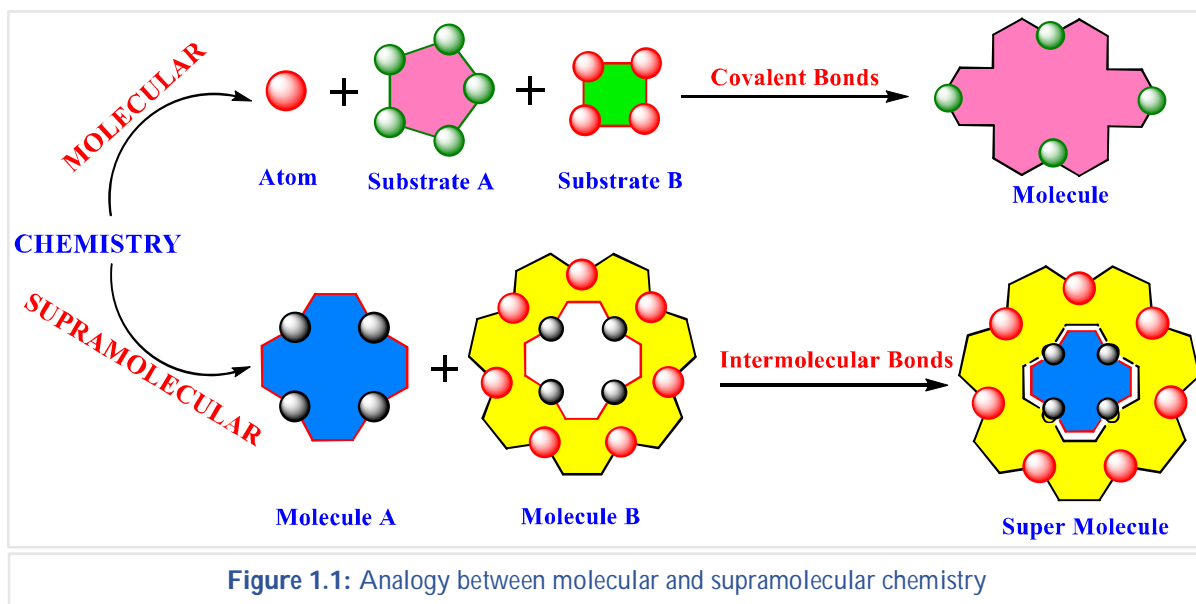
Introduction

1.1. Crystal engineering in supramolecular chemistry

A topic crystal engineering has emerged from crystallography. Designing new solid with desired properties becomes a challenging job without crystal engineering techniques. Supramolecular science is the main area of crystal engineering wherein the ‘supramolecular entity,’ intermolecular interaction decides the crystal packing. The supramolecular chemistry deals with molecular self-assembly, molecular recognition, host-guest chemistry through non-covalent interactions. It has originated from the concept of chemistry in a biological system such as hydrogen bonding^[1] and $\pi\cdots\pi$ stacking^[2].

1.1.1. Supramolecular chemistry

The term supramolecular chemistry is described in analogy with molecular chemistry: “Just as there is a field of molecular chemistry based on covalent bond, there is a field of supramolecular chemistry, the chemistry of molecular assemblies and the intermolecular bond” (Figure 1.1).^[3] Jean-Marie Lehn was awarded the Nobel Prize in 1987 along with Donald J. Cram and Charles J. Pedersen for their pioneering work in this field. Supramolecular chemistry is ‘chemistry beyond the molecules’ where two or more chemical species are associated by intermolecular forces or non-covalent interactions between a host and a guest molecule.



The term supramolecular chemistry is covered in the range of subjects from biological chemistry to material science and has potential in other fields.^[4] The main phenomenon of this term is molecular recognition according to their molecular complementary of host-guest binding sites and geometry. Only with the help of supramolecular entity, the giant molecular

structure could be predicted theoretically and experimentally. Crown ether is one of the earliest macrocyclic molecules in supramolecular chemistry.^[5] The first supramolecular polymer was reported by Lehn and co-workers.^[6] This polymer is an assembly of an equimolar mixture of repeat units uracil and 2,6-diaminopyridine via hydrogen bond interactions and constructed into hexagonal columnar extended network chain. This resulting network has been further grafted for rigid rod type frameworks in supramolecular chemistry.^[7] Parimal K Bharadwaj group has described in their review about the formation of discrete clusters of water molecules in various host metal-organic frameworks via the supramolecular entity.^[8] Vandana Bhalla has described the guiding forces for self-assembling process of supramolecular chemistry originates from the binding sites.^[9]

1.1.2. Crystal engineering

Crystal engineering is used for designing novel materials with desired properties by utilizing coordination bonding and intermolecular interactions such as hydrogen bonding.^[10] Gerhard Schmidt used the term crystal engineering in describing the cinnamic acid reaction in 1971.^[11] This term was also stated by Ray Pepinsky^[12] in 1955. Desiraju^[10] provided an ideal definition of crystal engineering which is described as “understanding of intermolecular interactions in the context of crystal packing and the utilization of such understanding in the design of new solids with desired physical and chemical properties.” This definition was universally accepted and appreciated in a similar way as the definition of “chemical bond” by Linus Pauling. Details of crystallization techniques, intermolecular interaction, and the history of crystal engineering are elaborated by G.R. Desiraju, J. J. Vittal and Arunachalam Ramanan in their well renowned textbook of crystal engineering.^[13]

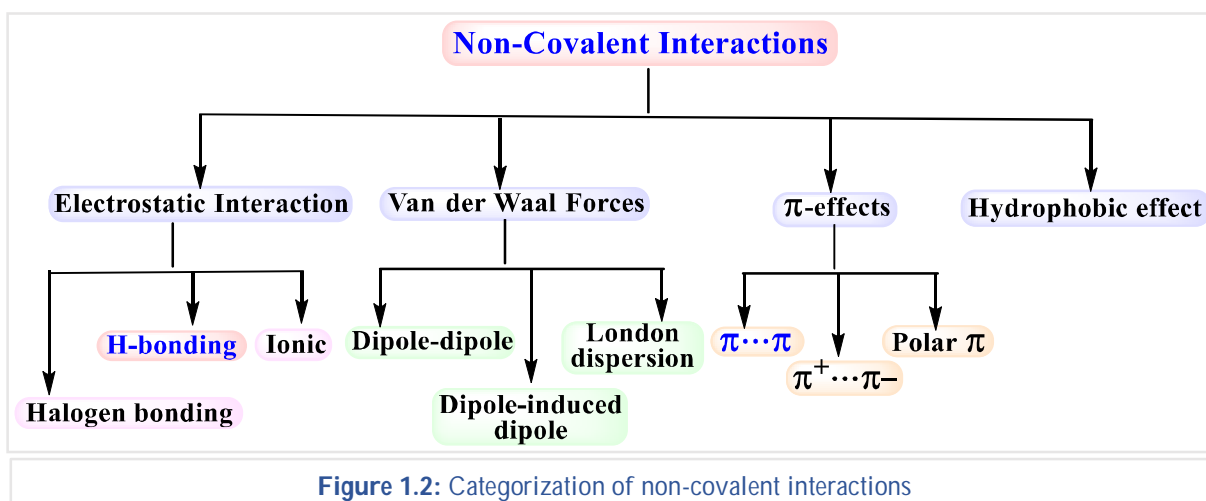
Hydrogen bond interactions are important tools in assembling molecules in designing crystal structures. Both the strong hydrogen bonds, like N-H•••O, O-H•••O, O-H•••N, N-H•••N and weaker C-H•••O and C-H•••N interactions play a vital role in arranging the molecules in the crystal and are important in determining the geometry of the network. Coordination bonding is another important interaction utilized in synthesizing new organic-inorganic hybrid materials. One of the important aspects in crystal engineering is the structural characterization by single crystal X-ray diffraction and analysing their properties.^[14] Cambridge structural database^[15] (CSD) is also explored widely to know about the supramolecular synthons and their possible arrangements in order to predesign any material. The chemist-crystallographer Robertson has made the correlation between the molecular structure and crystal structure by evaluation of

systematic experiments in crystal engineering.^[16] Thus, the crystal engineering technique leads the supramolecular synthon like it is an entity that is held together by intermolecular forces.

1.2. Backbone of supramolecular chemistry

1.2.1. Non-covalent interactions

Non-covalent interactions^[17] are the backbone of supramolecular chemistry, which helps in assembling the basic building blocks and holds the entire network architecture. These interactions can be categorised based on their strength and electronic factors. From the physics point of view, every interaction can be considered as an electrostatic effect due to the charge developed in species, which results in intermolecular forces between the molecules. Whenever these intermolecular forces are stronger than average kinetic energy of the molecules then assembling of supramolecular networks with a higher dimension will result. So, understanding such intermolecular interaction^[18] is the most important task for design of supramolecular architectures. Figure 1.2 summarizes the different categories of non-covalent interactions.^[19]



1.2.1.1. Hydrogen bond interactions

Hydrogen bonding is one of the most important non-covalent interaction and is described by Pauling's definition as, "Hydrogen bond is largely ionic in character and is formed only between the most electronegative atoms." There are many interpretations and descriptions of hydrogen bond interaction some of which considers partial covalent character in hydrogen bonding. Pimental and Mc Clellan studied the various hydrogen bonding and the definition given by them did not mention the chemical nature of atoms. Their definition also included the weak interactions C-H...N, C-H...O and so on.^[20] Steiner has defined "the X-H...A interaction as hydrogen bonding and mentioned it as a local bond, where X-H will behave like a proton donor to A (acceptor).^[21]

The IUPAC definition of hydrogen bonding was explored by Arunan et al., in 2011, where a list of six criteria defined the interaction and described hydrogen bond as “an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X-H in which X is more electronegative than H atom and an atom or group of atoms in the same or a different molecule, in which there is evidence of bond formation.” Figure 1.3 summarizes the definitions and descriptions of hydrogen bond interactions.^[22]

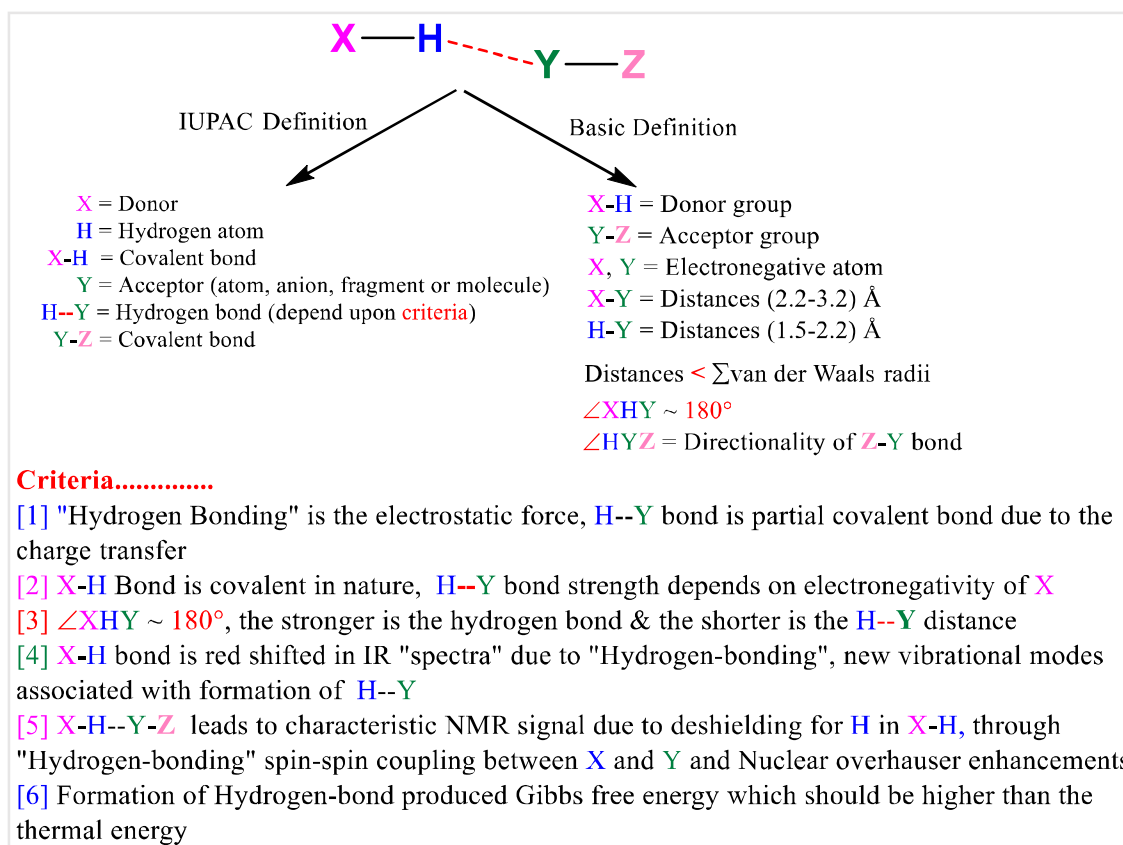


Figure 1.3: Comparison between IUPAC definition and basic definition

Hydrogen bond interaction being one of the most important tools in constructing supramolecular architectures, it is necessary to have a thorough understanding on the classification of hydrogen bond interaction based on strength.

The strength of hydrogen bonding depends on electronegativity of donor or acceptor atom. Based on strength, Jeffery has categorized the hydrogen bond interaction as ‘very strong’, ‘moderate’ and ‘weak’ hydrogen bond.^[23] G.R Desiraju characterized hydrogen bond interactions as ‘very strong’, ‘strong’ and ‘weak’ hydrogen bonds which extend from covalent limit (40 kcal/mol) to electrostatic limit (15 kcal/mol) upto van der Waals limit (0.25 kcal/mol) (Figure 1.4).^[24] Covalent character is observed rarely in very strong bond (20-40 kcal/mol), for example in an O-H...O hydrogen-bond interaction where the O...O distance is in the range 2.2

\AA -2.5 \AA . Strong hydrogen bonding functionalities such as O-H \cdots O, O-H \cdots N, N-H \cdots O, and N-H \cdots N have efficiently led to the formation of extended networks in MOFs/CPs.^[25] Weak hydrogen bond interactions such as C-H \cdots O, C-H \cdots N based on weak donor and O-H $\cdots\pi$, N-H $\cdots\pi$ based on strong donor is also equally effective in assembling of frameworks of MOFs/CPs.^[26]

C-H \cdots F-C and C-H \cdots Cl-C are denoted as the controversial hydrogen-bonding interactions due to non-polarizing nature of fluorine and chlorine atoms. These weak interactions are more prominent in hetero recognition (guest molecule interactions within a network) than in self-recognition.^[27] All these interactions are highly responsible for the crystal packing.

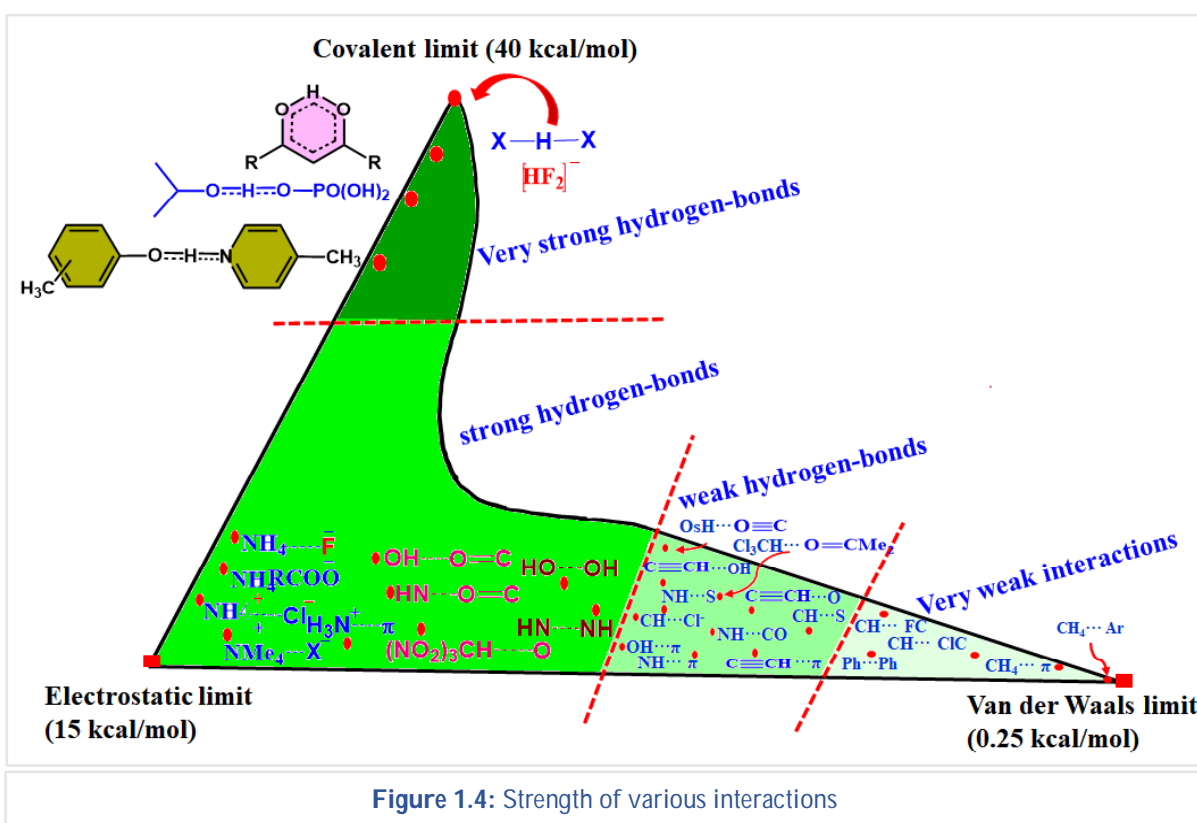


Figure 1.4: Strength of various interactions

1.2.1.2. π - π interactions

In 1990, Hunter and Sander have given a model on aromatic interaction which is considered as “a π system with an aromatic ring described as a positively charged σ -framework sandwiched between two regions of negatively charged $-\pi$ electron density”.^[28] $\pi\cdots\pi$ stacking can result in three types of orientations which are (i) *edge to face stacking* in a perpendicular manner known as T-shaped, (ii) *stacking in a parallel manner* and (iii) *stacking in offset parallel manner* (Figure 1.5a). The type of $\pi\cdots\pi$ stacking is decided by the quadrupole effect of two molecules.

The quadrupole moment arises from a partial negative charge above both the aromatic faces and a partial positive charge around the periphery (Figure 1.5b). π -interaction between lone pair and aromatic moiety is described by Martin Egli^[29] (water-hexafluorobenzene), Reyes et al^[30], (aromatic molecules- water), Jain et al^[31], ($>C=O \cdots \pi$ interaction in between formaldehyde and benzene) and Mak group^[32] ($>C=O \cdots \pi$) in different system. $\pi \cdots \pi$ interactions are effective in assembling of CPs. Recently, Zheng's group^[33] has synthesized a 1D coordination polymers based on π -conjugated pyrene moiety and established the mechanoluminescence property due to the existence of $\pi \cdots \pi$ interactions (Figure 1.6a). Another report on $\pi \cdots \pi$ stacking involves sewing of supramolecular architecture where 2D networks are connected to result in 3D networks (Figure 1.6b).^[34]

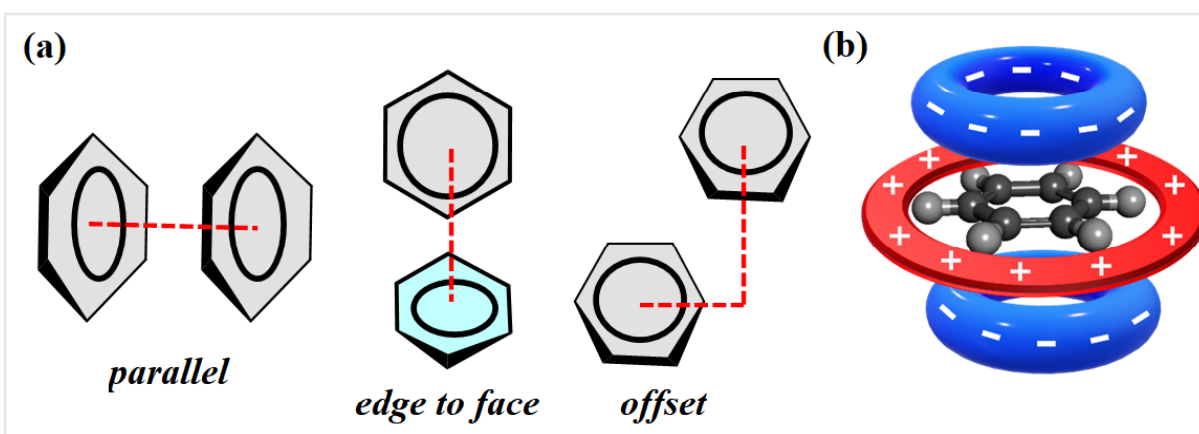


Figure 1.5: (a) Three conformers of benzene dimer for different π - π stackings, (b) Quadrupole moment of benzene

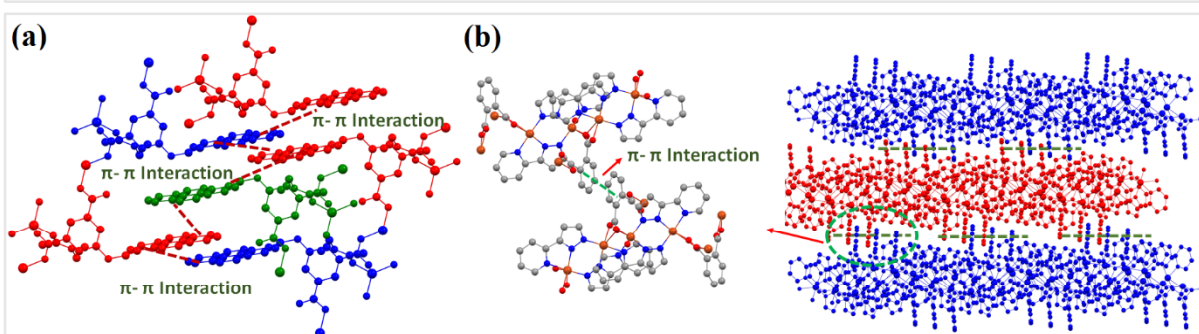


Figure 1.6: (a) $\pi \cdots \pi$ interaction in adjacent pyrene moiety in 1D CP (CCDC No. 1536824), (b) 2D network extending to 3D network through $\pi \cdots \pi$ interaction in a MOF of a pyrazole ligand (CCDC No. 925250)

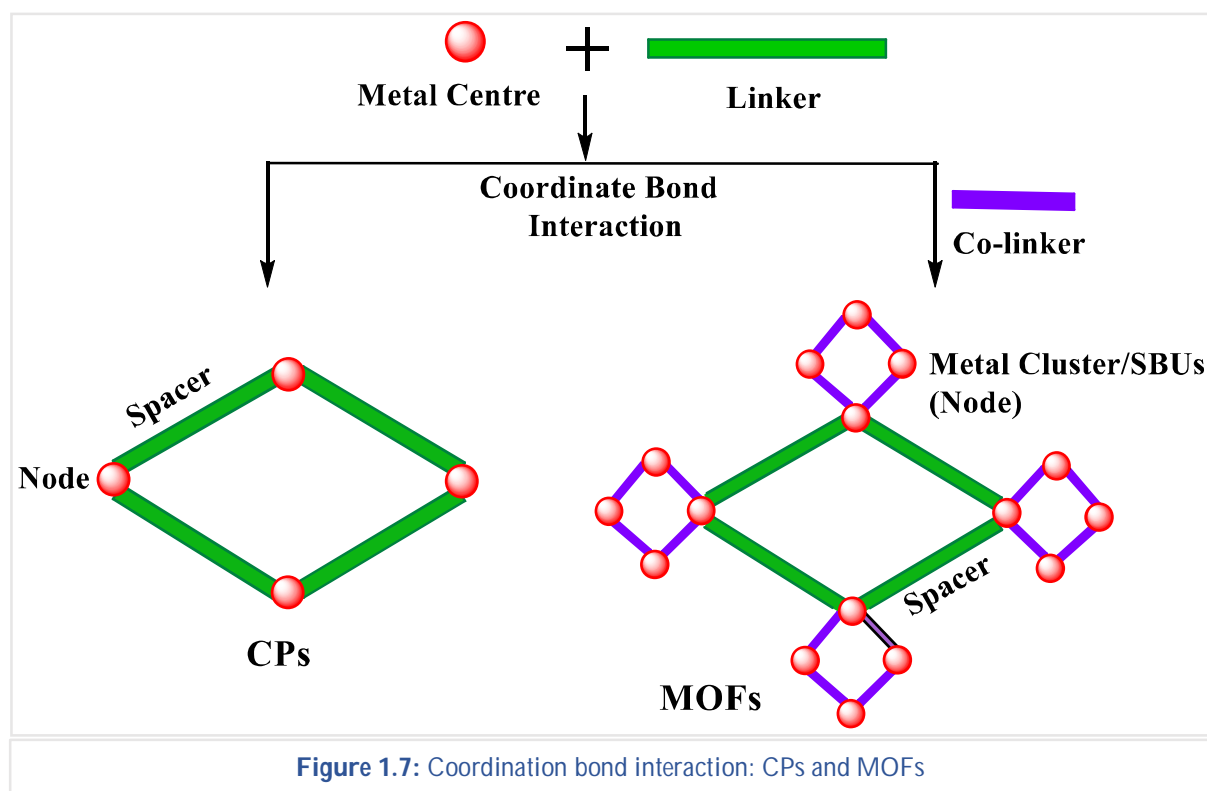
1.2.1.3. Coordinate bond interactions

Coordinate bond interactions arise between a metal (M) centre and organic ligand (L) and M-L interaction energy is in the range of 30-70 kcal/mol.^[35] The coordination preferences between metal and ligands are the primary phenomena for the frameworks in CPs as the basic understanding of coordination chemistry based on discoveries of Werner's coordination bond

in polymeric framework structures for position in different components. Structure directing phenomena of metal to ligand ratio, guest molecules, counter anions and reaction conditions are also decided the geometry in CPs.

1.3. Coordination polymers and Metal-Organic-Frameworks

Coordination polymers (CPs) are polymers where metal cations are linked by organic linkers. Robson and Hoskin described the CPs using ‘node’ and ‘linker’ approach.^[36] Reticular chemistry is described elaborately by Yaghi and co-workers^[37] and also introduced as the term secondary building units (SBUs) in metal-organic frameworks (MOFs) (Figure 1.7).^[38]



CPs/MOFs have shown to possess novel properties and are used in myriad application in all the field of chemistry. Reports on coordination polymers are started to appear from 1950s but their renaissance was in the 1990s when metal-organic framework (MOFs) drew attention due to their permanent porosities. The term MOF was defined by Yaghi et al., in 1995. They have synthesized a layered Co-MOFs where rigid disk-like conformation of molecular building unit of 1,3,5-benzentricarboxylic acid resulted in two layers of metal-carboxylate (MC).^[39] In 1997, Kitagawa et al., reported 3D CPs with permanent porosity, which also exhibited the gas sorption properties at ambient temperature. They have found a series of 3D interpenetrating (Section 1.3.4) networks where 4,4'-bipyridine (4,4'-bpy) was acted as pillar ligand and resulted

in ‘tongue and groove’ structure with channelling cavities which incorporated the small gas molecules.^[40] In 1999, Ian D. Williams and Yaghi groups reported MOFs, HKUST-1 and **MOF-5**, respectively. **HKUST-1**, $[\text{Cu}_3(\text{TMA})_2(\text{H}_2\text{O})_2]$ (TMA is 1,3,5-tricarboxylic acid), is a 3D open network with a pore size of 1 nm and BET surface area of $692.2 \text{ m}^2\text{g}^{-1}$. The large surface area in **HKUST-1** is due to the in situ formation of large SBUs of dicopper tetracarboxylate.^[41] Yaghi’s group has reported an exceptional stable and highly porous **MOF-5**, $[\text{Zn}_4\text{O}(\text{bdc})_3]$, where bdc = 1,4-benzenedicarboxylate linker resulted in the construction of tetrahedron cluster (Zn_4O), which constructed into a 3D framework. **MOF-5** showed a high Langmuir surface area of $2900 \text{ m}^2\text{g}^{-1}$ and a pore volume $1.03\text{-}0.92 \text{ cm}^3\text{g}^{-1}$ which is more than that of zeolite pores ($0.007\text{-}0.175 \text{ cm}^3\text{g}^{-1}$).^[42]

Structural flexibility of dynamic MOFs combined with several other unique characteristics is an added advantage to allure the field and distinguishing the MOFs from traditional porous solids. In 2002, Ferey’s group has reported a flexible open frameworks **MIL-47**^[43] and **MIL-53**^[44]. **MIL-47** is $[\text{V}^{+3}(\text{OH})[\text{O}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2] \cdot (\text{HO}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2\text{H})_{0.75}] / [\text{V}^{+4}(\text{OH})[\text{O}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2]]$, crystallized in 3D orthorhombic structure from the VCl_3 and terephthalic acid in water. The phenylene group acted as walls of the **MIL-47** pores and vanadium octahedron connected the walls to give corner support of the chains and resulted in large pore size with a BET surface area of $930 \text{ m}^2\text{g}^{-1}$. **MIL-53**, $\text{Cr}^{+3}(\text{OH}) \cdot [\text{O}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2] \cdot [\text{HO}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2\text{H}]_{0.75}$, isostructural with **MIL-47** and is built from Cr-III octahedra and terephthalate dianion resulting in 3D network having an array of 1D large pore channels ($1500 \text{ m}^2\text{g}^{-1}$ Langmuir surface area) with disordered terephthalic or water molecules. Both **MIL-47** and **MIL-53** showed antiferromagnetic properties at Neel temperature (T_N). Kim’s group^[45] reported a Zn dicarboxylate MOFs based on the mixed-linker $[\text{M}_2(\text{dicarboxylate})_2(\text{diamine})]$, where $\text{M} = \text{Zn}, \text{Cu}$, which showed versatile properties by varying the two linkers. Rowsell and Yaghi explored the adsorption-desorption properties of MOFs (especially the inclusion of $\text{CH}_4, \text{N}_2, \text{H}_2, \text{CO}_2$) based on chemically diverse carboxylate ligands and $\text{Zn}_4\text{O}(\text{CO}_2)_6$ cluster as SBUs unit.^[46] The different substituent of ditopic linker^[47] has resulted in cubic topologies in the MOFs, **IRMOF-1**, **IRMOF-8** and **IRMOF-18**, with octahedrally bound zinc metal ion. A tritopic linker has resulted in the construction of **MOF-177** with (3,6) connectivity which possesses a surface area of $4500 \text{ m}^2\text{g}^{-1}$.^[48] Czaja’s group has found a catalytic activity in **MOF-48** and **MIL-47** for the conversion of methane to acetic acid. **MOF-48** $(\text{VO}(\text{DMBDC})(\text{H}_2\text{DMBDC})_{0.4})$ where DMBDC is 2,5-dimethylbenzendicarboxylate, has VO_6 as SBUs and is connected with DMBDC chains resulting in the formation of 1D pores, where methyl groups are protruding out of the pores.^[49]

Kitagawa et al., classified the porous coordination polymer into three categories first, second and third generation of coordination polymers.^[50] The first-generation compounds sustained only with the presence of guest molecules in the pores/channels and removal of guest molecules resulted in irreversible framework collapse (Figure 1.8a). The second-generation compounds have stable and robust porous frameworks, which show permanent porosity even when the guest molecules are removed from the pores (Figure 1.8b). The third-generation compounds have flexible and dynamic frameworks, which respond to external stimuli, such as light, electric field, guest molecules, and change their channels or pores reversibly. Initial research in MOFs resulted in a wide range of first-generation frameworks (Figure 1.8c). But the lack of stability in first-generation MOFs upon guest removal is one of the major drawbacks. In the last few years, several examples of MOFs are afforded by the studies in crystal engineering, which are thermally stable and have robust frameworks even on the removal of guest molecules. The porous functionalities of these second-generation MOFs have been explored in the field of gas adsorption,^[51] separation,^[52] and catalysis^[53]. The porous functionality has been succeeded due to scaffold networks. Pre-design synthesis and construction of the frameworks have resulted in a stable scaffold structure. Robson's group has synthesised the diamond-structure with adamantane cavities by pre-examined the structure of $Zn(CN)_2/Cd(CN)_2$.^[36] Interpenetrate-structure, pillaring-structure, 'tongue and groove' structure are retained the structural frameworks even after the guest induced transformation/reformation successfully in the 2nd generation MOFs.^[40, 54] A 2nd generation CP $[Cu^{II}SiF_6(4,4'-bpy)_2]_n$ was reported by the Kitagawa's group, where 3D network is constructed from a square grid of $[Cu(4,4'-bpy)_2]_n$ and pillar of SiF_6 building blocks. The micropore channels in the CP held eight crystallized water

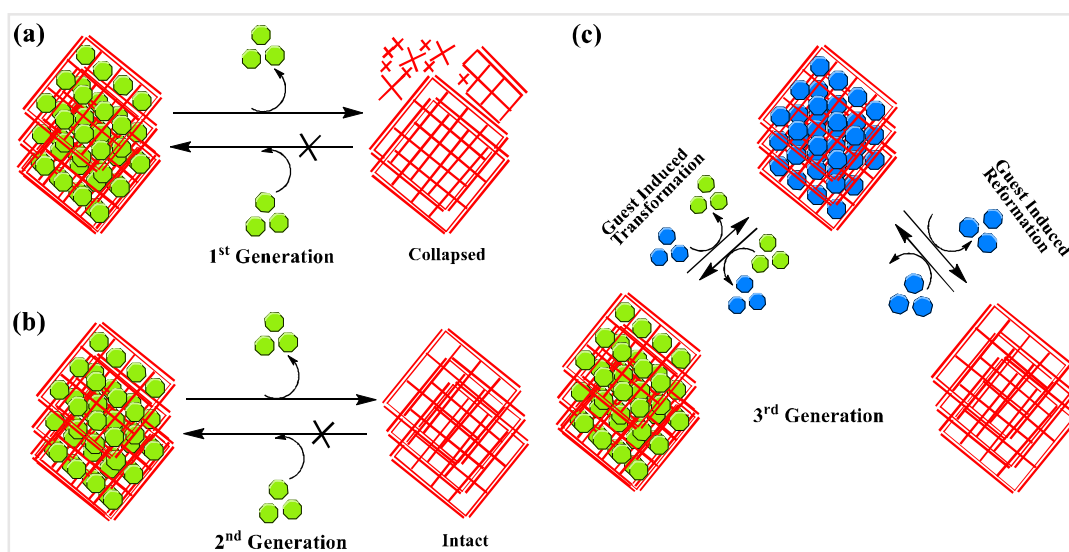


Figure 1.8: (a) Schematic representation of first-generation porous network MOFs, (b) third-generation porous network MOFs

molecules per Cu^{II} ion and adsorption- desorption of guest molecules were observed without any disintegration of the network.^[55]

Third generation^[56] CPs are categorized into three types: Type I: “Recoverable Collapsing”, Type II: “Guest Induced Transformation” and Type III: “Guest Induced Reformation”. Type-I, recoverable collapsing, is attributed to the crystalline to amorphous transformation during guest adsorption-desorption and some of the examples under this category includes: 2D porous frameworks $[\text{Co}(\text{NCS})_2(3\text{-pia})_2 \cdot 2\text{EtOH} \cdot 11\text{H}_2\text{O}]_n$, $[\text{Co}(\text{NCS})_2(3\text{-Pia})_2 \cdot 4\text{Me}_2\text{CO}]_n$, $[\text{Co}(\text{NCS})_2(3\text{-pia})_2 \cdot 4\text{THF}]_n$, where 3-pia = *N*-(3-pyridyl)isonicotinamide. The network changes observed during the removal of guest molecules ($\text{C}_2\text{H}_5\text{OH}$, $(\text{CH}_3)_2\text{CO}$ and THF).^[57]

A series of Type I - 3rd generation CPs were reported by Biradha et al., which are open square grid networks and interpenetration of frameworks are eschewed due to the presence of guest molecules in the pores. In one of their reported CPs, $([\text{M}(\mathbf{B1})_2(\text{NO}_3)] \cdot \text{Guest})_n$ where $\text{M} = \text{Ni}(\text{II})$ and $\text{Cu}(\text{II})$ and $\mathbf{B1} = 9,10\text{-bis}(4\text{-pyridyl})\text{anthracene}$, guest molecules nitrobenzene and cyanobenzene are connected as the 1D columnar way through $\text{C-H} \cdots \pi$ aromatic interaction with the anthracene moiety of the linker and resulted in an open square grid framework (dimension $15 \text{ \AA} \times 15 \text{ \AA}$). 4,4'-bpy and its analogue 1,4-bis(4-pyridyl)benzene ($\mathbf{B2}$) also resulted in square grid networks with benzene as guest molecule inside the layers in $([\text{Ni}(\mathbf{B2})_2(\text{H}_2\text{O})] \cdot (\text{Guest}) \cdot 5\text{MeOH} \cdot 2\text{NO}_3)_n$.^[58]

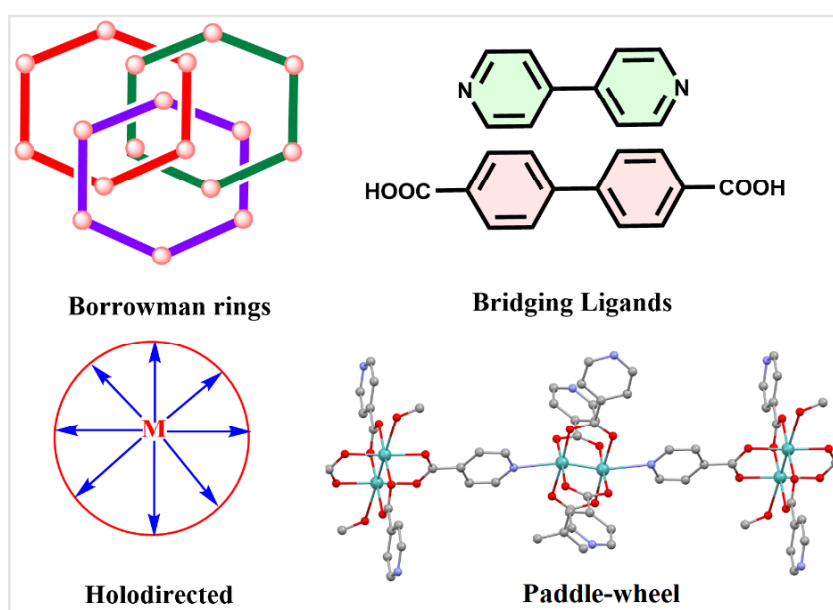
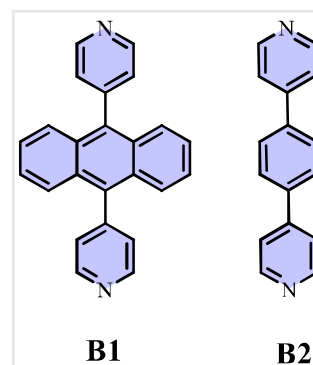


Figure 1.9: Different architecture of 1D CPs/MOFs (Paddle-wheel: CCDC No. 1850472)

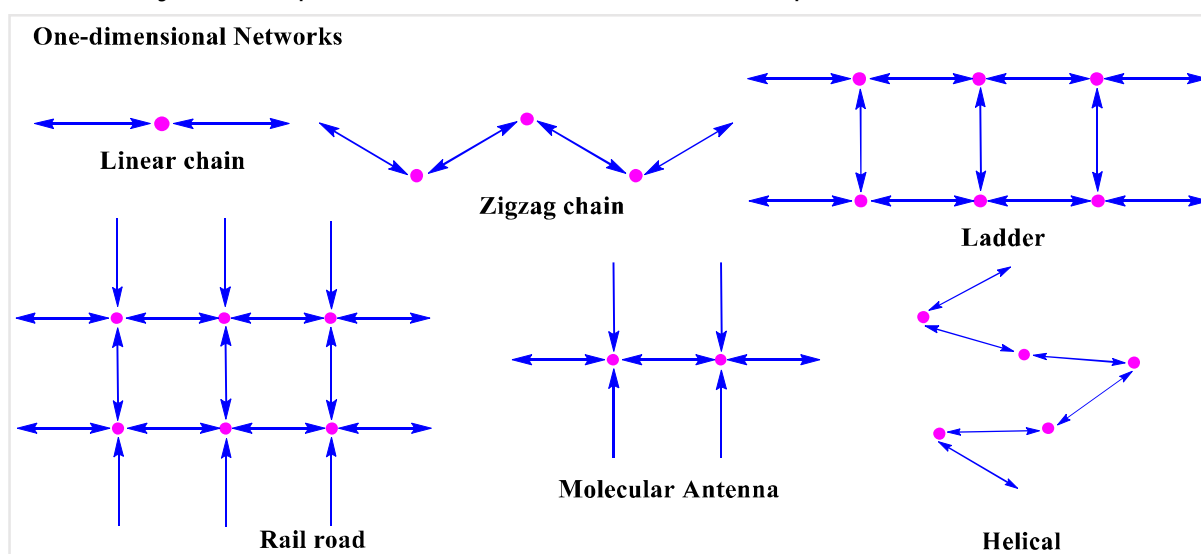
There are vast reports on MOFs/CPs using 4,4'-bpy, and dicarboxylic acid due to their attractive connecting networks like bridging, pillaring, layering, (borromean, holodirected, paddle-wheel, etc., (Figure 1.9). The miracle supramolecular materials, “metal-organic frameworks”, a subclass of coordination polymers are organic-inorganic hybrid solids with infinite uniform 1-dimensional (D), 2-D, and 3-D framework structures built from organic linkers and inorganic metals as secondary buildings units (SBUs).^[59] 1D CPs/MOFs include linear chain, zigzag, ladder, rail-road, molecular antenna, helical while 2D has brick wall, honeycomb, bilayer, square grid, herringbone and diamond, cubic and Lincoln logs are some of the networks under 3D CPs/MOFs (Figure 1.10).^[60] Various geometries of CPs/MOFs are triggered by reaction conditions such as temperature, pressure, solvent and metal-ligand ratio. Metal valency and coordination preference of metal centre have a significant role in directing the network architecture of the CPs.

1.3.1. One dimensional networks (1D CPs/MOFs)

The 1D CPs have the simplest geometry and most of them possess interesting properties like magnetic, electrical, mechanical, and optical properties. Zigzag, helical, molecular antenna, railroad, ladder, rotaxane, and ribbon/tape types 1D geometries are formed when ligands are bound with the metal ions in a particular ratio and some specific conformation.

1.3.1.1. Linear geometry

One of the earliest 1D coordination polymer of 4,4'-bpy with Co(II) was reported in 1982 by Kubel et al., (Figure 1.11a).^[61] Hosseini group has reported double-stranded linear CPs of $[AgB3(CIO_4)]$, where **B3** is the derivative of 4,4'-bpy type with hexaethylene glycol functionality and this part formed circular conformation loop on a linear chain, further such



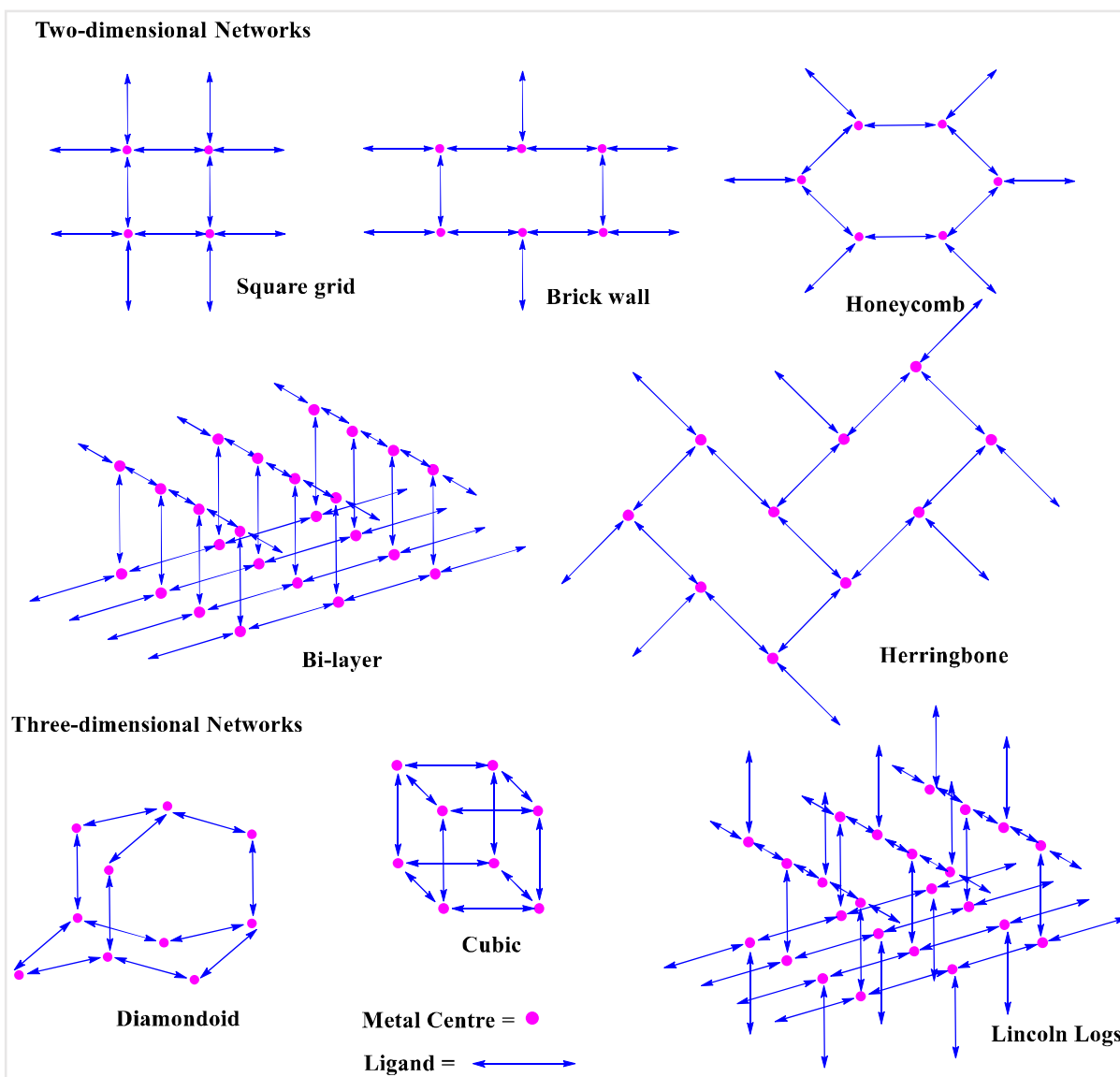
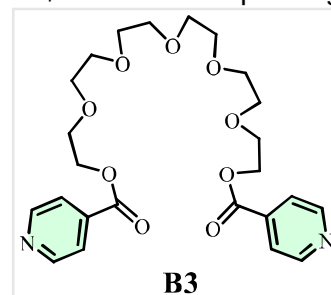


Figure 1.10: Overview of different types of geometries in 1D, 2D, and 3D networks

two chains propagated in a parallel fashion resulted in double-stranded by hugging each other (Figure 1.11b).^[62] Under the category of 1D linear networks of CPs, the different packing patterns of the CPs was observed, which include ‘stacking of polymeric chains’^[63], ‘crisscross’ (Figure 1.11c)^[64] ‘layers from different chains’ etc. Jin’s group has reported unusual interesting pipelike 1D polymer where 1D linear chains are connected by four different 4,4'-bpy to form square-based hollow pipes.^[65]



1.3.1.2. Zigzag geometry

Ligand to metal ratio is greatly influences the resultant geometry of CPs, such as zigzag, helical needs 1:1 ratio. Zigzag conformations are designed from the flexible exoditopic ligands.

Morsali and co-workers have reported a series of 1D zigzag CPs based on Zn and dipyridyl ligands (Figure 1.12a).^[66] Long bis(4-pyridyl) ligand also resulted in interesting supramolecular zigzag arrangement. For example, in a CP of 4,4'-bis(pyridin-4-ylmethoxy)-1,1'-biphenyl (**B4**) ligand, one **B4** is perpendicular and another **B4** is parallel to the plane of zigzag chain with dihedral angles 81.5° and 4.3° .^[67] Zigzag geometry can

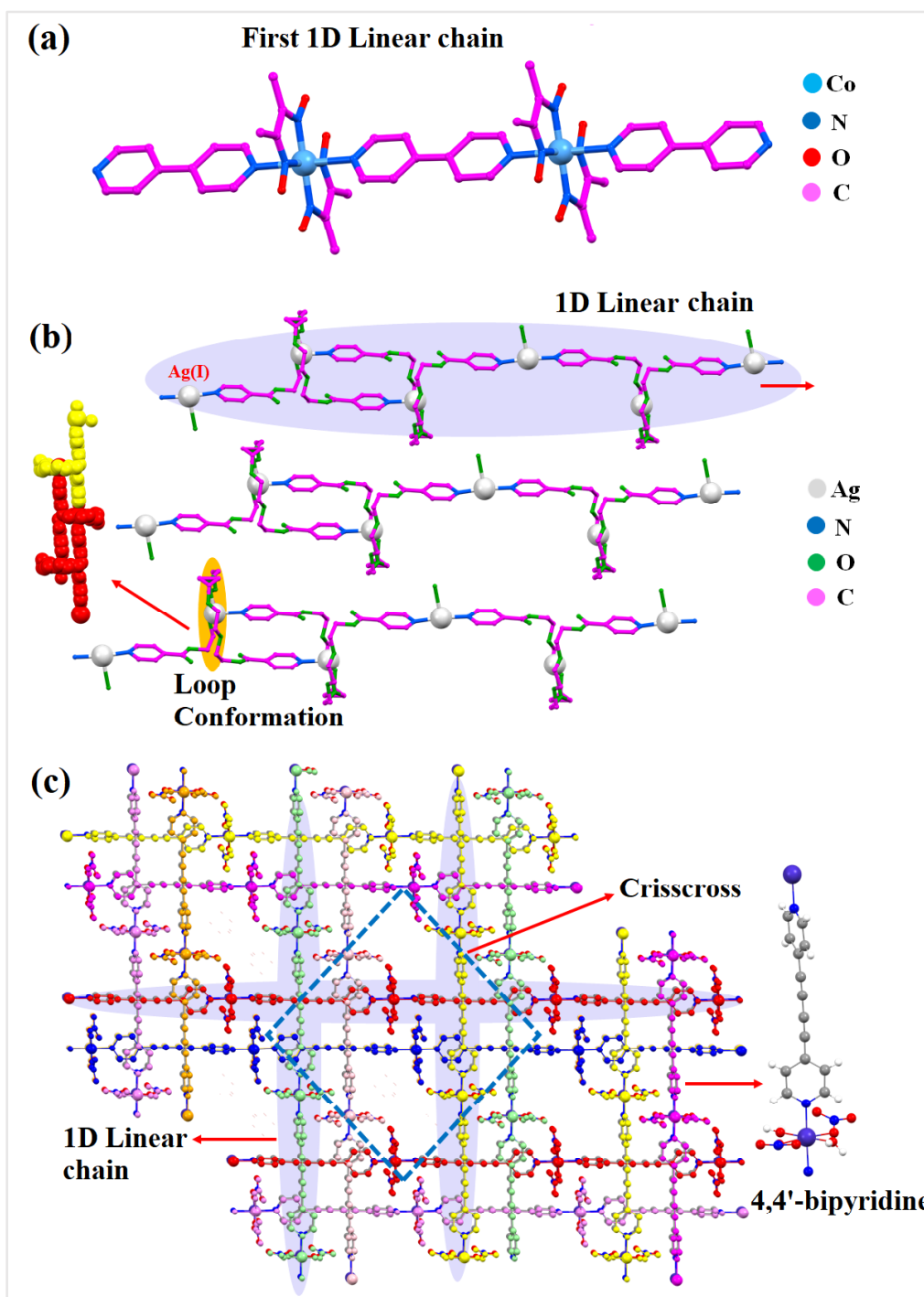
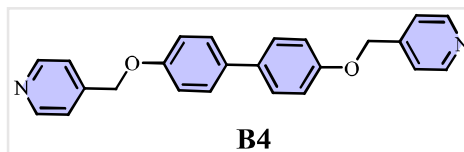


Figure 1.11: (a) 1D Linear chain CP (CCDC No. 1108424),^[61] (b) 1D Linear chain CP with hugging helical type conformation (CCDC No. 163024)^[62], (c) Crisscross pattern in 1D Linear chain CP (CCDC No. 179774)^[64]

be assembled into different types of sheet/layers like 2D corrugated sheet,^[68] laminated sheet^[69] and interwoven entangle, double-stranded, undulating-layer architectures.^[70] Ciani's group has shown the formation of 1O/1U (one over /one under) interwoven 2D architecture in rigid 1D CP of zigzag geometries.^[71] Loye's group has also reported a 2O/2U (two over /two under) interwoven 2D fabric structure constructed from a 1D zigzag chain (Figure 1.12b).^[72] [Zn(phen)(sdc)] where **H₂sdc** is *trans* stilbene-4,4'-dicarboxylic acid, formed 1D zigzag chain and two such chains interwoven as warp and woof like 2D sheet and further two 2D sheets interlocked in perpendicular fashion resulted in 3D networks.^[73]

1.3.1.3. Helical geometry

Helical geometry gets more attraction due to biological similar structural conformation. Flexible and chiral/achiral building blocks have been used for the construction of single, double, triple, and multiples stranded helical CPs. Using 4,4'-bpy ligand, Zaworotko's group has synthesized homochiral helical CPs.^[74] Biradha's group have reported a 1D double helix

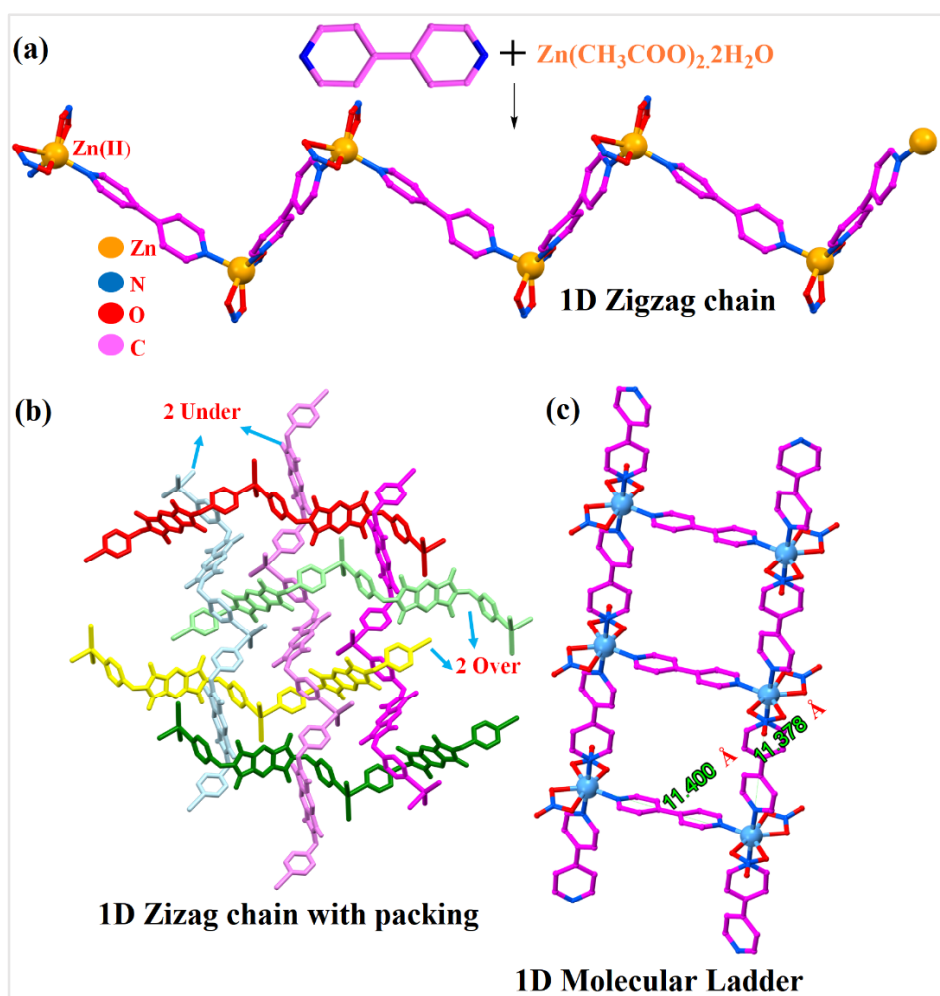


Figure 1.12: (a) 1D Zigzag CP (CCDC No. 629972),^[66] (b) 1D Zigzag CP with 2 Over and 2 Under type packing (CCDC No. 207401),^[72] (c) 1D Molecular Ladder CP (CCDC No. 1248145)^[76]

CPs in 1:1 metal:ligand ratio from exo-bidentate N^1, N^2 -bis(1-(pyridin-3-yl)ethyl)ethane-1,2-diamine ligand which is a higher analogue of 4,4'-bpy.^[75]

1.3.1.4. Ladder geometry

T-shaped coordination environment of metal centre results in ladder while square planar coordination mode of metal can lead to the molecular antenna and railroad network (Figure 1.10).

Spacer ligand as 'rails and rungs' and metal ions as 'nodes' are used in versatile ladder-type architectures. Square cavity within a non-interpenetrated molecular ladder was reported by Zaworotko's group using 4,4'-bpy (Figure 1.12c).^[76] Four-fold interpenetrated of molecular ladders with a large cavity of 16.4 Å × 16.6 Å dimensions was reported by Fujita et al.^[77] Polycatenated interpenetrated,^[78] polycatenated interwoven-flattened undulating,^[79] and interlocking lamellar^[80] network of molecular ladder are constructed by using 1,4-bis[(4-pyridyl)-ethynyl benzene], 1,4-bis(4-pyridyl)-butadiyne and derivative of 4,4'-bis(pyridyl) respectively. These structures are stabilized through the $\pi \cdots \pi$ interaction. The first unusual three-stranded molecular ladder was reported by Cao's group wherein 4,4'-bpy is bridged with three Zn(II) for the formation of rails and acetate anions connected to this Zn(II) atom as rungs.^[81] Several types of molecular ladder of CPs are reported with different applications.^[82] Vittal's group has listed the 4,4'-bpy derivative ligands which are specially involved in construction of ladder type 1D CPs.^[83]

1.3.1.5. Molecular railroad geometry

A 1D molecular railroad network of CP having a large pore size of 11 Å × 11 Å dimension was prepared by Yaghi's group through the combination of 4,4'-bpy and nickel perchlorate (Figure 1.13b).^[84] Later on, Zaworotko has reported a molecular railroad network by using 4,4'-bpy with cobalt nitrate.^[85]

1.3.1.6. Molecular antenna geometry

Seidel et al., have reported the molecular antenna network by using 4,4'-bpy and cadmium perchlorate (Figure 1.13a).^[86] Other geometries of 1D CP, rotaxane, looped, ribbon/tape type are explored by other ligands.^[87]

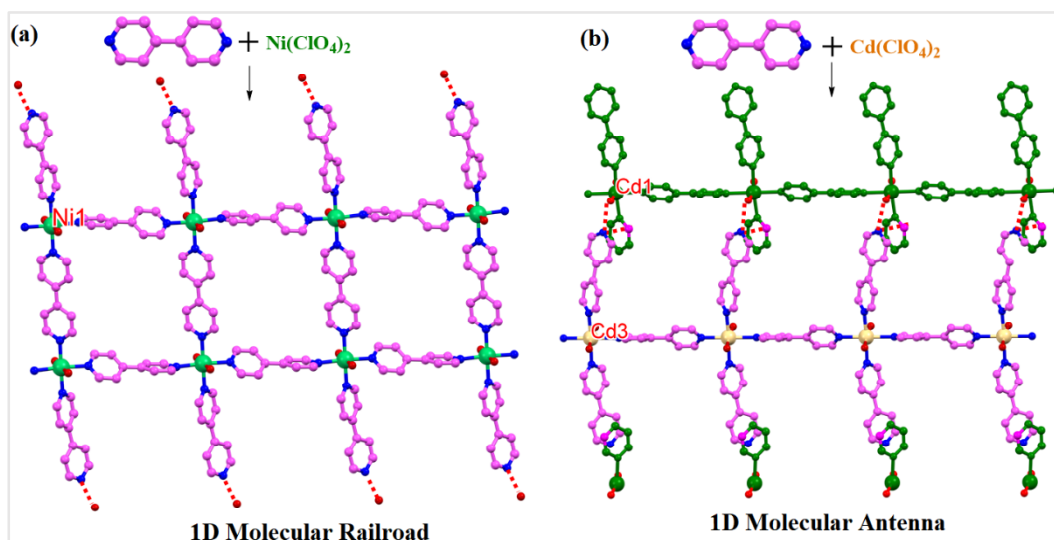


Figure 1.13: (a) Represents the sidewise extension of 1D molecular railroad (CCDC No. 1222031),^[84] (b) Pink color single chain represents 1D molecular antenna; where red dotted lines are shown noncovalent interaction (CCDC No. 836453)^[86]

1.3.2. Two dimensional networks (2D CPs)

Network topology to describe any geometry is by the symbolic general formula (n,p), where n represents the number of nodes in minimum closed net and p represents the number of connections to the neighbour. For example, in Figure 1.14, (6,3) topology represent 6 smallest complete circuit in the net and each node is further connected with 3 other nodes. Most widely observed 3-connected 2D geometries are ‘bilayer’, ‘herringbone’, and ‘honeycomb’, while the 4-connected nets include square grids and rectangular grids.

1.3.2.1. Square grid networks

[Zn(4,4'-bpy)₂(H₂O)₂(SiF₆)_n] is one of the earliest square grid interpenetrated CP reported by Robson's group.^[88] Fujita and co-workers first observed a non-interpenetrate or open square grid polymer with bpy in ([Cd(bipy)₂(NO₃)₂].2(*o*-dibromobenzene))_n.^[89] There are many

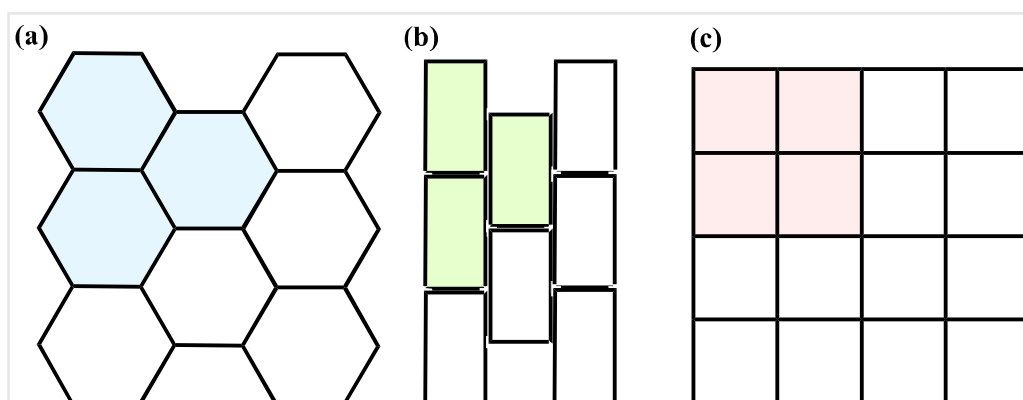


Figure 1.14: (a) and (b) two different geometrical with (6,3) representation in 2D infinite nets, (c) (4,4) representation in 2D infinite nets

reports on square grid with wide ranges of pore size ($15 \text{ \AA} \times 15 \text{ \AA}$,^[58] $20 \text{ \AA} \times 20 \text{ \AA}$,^[90] and $25 \text{ \AA} \times 25 \text{ \AA}$ ^[91]) and selective inclusion of guest molecules.^[92] Zaworotko has synthesized square grid networks with bipyridine, which has captured many guest molecules.^[93] The size and shape of the square grid network can be tuned by analogues of 4,4'-bpy to get a desirable cavity. Biradha's group^[94], Wang's group^[95], and Gong's group^[96] have reported the interpenetrated square grid networks based on bis(pyridyl)-diamide ligand.

1.3.2.2. Rectangular grid networks

Fujita's group and Mak's group have synthesized very rare rectangular grid with the combination of 4,4'-bpy and a higher analogue of 4,4'-bpy. Mak et al., have used pyrazine as co-ligand with 4,4'-bpy to get rectangular grids with $6.8 \text{ \AA} \times 11.1 \text{ \AA}$.^[97] Biradha et al., have synthesized a rectangular grid cavity of $11.34 \text{ \AA} \times 15.56 \text{ \AA}$ dimension which synthesized from 1,4-bis(4-pyridyl)benzene and 4,4'-bpy which has shown the ability to capture benzene molecule as a guest into its cavities (Figure 1.15).^[98]

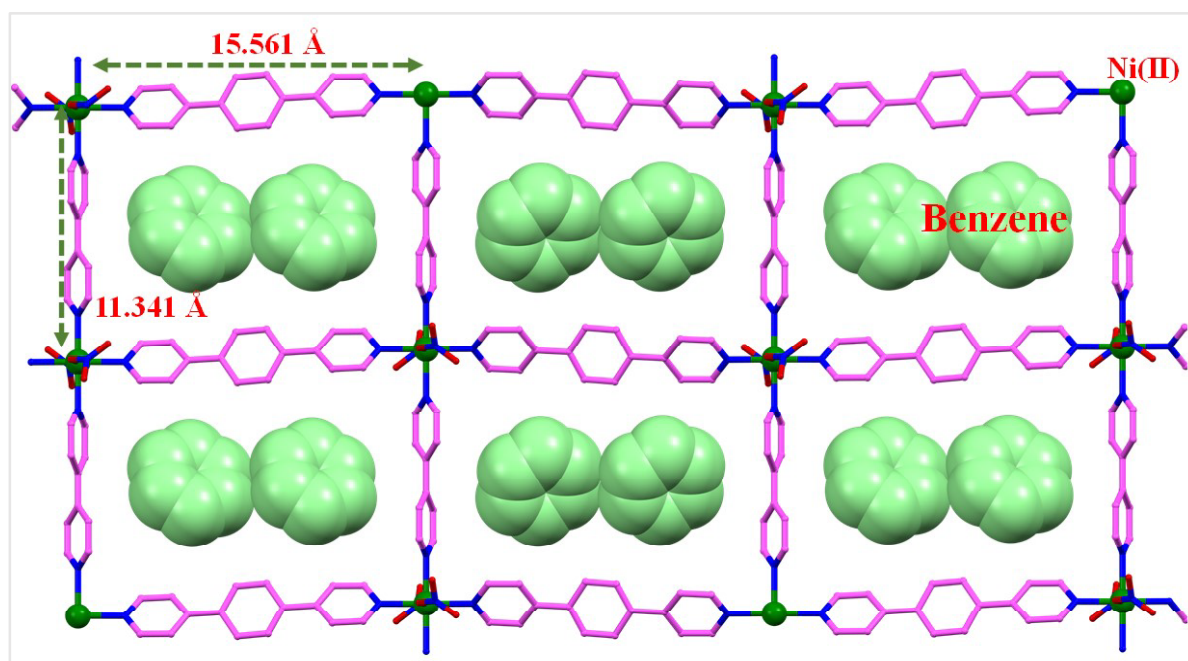


Figure 1.15: 2D Rectangular grid network by 4,4'-bpy and its analogue where the cavities are encapsulated with benzene molecules (represented in space-fill model) (CCDC No. 156766)^[98]

1.3.2.3. Bilayer network

2D network of bilayer, honeycomb, brick wall is constructed from T-shaped metal geometry. Conventional definition of bilayer is coming from lyotropic liquid crystal where network is arranged by the layers of hydrophobic and hydrophilic in an alternate fashion. Bilayer network

of CPs can be represented as two layers lying in a parallel manner and are connected through spacer ligand perpendicularly. The first bilayer CP $[\text{Co}(\text{NO}_3)(\text{B5})_{1.5}]_n$ was reported by the Zaworotko et al., where **B5** (1,2-bis(4-pyridyl)ethane) is the analogue of 4,4'-bpy (Figure 1.16).^[99]

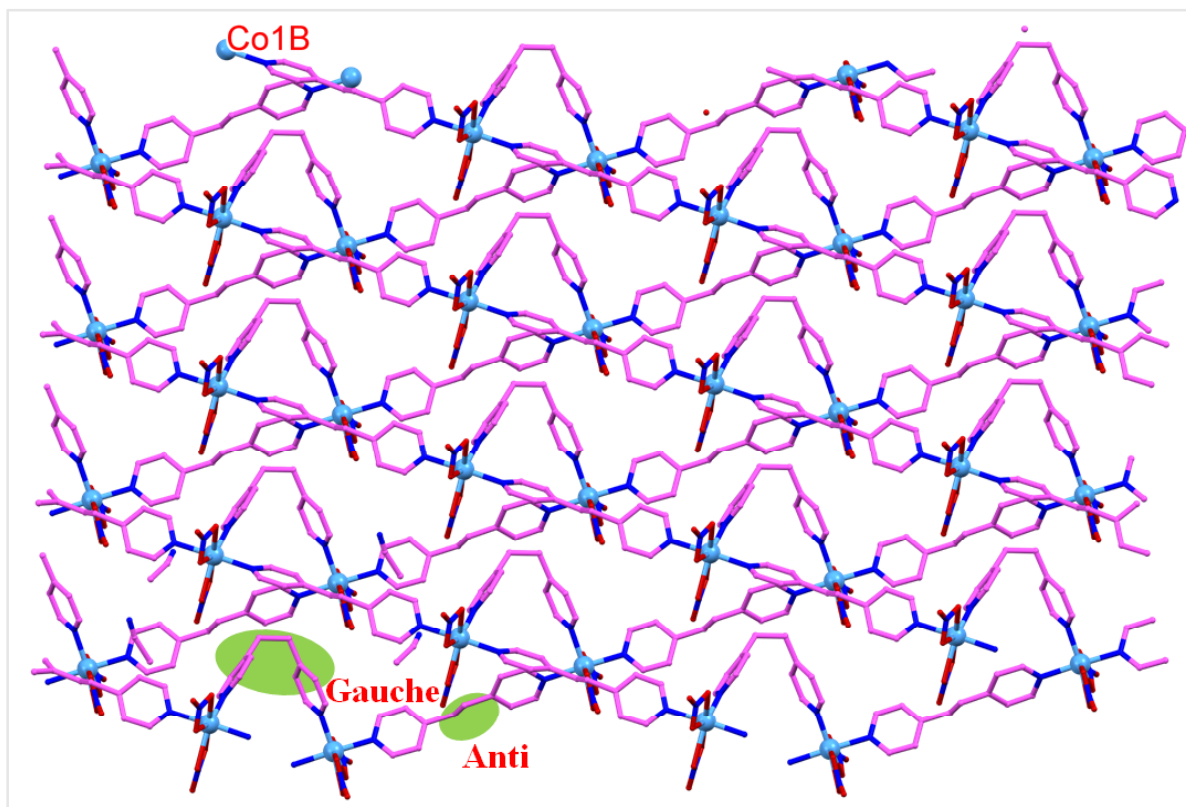
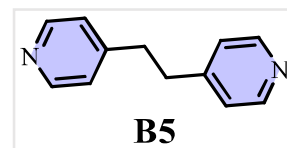


Figure 1.16: The net view of a 2D molecular bilayer of $[\text{Co}(\text{NO}_3)(\text{L})_{1.5}]_n$, (CCDC No. 120532)^[99]

1.3.2.4. Herringbone network and brick wall network

Herringbone network was prepared by Lin's group from combination of ligands: 4,4'-bpy and pyridine-2,4,6-tricarboxylic acid, which is coordinated with Zn(II) metal ion (Figure 1.17).^[100] Another interesting 2D herringbone network was constructed by trans-4,4'-azo-bis(pyridine) ligand with Cd(II)/Co(II) in dichloromethane. In this network, a sheet of parallel interpenetrated 2D grids of (6,3) topology resulted in a herringbone motif.^[101]

1.3.2.5. Honeycomb network

Trigonal and trigonal bipyramid geometry in metal center resulted in honeycomb network. This network was explored by Zaworotko et al.,^[102] and Yaghi et al.,^[103] using pyrazine ligand with Cu(I)SiF₆ salt and 4,4'-bpy with Cu(I)Cl salt respectively (Figure 1.18a & b).

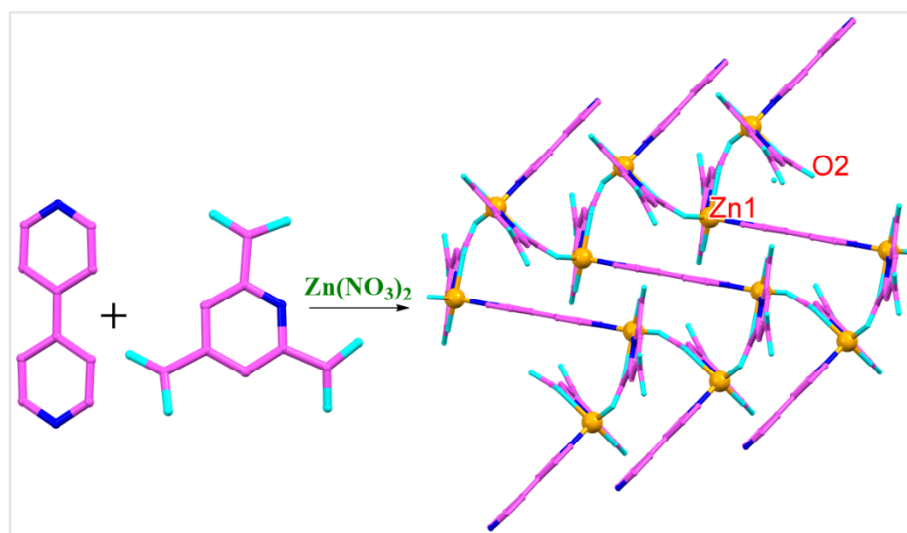


Figure 1.17: 2D herringbone network from mixed ligand (CCDC No. 614666)^[100]

1.3.3. Three dimensional networks (3D CPs)

There are many reports on 3D networks synthesized using a wide range of ligands. The current discussion is limited to bidentate ligands with different metal salts. One of the earliest examples of 3D network was reported by Zaworotko's group where linear 4,4'-bpy and Ag(I) resulted in a Lincoln Log 3D networks with T-shaped coordination environment, which is a

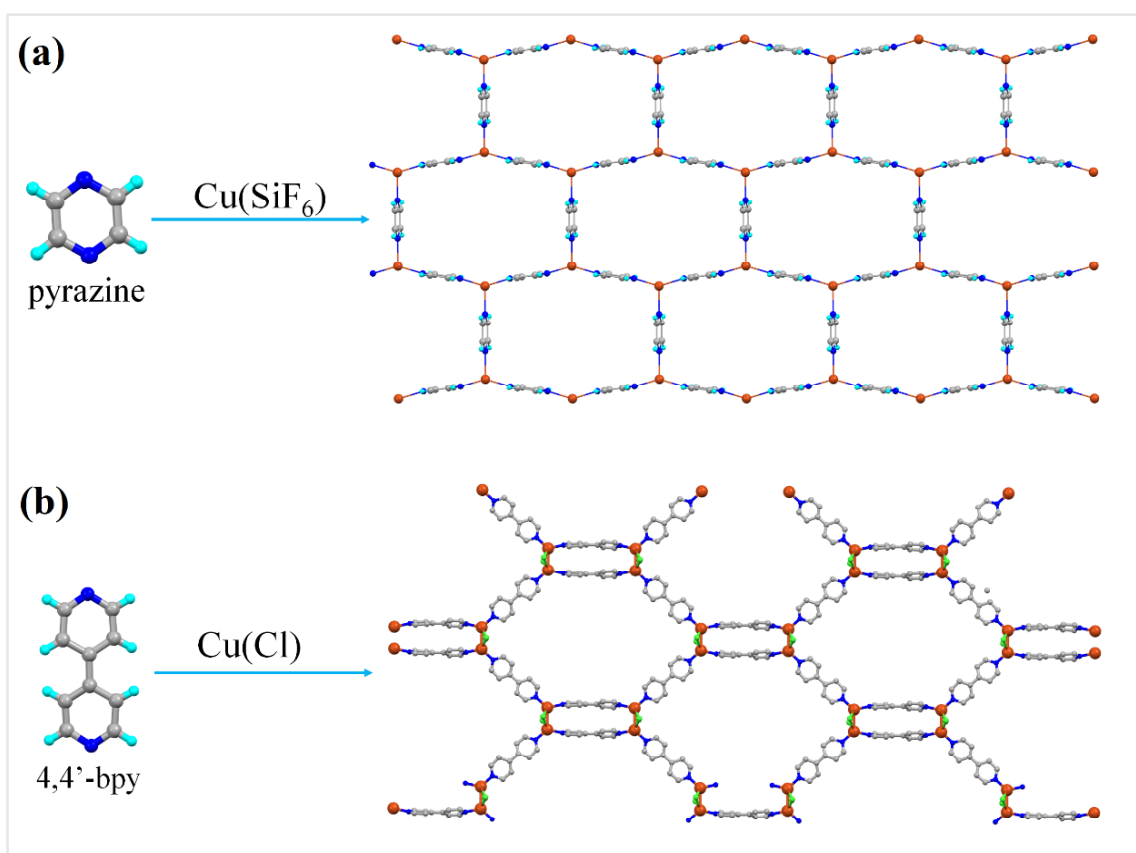


Figure 1.18: 2D honeycomb network from (a) pyrazine (CCDC No. 1206001),^[102] and (b) 4,4'-bpy (CCDC No. 1302600)^[103] ligands

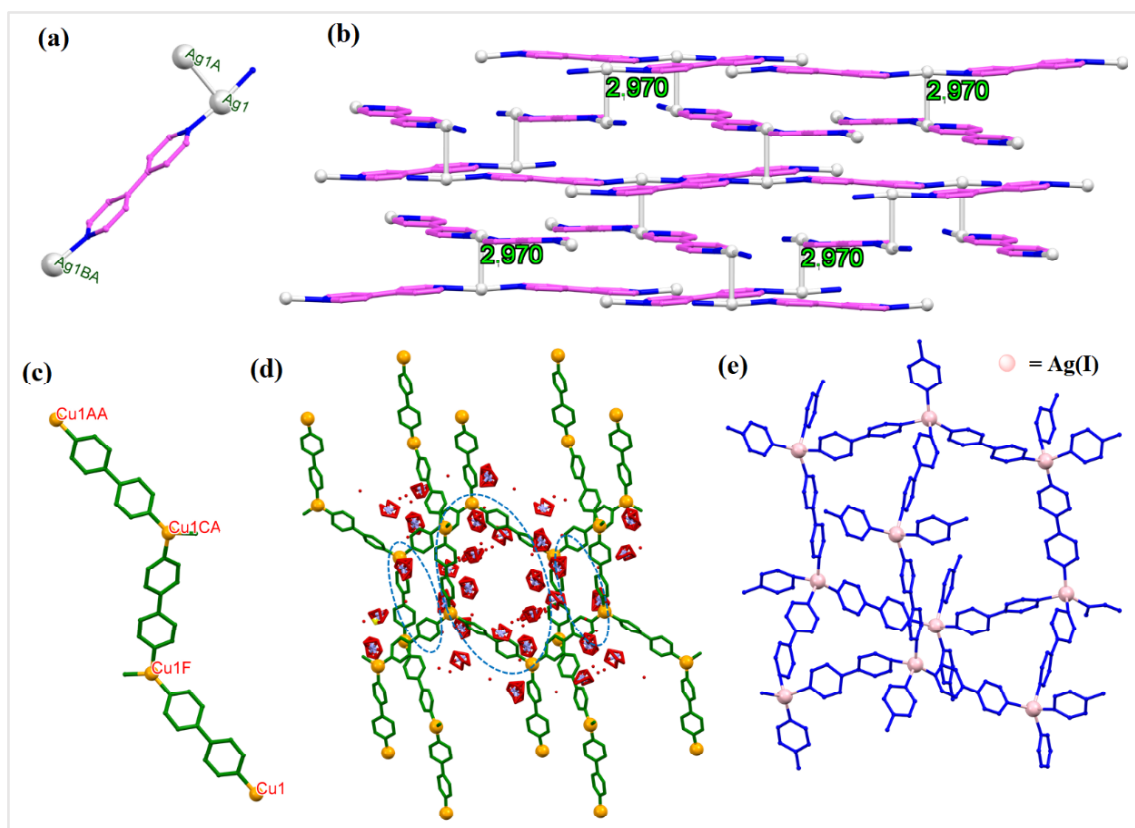


Figure 1.19: (a) Three -connected T-shaped geometry, (b) 3D Lincoln Log networks by Zaworotko group (CCDC No. 1321203),^[104] (c) Three -connected Cu(II) center with 4,4'-bpy,^[106] (d) Rectangular shape of three different size channels in 3D networks with nitrate anions (CCDC No. 1311992),^[106] (e) Adamantanoid cage of 4,4'-bpy with Ag(I) by Ciani group (CCDC No. 1302198)^[105]

interpenetrated triple network (Ag–Ag bond distance of 2.97 Å) (Figure 1.19b).^[104] Four connected nodes can result in diamondoid network. Zaworotko^[102] and Ciani^[105] have reported a diamondoid network with the combination of 4,4'-bpy and Cu(I) and Ag(I) respectively. One equivalent of 4,4'-bpy oriented with the two equivalents of Ag(CF₃SO₃) in such a way that they formed four interpenetrated diamondoid lattices. Ciani's group has represented the diamondoid network in a single adamantanoid cage (Figure 1.19e).^[105] Yaghi's group has reported the three connected node-based interpenetrated porous 3D-framework of Cu(II)–4,4'-bpy which was large rectangular different size of three channels with dimensions 26 Å × 20 Å, 10 Å × 12 Å, 43 Å × 18 Å along the [100], [010], [001] crystallographic axes (Figure 1.19d).^[106] Besides this, cubic topology are reported in 3D networks. Zaworotko et al., have reported the non-interpenetrated square grid octahedral CP based on the 4,4'-bpy with Zn(OH)₂SiF₆ wherein SiF₆ resulted in linear bridges.^[107] In this CP, the four equivalent of 4,4'-bpy are bridged with the Cu(II) ion and formed 2D square grid layers. These layers are further connected with two equivalents of SiF₆ through the coordination bond of Cu-F and propagated into a 3D network without interpenetration.^[55]

1.3.4. Interpenetration of networks

Interpenetrated network is defined as ‘the polymeric nets are connected to each other without covalent bond, but it is impossible to separate without breaking the any bond’.^[108] It can be defined also as a way which ‘reduces the void spaces in the framework by self-catenation or self-entanglement in absence of suitable guest molecules and resulted in entwining multiple lattices (interpenetration)’. Initially, the interpenetrated CPs/MOFs considered as disadvantages in application due to the decrease in surface area. Majhi’s group had listed the several interpenetration CPs in their review article.^[109] Figure 1.20 shows the classification of interpenetration. Solvent, temperature, time period and steric factor of ligand are regulated the degree of interpenetration. Ma’s group had discussed the regulation of degree of interpenetration in different depiction into CPs from two-fold, three-fold, four-fold, five-fold, six-fold, seven-fold, eight-fold up to multiple fold.^[110]

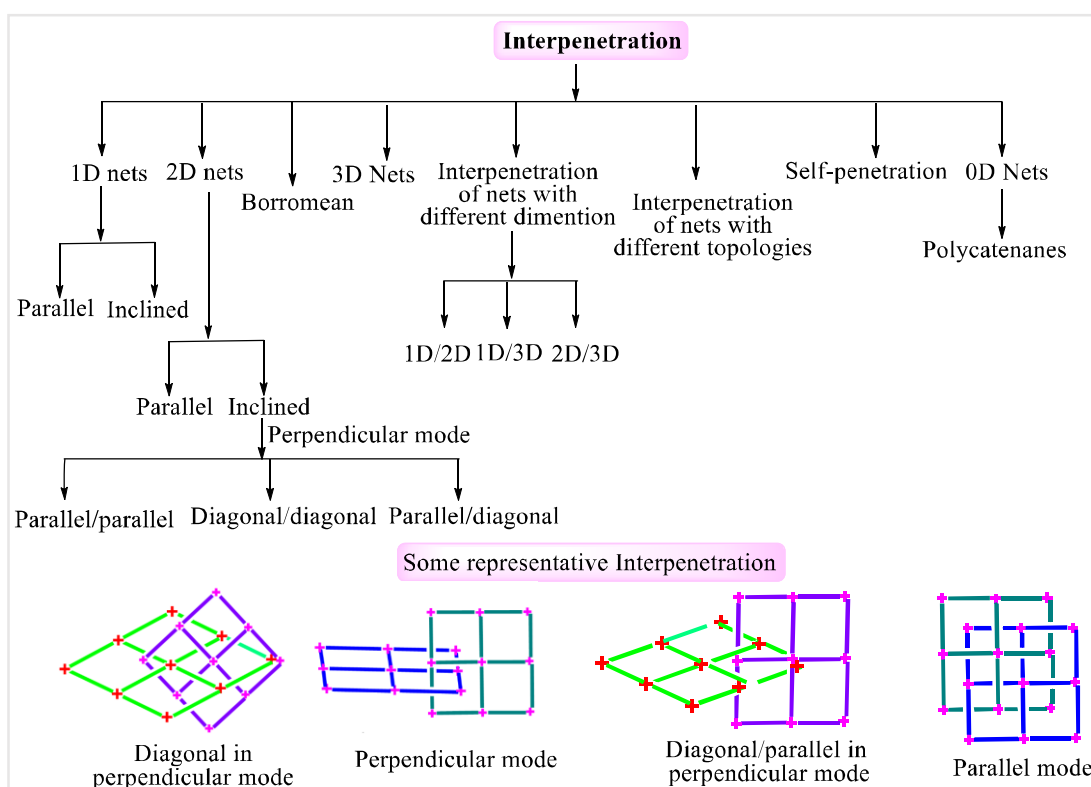


Figure 1.20: Classification of interpenetration in CPs/MOFs networks

1.4. Connecting tool synthon to construct CP/MOF

Many factors such as ligands, metal ions, counterions, crystallization techniques have greatly influenced the CPs architecture. Coordinate bond and hydrogen bond interactions are the main connecting tools to assemble the CP/MOF. Incorporating heteroatoms and other hydrogen bond functionalities into ligands have resulted in different architecture in supramolecular chemistry.

In this section, the discussion on CPs of ligands with amide functionality and imine functionality will be carried out.

1.4.1. CPs/MOFs of imine functionality

Focus on Schiff bases arises due to the presence of imine functional group in the spacer which may lead to the various interesting topology in networks through non-covalent interaction or direct coordination with metal ion where spacer can be mono-imine, di-imine, tri-imine with aryl, etc. In some of the CPs, Schiff base is used as a coligand/auxiliary ligand with the carboxylate acid, amide, mixed functional linker, etc., and resulted in interesting topologies. In 1973, Naphthal Dunski and Thomas. H. Crawford prepared many coordination complexes of Cu(II), Co(II) and Ni(II) from mono-imine, di-imine Schiff bases of *N*-salicylidine-*o*-methylthioaniline and characterized their magnetic, spectral and analytical properties.^[111] The *exo*-bidentate imine functionality can lead to novel networks of CPs/MOFs. Li's group has prepared doubly interpenetrated CPs based on imine and amide functionalized *exo*-bidentate ligands. Later they have synthesized homometallic-mixed valence copper (I/II) CPs for long-distance electron transfer entities that enable their application in electrochemical sensors and ferrimagnets.^[112] Using the similar mixed functionality of ligand, Xue-Qin's group has constructed a 1D zigzag Mn(III) CPs. Two 1D chains are formed a puckered 2D supramolecular network which showed antiferromagnetic property.^[113] G. Mahmoudi reported mixed functionalized bis(pyridyl) CPs with holo-directed lead coordination sphere, wherein different networks (4,6-connected and 4,7-connected underlying topologies) constructed by varying the nitrogen position on the benzene ring in $[\text{Pb}_2(\mathbf{B6})\text{Cl}_4]_n$, where **B6** = 1,4-bis(3-pyridyl)-2,3-diaza-1,3-butadiene. 2-Pyridyl nitrogen obtaining ligand (Z)-N-((E)-1-(pyridin-2-yl)ethylidene)picolinohydrazonic acid (**B7**) formed a 1D zigzag CPs $[\text{Pb}_2(\mathbf{B7})\text{Cl}_3]_n$.^[114] Lee's group introduced a pyridyl based carboxylate terminal group with imine functionality, which tuned the coordination mode of ligand to chelating (construct interwoven pattern sharing of 8 member ring) and bridging, and resulted in 2D and 3D CPs.^[115]

Mono-imine functionality as spacer in bis(pyridyl) has also resulted in varied CPs of attractive properties. Dang's group has reported a novel 1D $[\text{Ag}(\mathbf{B8})(\text{NO}_3)]_n$ CP showed a seesaw metal geometry where the mono-imine functionality of 4-benzoylpyridine hydrazone (**B8**) are attached to three silver metal-ion. The metal to ligand coordination has resulted in luminescence property at room temperature.^[116] Safari's group has shown the formation of 1D network topologies by anion exchange reaction. Mono-imine constructed a 1D zigzag chain with $\text{Hg}(\text{X}_2)$ where $\text{X} = \text{Br}^-/\text{Cl}^-$. This zigzag topology was changed to helical geometry by

changing the halide anion from bromide/chloride to iodide. Zigzag to helical structural array was observed due to bifurcated H-bonding of C-H...I-Hg along with π - π interactions (Figure 1.21).^[117]

Di-imine can increase the coordination site on the linker group. Especially when the linker is decorated with bis(pyridyl) and resulted in variation in topologies of CPs. The useful functionality of the di-imine Schiff base is salen. By introducing the dicarboxylate group at the terminal of metal-salen linker has developed heterogeneous MOF catalysts. Loye's group have introduced several novel building blocks into CPs using di-imine functionality like, '3D non-interpenetrated polyclohexane structural motif of $[M(\text{NO}_3)_2(\mathbf{B6})_{1.5} \cdot \text{CH}_2\text{Cl}_2]_n$, with pore size $28 \text{ \AA} \times 15 \text{ \AA}$, where $M = \text{Cd}(\text{II})/\text{Co}(\text{II})$ based on T-shape building blocks',^[118] 'interpenetrated 2D brick wall of $[\text{Cd}(\text{NO}_3)_2(\mathbf{B6})_{1.5} \cdot 0.5 \mathbf{B6}]_n$ constructed from distorted T-joint by 1,4-bis(3-pyridyl)-2,3-diaza-1,3-butadiene (**B6**)', same ligand they got '3D interpenetrated network of $[\text{Co}(\text{NO}_3)_2(\mathbf{B6})_{1.5} \cdot \text{H}_2\text{O}]_n$ with F-joint connector just replaced the Cd(II) by Co(II) (Figure 1.22). By changing nitrogen position on the pyridyl ring from 3-pyridyl to 4-pyridyl, they got '2D non-interpenetrated brick wall CP with T-shape metal center of Co(II)', '3D rhombus grid CP based on propeller Ni(II) metal center'.^[119] Due to the aza functionality of imine group, ligand itself extent in zigzag fashion towards the metal center. 'Non-interpenetrating 2D square grid propeller type' metal center of CP and 'non-interpenetrating 1D ladder packed in herringbone' array of CP are

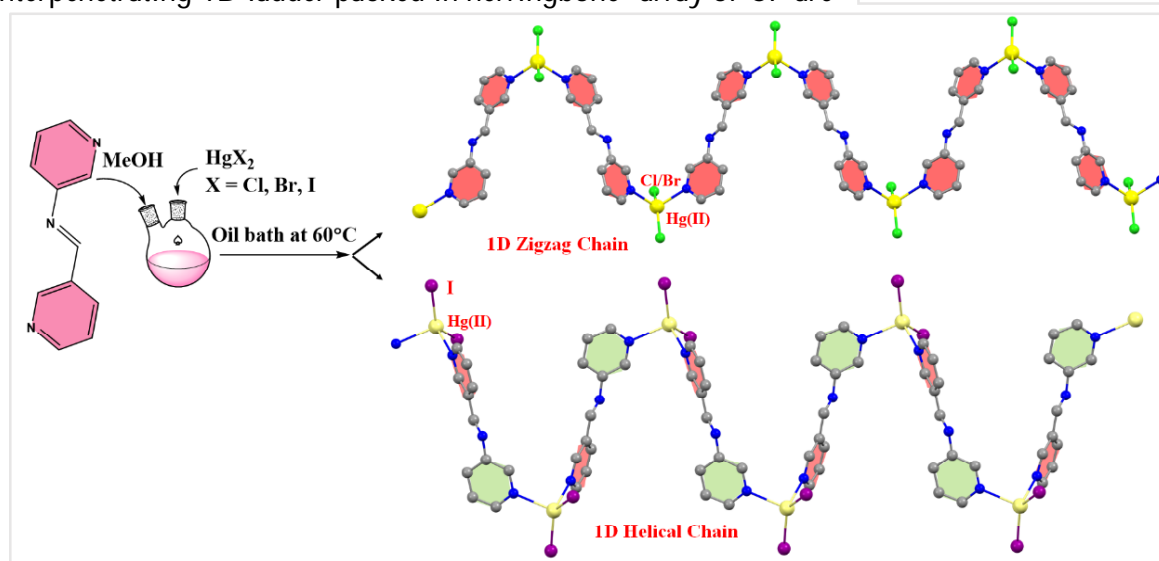
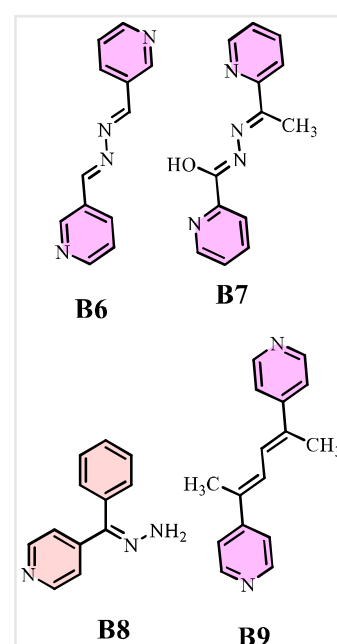


Figure 1.21: Bis(pyridyl)-mono-imine directed zigzag and helical chain (HgI_2 CCDC No. 835329 and HgCl_2 CCDC No. 835327)¹¹⁹

constructed from 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadine (**B9**),^[120] This minor change has shown a drastic topology change with hepta to pseudo octa coordination in CPs while keeping the same solvent, and metal to ligand ratio.

Morsali's group has synthesised wide range of MOFs like **TMU-4**, **TMU-5**, **TMU-6**, **TMU-7**, **TMU-21**, **TMU-33**, **TMU-40**, **TMU-42**, **TMU-60** with bis(pyridyl)-di-imines.^[121] In the construction of 3D MOFs, linear di-imine acts as pillar linker, and non-linear V-shaped carboxylate act as connector/SBUs. One of the CPs of **B6** synthesized by Morsali's group include 1D zigzag chain of $[\text{Hg}(\mu\text{-B6})(\text{CH}_3\text{COO})_2]_n$ while **B11** was shown to form 2D CPs $[\text{Hg}_2(\mu\text{-B11})_{1.5}(\mu\text{-CH}_3\text{COO})(\mu_{1,1}\text{-SCN})(\mu_{1,3}\text{-SCN})(\text{SCN})]_n\text{-CH}_3\text{CN}$.^[122] Further, they have used CPs as a precursor like $[\text{Pb}_2(\mu\text{-B6})(\mu\text{-}(\text{NO}_3)_3(\text{NO}_3))]_n$ to synthesize the nano-sized Pb(II) CPs for nanopores.^[123] 3D porous MOF with azine functionality of **TMU-4** and **TMU-5** have synthesized from **B6** and **B9** respectively along with 4,4'-oxydibenzoic acid. In **TMU-4** dicarboxylate formed 2D sheet with Zn(II) which is being held by the connection of pillar linker **B6** and resulted in the double interpenetrated 3D honeycomb network of MOF. Binuclear paddle-wheel Zn(II) as SBUs in **TMU-5** formed 2D layers which is pillared by **B9** to give interconnected 3D MOF. Three-

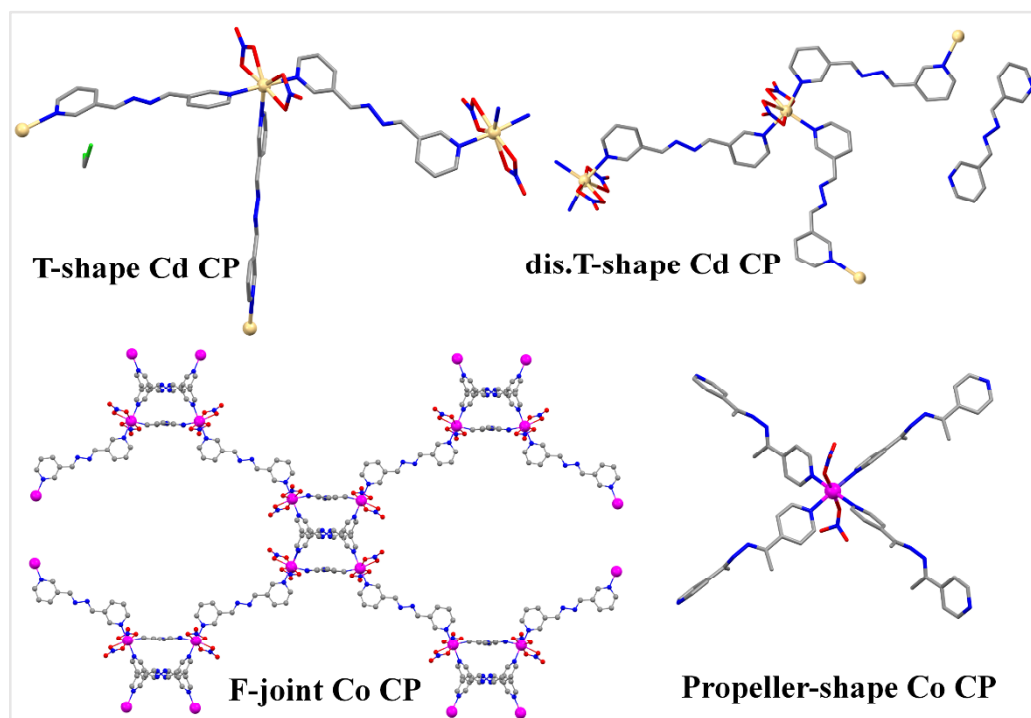
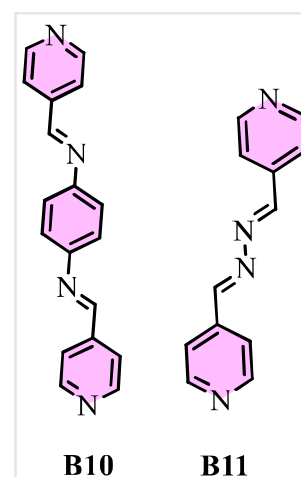
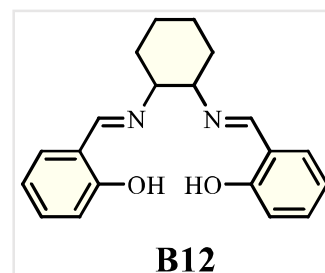


Figure 1.22: Different geometry in CPs (T-shaped Cd CP: CCDC No. 154668, distorted T-shaped Cd CP: CCDC No. 154667, F-joint: CCDC No. 154667, Propeller-shape: CCDC No. 166629)¹¹⁸

fold interpenetrated **TMU-6** was synthesized from linker **B10**.^[124] While, **TMU-21** was prepared by introducing a naphthyl ring in place of benzene in the ligand moiety which resulted in extended π -electrons in the pillar system for better catalytic activity.^[125] Su's group has used phenylene spacer in **B10** synthon as a supporting rod-like ligand to build the 2D borromean network of CPs.^[126] Shabani's group has found a 2D holo-directed lead CPs, where each distorted octahedral (X_4N_2) Pb(II) center is bridged by two bis(pyridyl)-di-imine linker and four halides (X) ions. Luminescence property was observed in these CPs due to effective orbital interactions that occurred between Pb(II) and halide ions.^[127] Later on, they have used hydrazine, phenylene and naphthylene spacer of bis(pyridyl)-di-imines to synthesize the 1D linear Co(II) and Zn(II) CPs. The electronic effect of these spacer group on intermolecular interactions (C-H \cdots O, C-H $\cdots\pi$, and π - π) stabilized to construct the 2D supramolecular networks.^[128] Ghoshal's group has synthesised diverse topological CPs like 'interpenetrated 3-fold', 'interpenetrated 5-fold diamondoid net 6⁶ topologies', '3-connected net 6³ topologies', '3D paddle-wheel with $M_2(CO_2)_4$ SBUs (M = Cu(II) and Zn(II))', '3,5-connected binodal with (6³) (6⁹.8) Schlafli symbol', '2D bilayer frameworks' by introducing different dicarboxylate alkyl to aryl as the precursor of SBUs, which is further pillared by linear/bent linkers of **B6**, **B9**, **B11**.^[129] Konar's group explored the structural topologies in MOFs by used the phenylene dicarboxylate as SBUs wherein made variation in geometry by using **B6** and **B11** as pillar ligands.^[130]

In 2007, Belghoul et al., synthesized ultra-thin films of metal-Schiff base coordination polymer. They used bi, tri, and multidentate Schiff base ligands.^[131] Yan et al., prepared $[Ln(H_2B12)(NO_3)_3(MeOH)_2]_n$ lanthanide 1D CPs based on *N,N*-bis(salicylidene)-1,2-cyclohexanediamine (H_2B12) which showed luminescence properties.^[132]



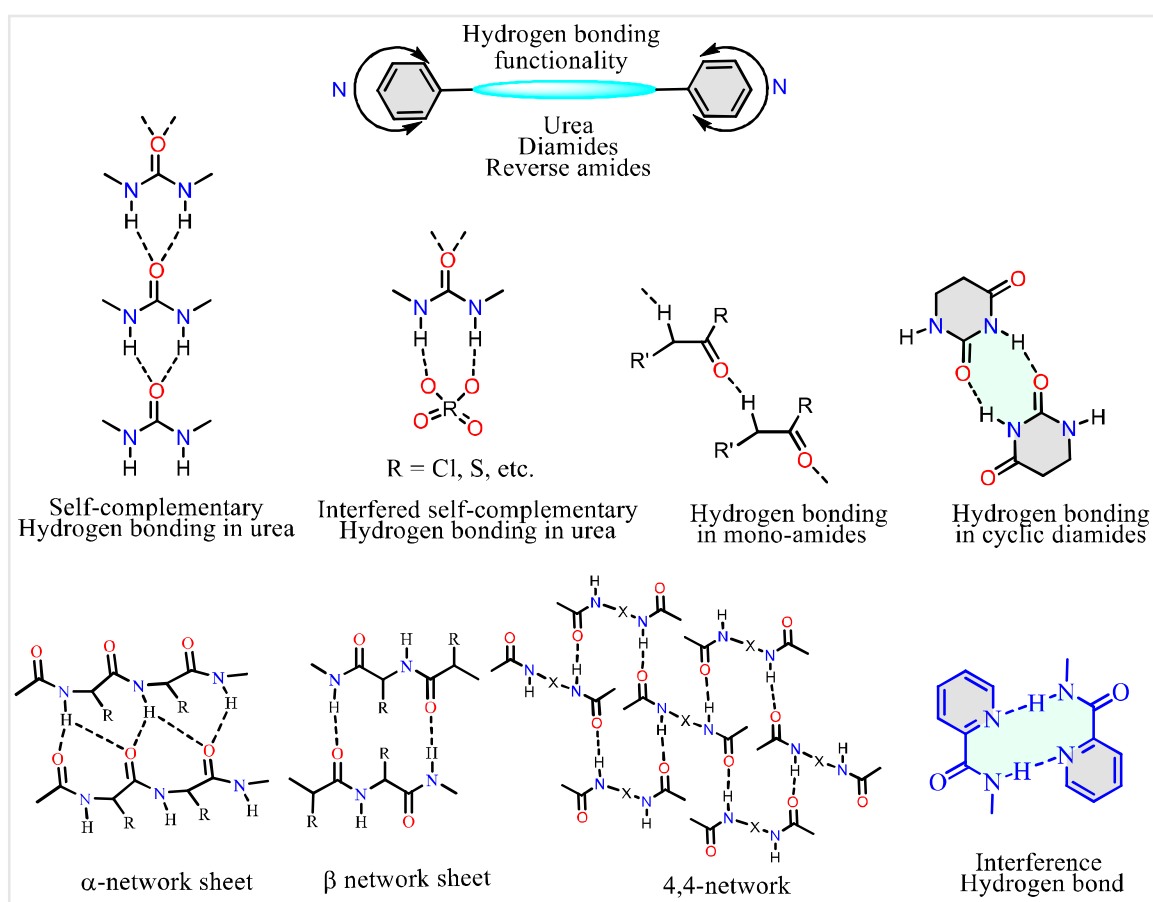
In 2008, Khalaji et al., reported 1D zigzag CPs prepared from Co(II) and *N,N*-bis(salicylidene)-1,3-diamino propane, where ligand acted as bridging linker between Co(II) and Na(I) metal ion of co-ligand NaN_3 .^[133] In 2012, this group further reported two 1D polymers with Schiff base ligands are $([AgL(H_2O)]_2[AgL(NO_3)]_2L(H_2O)_2)_n$ and $[ZnL(Cl)_2]_n$ where the ligand L is *N,N*-bis(1-pyridine-4-yl-ethylenedene)hydrazine. Biradha and co-workers have found 1D double helix CPs of 2,7-bis(3-pyridyl)-3,6-diaza-2,6-octadiene with Ag(I).^[75]

Our group has synthesized bis(pyridyl)-di-imine CPs with Cd(II).^[134] Three-fold interpenetrated 3D Cd(II) CPs have been reported with the combination of **B6** and benzene-

1,3-disulfonate ligands. In this CP, **B6** adopted a seesaw geometry in Cd(II) metal center and formed in a 2D staircase network of 4,4-topology which resulted in an interpenetrated 3D network.^[135]

1.4.2. CPs/MOFs of amide functionality

Amide based ligands in designing the CPs/MOFs will lead to novel architectures due to the presence of hydrogen bonding functionality which may lead to N-H...O and other hydrogen bond interactions. The current thesis is focussed on bis(pyridyl)-diamide where the presence of nitrogen coordinating site will help in extending the network in higher dimensions. While the amide functionality can be involved extensive hydrogen bonding interactions (Scheme 1.1). There are many reports on urea functionalized CP which has been extended via α -network (where one N-H interacted with two C=O group) of hydrogen bonding with combination of one C=O group with two N-H groups. Although there are possibilities of self-complementary hydrogen bonding of amide groups in CPs but different external factors like solvents, guest molecules and anions can interfere with this hydrogen bonding and may lead to varied geometries and novel properties. There are various reports on CPs based on bis(pyridyl)-

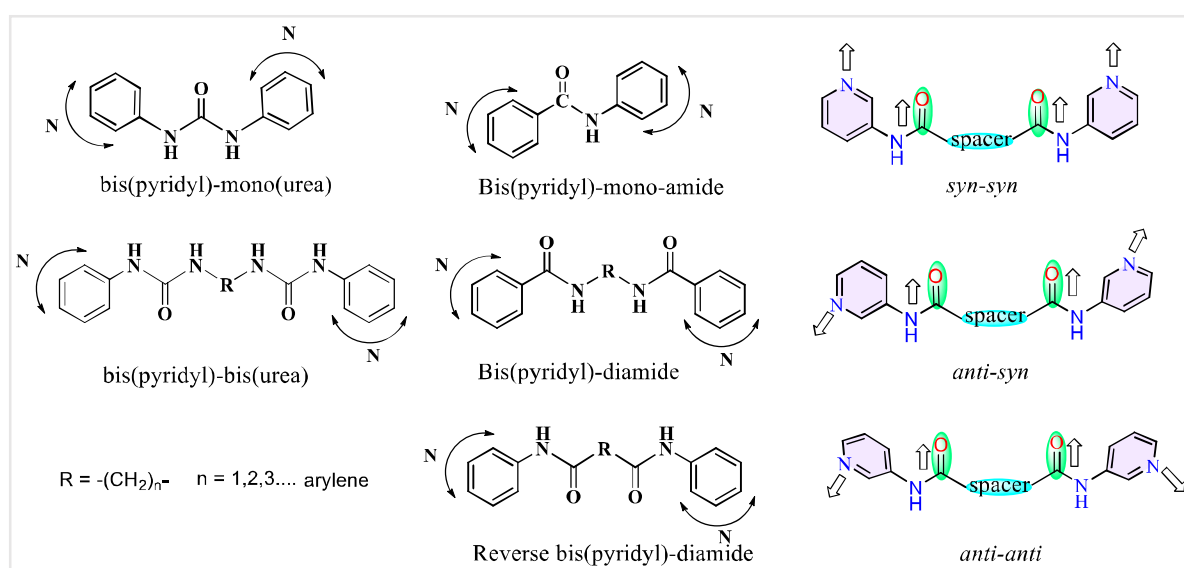


Scheme 1.1: Different hydrogen bonding motifs

mono(urea), bis(pyridyl)-bis(urea), bis(pyridyl)-mono-amide, bis(pyridyl)-diamide and reverse bis(pyridyl)-diamide (Scheme 1.2).^[57,69,136] Presence of $-(CH_2)-$ backbone in the spacer of bis(pyridyl) ligands and bis(pyridyl)-diamide give flexible features to the framework while semi rigid flexibility can be attained from aromatic backbone spacer. Pyridyl nitrogen position also leads variations in conformation of ligands and may enhance the formations of acquiring possibilities of *anti-anti*, *syn-anti*, *syn-syn* conformation with different possible orientation of nitrogen with amide $C=O$ group. Also, the orientation of $C=O$ and $N-H$ will result in different geometrical variations within the network. Thapa et al., reviewed bis(pyridyl)-diamide ligands and categorized the CPs of these ligands on the basis of their dimensionalities as 1D, 2D and 3D.^[137] Dastidar's group reviewed the development of diverse ligating topologies of N-donor ditopic ligands [bis(pyridyl)-amides].^[138]

In 1994, Jhon C. MacDonald and George Whiteside in their review paper discussed various motifs that were possible using hydrogen bonding functionality of amide group, especially "tape" arrangement based on cyclic diamides.^[139] In 1983, amide based polymer is known in the form of polymer resin that is used as ink for printing electronic circuits.^[140] In 1988, the polymer form of amide was achieved by using alkyl amide moiety in a linear conjugated porphyrin polymers.

Bis(pyridyl)-diamide has an important contribution to synthesize the versatile topological networks of CPs/MOFs with their different flexible and rigid skeleton of alkyl to aromatic functionality. Several leading research groups, Kitagawa, Dasitdar, Biradha, Puddephatt, and Wang group have developed CPs by using these diamide linkers.^[141]



Scheme 1.2: Different bis(pyridyl) moieties with amide spacer and their conformation

In 2002, Kitagawa's group has published a crystalline porous 2D CPs from *N*-(3-pyridyl)-isonicotinamide bridging unsymmetrical ligand.^[57] Further this group, in 2006, showed selective guest adsorption by using a CP of tridentate amide ligands.^[142] In 2004, Puddephatt's group has shown self-assembly of CPs which was constructed by Hg(II) and bis(amido)-pyridyl using dynamic coordination and hydrogen bonding.^[143] Also, this group discovered lantern complex prepared from a diamide ligand and PdCl₂ (NPh)₂ which exhibited host-guest recognition and can encapsulate cations, anions and water molecules due to the interaction of guest species with either the electrophilic NH or nucleophilic CO of the amide group.^[144] Sun's group has extended the properties of CPs by including the rare-earth element, flexible tripodal acid with additional amide group, and flexible bis(pyridyl).^[145]

Dastidar's group has reported bis/tris(amide) based CPs that showed metallogel property.^[146] They have also derived a 3D CPs from different chiral amino acid-based bis(pyridyl)-diamide ligands.^[141d, 147] Wang's group has explored different architecture of CPs like helical structure (from tris(pyridyl)-diamide ligand).^[141e] From the semi-rigid bis(pyridyl)-diamide ligand, they have also prepared a series of CPs.^[148] They have investigated properties of bis/tris(pyridyl)-diamide in fluorescent sensing and in selective photocatalysis. Figure 1.23 showed a 1D left-/right-hand helical structure in CP of [Cu(4**bpah**)(5-**MIP**)(H₂O)], where **bpah** = *N,N*-bis(4-pyridinecarboxamide)-1,2-cyclohexane and **5-MIP** = 5-methylisophthalic acid.^[148a]

Majhi's group has reported amide based lanthanide CPs that showed unique properties of low molecular weight gelator.^[149] Mukherjee's group synthesized an organometallic building block by using diamide ligands and showed its application in luminescence properties.^[150]

Biradha's group prepared a series of copper CPs with different packing modes namely mixed, offset-offset, and trigonal, doubly interpenetrated networks, 1D looped chain, 2D with guest inclusion, 2D interpenetrated, and 3D network.^[151] In one of the works they have observed two types of SBUs with

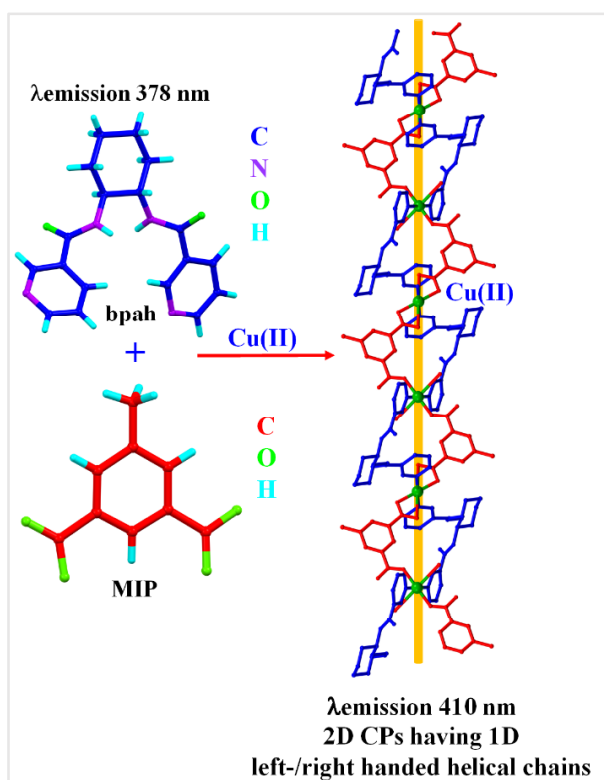


Figure 1.23: Left-/right handed helical CPs by bis(pyridyl)-diamide as co-ligand (CCDC No. 954315)

interpenetrated and non-interpenetrated 2D networks from the same ligand *N,N'*-(ethane-1,2-diyl)dinicotinamide (Figure 1.24).^[152] They have also reported 1D Cu(II) CPs of rectangular cavities based on the bis(3-pyridyl)-diamide with flexible ethylene spacer which has resulted in structural transformation upon exchange of ClO_4^- with PF_6^- anions.^[94, 153]

Our group has developed flexible CPs by using bis(pyridyl)-diamide linkers. Suman et al., have reported 1D looped chain with $\text{Cu}(\text{PF}_6)_2$ metal salt and bis(3-pyridyl)-diamide. They observed reversible guest inclusion of benzonitrile and nitrobenzene which was triggered by anion exchange.^[154] Changing the ethyl spacer to more flexible butyl spacer in bis(3-pyridyl)-diamide resulted in 2D interpenetrated network^[155]

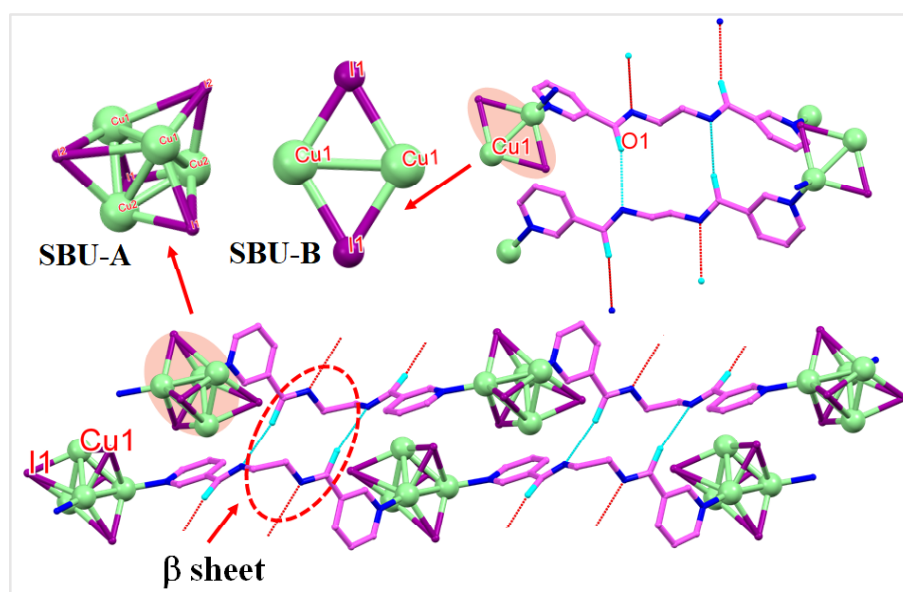


Figure 1.24: Two types of SBUs from the same ligand with β sheet recognition (CCDC No. 253152 and 253151)

1.5. Tuning methods in CP/MOF

Reversible and controllable structural changes can be brought by general physical stimuli such as light, mechanical deformation, thermal, electrical, or magnetic stimuli. Some of the reports which can lead to the development of CPs/MOFs with novel architectures and interesting properties are mentioned below:

1.5.1. Post-synthetic modification in CP/MOF

The integral parts of MOFs could be modified after the synthesis of MOFs, which is termed as Post-synthetic modification (PSM). Post-synthetic modification has emerged as an important tuning property of MOF where the nature of parent MOFs directs the structural arrangement resulting in MOFs of interesting outcomes. Post synthetic modifications can be considered as an important synthetic methodology when direct synthesis could not afford the desired MOFs.

Several modifications can be done in PSM that are not possible in the direct synthesis of MOF. Post-synthetic modification can be classified into covalent PSM, dative PSM and post-synthetic deprotection (PSD) according to the Seth M. Cohen review article.^[156] Covalent PSM deals with the formation of a new covalent bond, dative PSM deals with the formation of coordinate bonds like metal-ligand bonds and PSD considers the cleavage of the chemical bond (Figure 1.25).

PSM is attractive because of the reagent accessibility into the exterior and interior of the solid porous MOFs, this interior modification is not possible of many inorganic materials like microporous silicon, gold nanoparticles, and quantum dots. Hence, organic transformation developed by this PSM.

Post-synthetic modification transformations where the crystallinity is intact with structural changes is considered as single-crystal-to-single-crystal (SC-SC) transformation. The exchange reactant, solvent and temperature are the key factors of this process.^[157] Ma's group has shown that controlled heating parameter led to the synthesis of metalloporphyrin based Co(II)-MOF by SC-SC transmetalation of Cd(II)-MOF.^[158] Long and co-workers have shown metal exchange into the interior framework with charge balancing due to tightly bound the

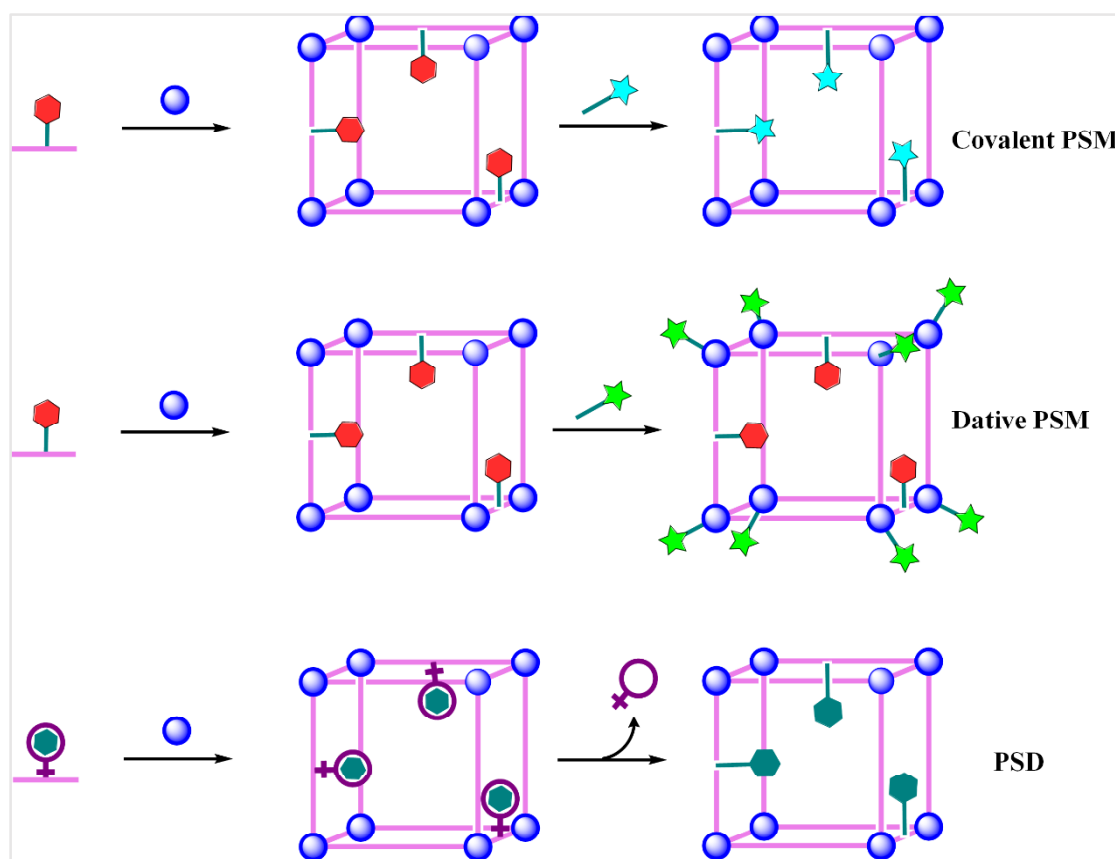


Figure 1.25: Possible types of PSM

metal nodes. SC-SC also leads the dimensionality of MOF, a 2D MOF was transformed into 3D MOF in the solid state by releasing the iodine molecules (Figure 1.26).^[159] Dinca's group has synthesized Mn(II)-MOF where Mn(II) ion was exchanged by Fe^{+2} , Co^{+2} , Ni^{+2} , Cu^{+2} , Zn^{+2} , and Li^+ while retaining the structural framework.^[160] Evans et al., have published a review post-synthetic metalation of MOFs which described the benefits of PSM.^[161] Farha's group in their feature article has discussed transmetalations in MOFs. Darren W. Johnson and co-workers have also reviewed the transmetalation of self-assembled supramolecular complexes and described a direct substitution exchange of metal while keeping structural integrity and also described about the transmetalation which resulted in a disruptive exchange of metal with a major change of supramolecular assembly (Figure 1.27).

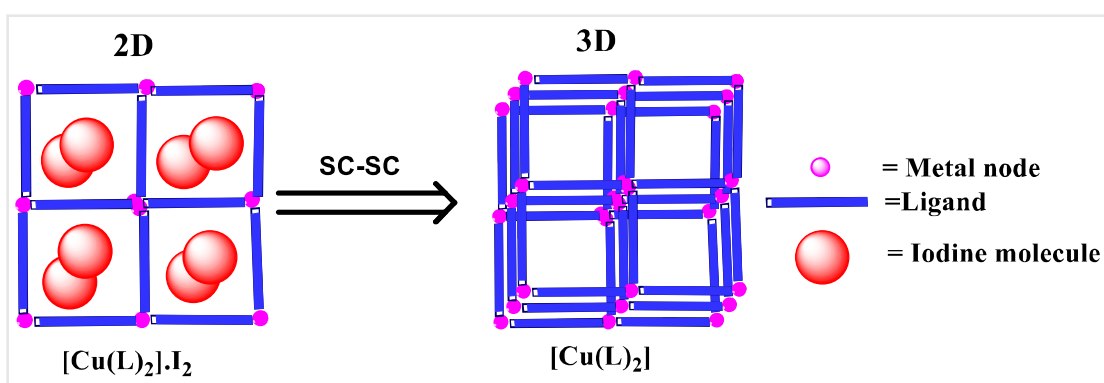


Figure 1.26: SC-SC leads the 2D to 3D transformation by removable of I_2 molecules

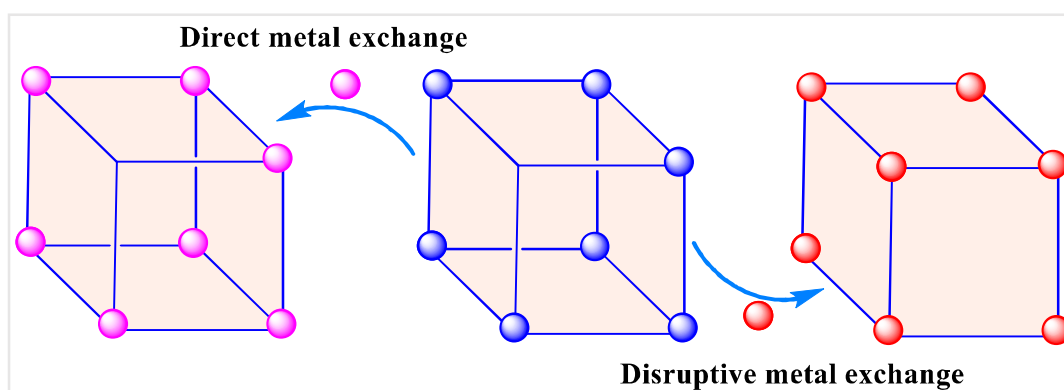


Figure 1.27: Representation of two different routes of transmetalation

1.5.2. Guest exchange

Flexible framework in MOFs leads to guest exchange processes. The non-covalent interaction provides the supporting role for guest molecules in the network. External stimulus such as temperature, pressure, light, and solvent act as the main parameter for guest exchange processes from the pores of CPs/MOFs. These parameters are needed in sufficient level to break the non-covalent interactions of the inbuilt guest molecules with the network while keeping structural

integrity. Chen et al., have reported Co(II)-MOFs which showed a switchable gate effect by encapsulation or release of guest molecules ($\text{NH}_3/\text{H}_2\text{O}$) during the transformation process into the frameworks.^[162] Guest exchange studies are effective when inbuilt solvent as a guest molecule could be removed successfully from the framework giving a lot of scope for incorporating external guest molecules into that framework. Biradha's group has developed such CPs in which a wide range of aromatic guest molecules such as pyrene, naphthalene, anthracene, benzene, and several aromatic solvent molecules were inserted (Figure 1.28).^[94]

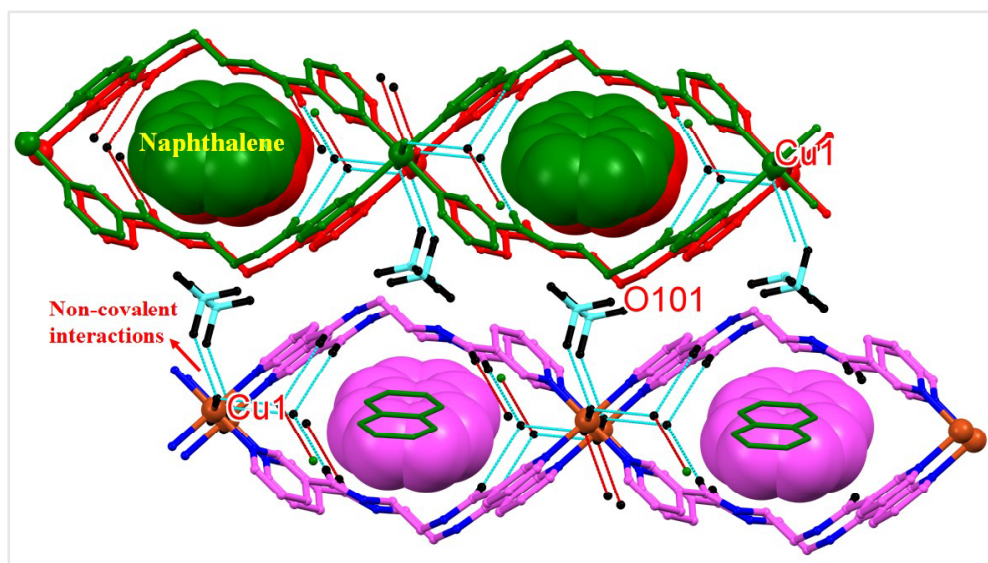


Figure 1.28: Insertion of naphthalene guest molecules (CCDC No. 630422)^[94]

1.6. Current applications of MOF/CP

A crystalline solid material MOF is being exploited in several applications which includes gas adsorbent, sensor, catalyst, light emitting device, magnet, conducting device, nano-MOF architecture material, etc., because of the effectiveness in attaining tunable pore size and controllable shape in the range of microporous to mesoporous, post-synthetic modification, pre-designed material with the help of flexible, rigid, and semi-rigid organic linkers (Figure 1.29).^[141a, 163]

1.6.1. Gas adsorbent

One of the most important applications of MOFs is in the energy-related technologies (Adsorption Properties) (e.g., H_2 , CH_4 , and CO_2), where MOFs are explored widely.^[164] In MOFs/CPs, one of the challenges is the predictability of polymeric networks and dimensionalities, because of the varied possibilities of coordination geometry of the metal ions, the metal/ligand ratio, the flexibility of the backbone of the ligands, as well as the counterions and solvents, and finally the reaction conditions (e.g., temperature).^[14] Tailoring pore size and

shape of MOF is helpful to detect selective gas adsorption which is observed in example- $Zn_2(\text{atz})_2(\text{ox})$ where **atz** is 3-amino-1,2,4-triazole and **ox** is oxalate.^[165] **MOF-5** is the first example of hydrogen adsorbate MOF.^[42] **MOF-177** has a large pore size around 11.8 Å in diameter and resulted in high H₂ adsorption on that guest surfaces.^[166] Different MIL-MOF have shown to possess high surface area in the range of (2280-1719) m²/g for effective in selective gas adsorption.^[167] **IRMOF-3** showed H₂ adsorption behaviour due to 3062 m²/g surface area.^[168]

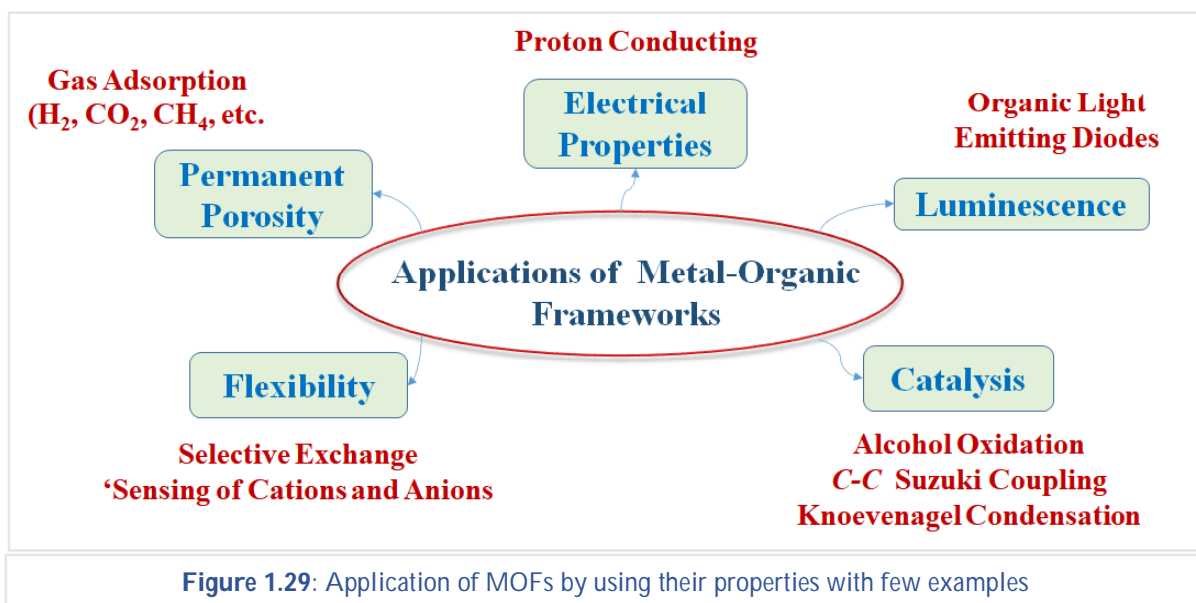


Figure 1.29: Application of MOFs by using their properties with few examples

1.6.2. Sensor

Selective exchange and sensing of cations and anions (Sensing and host-guest interaction) are another important application of MOFs, one example is $NaLa(\text{H}_4\text{pmtp})$, where **H₄pmtp** is 1,4-phenylene-bis(methylidyne)tetrakis(phosphonic acid).^[169] In aqueous solution, Na ion present in the channel of the MOF, so it can be changed by monovalent Li⁺, K⁺, and Rb⁺ and divalent metal ion Mg⁺², Ca⁺², Sr⁺², Ba⁺², Ni⁺², Cu⁺², Zn⁺², and Mn⁺².^[170] Reversible color changes are observed when the structural transformation occurred by absorption of the selective guest molecule.^[171] Deep's group has described the application of MOFs as potentially active for toxic gas H₂S detection.^[172] MOFs are also used as luminescent material for sensing small molecules.^[173] Solvatochromism study was done in Cu-MOF by Lu et al., wherein blue shift in absorption band was observed for two distinct groups of solvents.^[174]

1.6.3. Catalysis

MOFs are used as catalysts because of the presence of different pore functionalities, high surface area and high thermal stability. MOFs are potential candidates for heterogeneous catalysts which are easily separated from reaction mixture and enhances the reusability.^[175]

Many reports are available with MOF-catalysts having a high turnover number (TON). Pd-MOF [Pd-(2-pymo)]_n, where 2-pymo = 2-hydroxypyrimidinolate showed good catalytic activity in alcohol oxidation, C–C Suzuki coupling, olefin hydrogenation.^[53] Other organic transformation reactions such as Friedel-Crafts,^[176] transesterification,^[177] cyanosilylation,^[178] Henry reaction,^[179] Knoevenagel condensation,^[180] etc., are well catalysed by MOFs. Calleja and co-workers explored **Cu-MOF-74** as catalyst for Friedel-Crafts acylation with high reusability.^[181] Some other examples of MOFs as catalyst include, **HKUST-1** for cyanosilylation,^[182] Cu(II)-MOF for Henry reaction,^[179] **IRMOF-3** for Knoevenagel condensation,^[183] etc. MOF/CPs are also used as a catalyst in organic dye degradation.^[184]

1.6.4. Luminescence

Photophysics is concerned with the processes that involve changes in characteristic physical properties under light irradiation. Luminescence is one of the photophysical properties which is not only due to composition and concentration of species but is also affected by the intermolecular packing of molecules and their energy transfer processes. When a molecule absorbs energy, it gets excited from ground state (S_0) to excited singlet state (S_1) and on radiative deactivation, luminescence in the form of fluorescence ($S_1 \rightarrow S_0$) will occur within a timescale of nanosecond. While in phosphorescence, radiative decay ($T_1 \rightarrow S_0$) from the different triplet state (T_1) to ground state within microsecond to second will result through intersystem crossing ($S_1 \rightarrow T_1$). These two radiative processes are shown in the schematically drawn Jablonski diagram in Figure 1.30.

MOFs are well investigated in the fields of organic light-emitting diodes (OLEDs), chemical sensors, biomedical imaging, and optoelectronic devices.^[185] Especially the luminescence of MOF could be tuned by ligand, metal and guest molecules. An example is discussed here. Ramamoorthy Boomishankar and co-workers explored CuI-MOFs for photophysical properties. CuI-MOFs ([Cu₆I₅(thiophosphorous amide)]-(OH)·3DMF·2.5MeOH)_n emitted blue fluorescence at 298 K ($\lambda_{em} = 419$ nm) and an orange-yellow phosphorescence at 77 K ($\lambda_{em} = 594$ nm).^[186]

1.6.5. Conductivity

MOF can be used as a conductor if ionic species can be incorporated into porous networks.^[187] Givaja et al., have explained possible mechanism pathway of conductivity of CPs in their review article.^[188] The most prominent application of MOF is as an electrolyte in fuel cells due

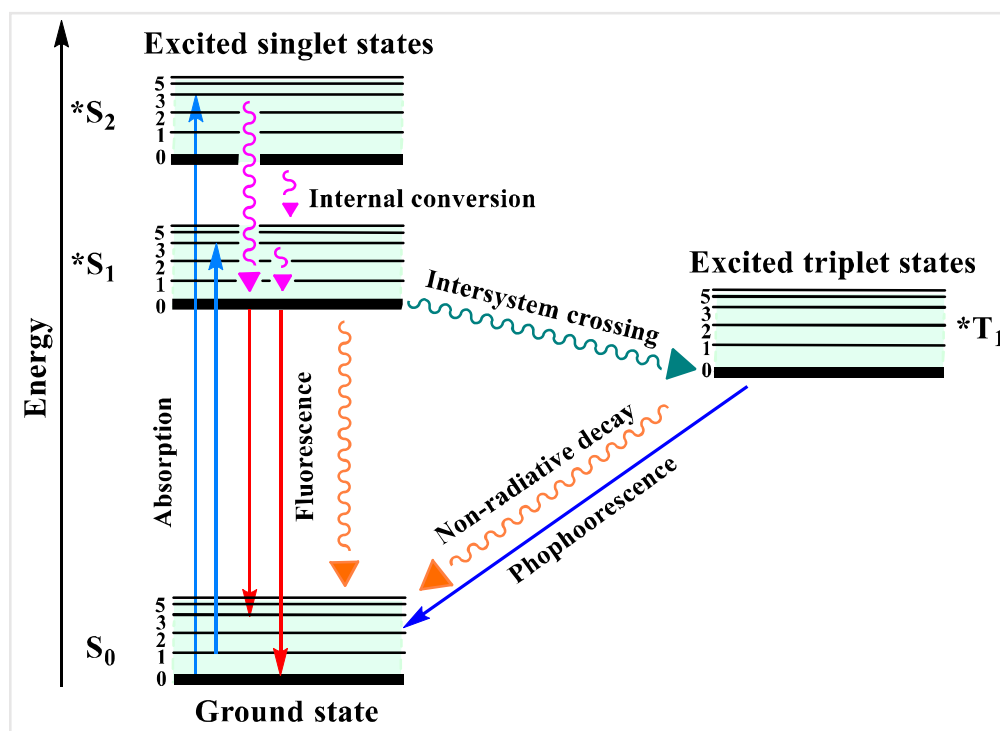


Figure 1.30: Jablonski diagram

to their ability for proton conduction. Ramaswamy et al. have discussed the proton conduction mechanism of CPs in their review.^[189] Mainly proton conduction can occur by lattice water/solvent as a guest and due to the presence of hydrogen-bonded network. Kitagawa et al., have reported several proton-conducting MOFs based on oxalate ligands.^[190] Kanda et al., have explored a series of proton conducting 2D CPs based on dithiooxamido ligands.^[191] $Zr_6O_4(OH)_4$ and carboxylate based UiO-66 MOFs were also explored as efficient proton conduction material by Hiroshi Kitagawa,^[192] Gong,^[193] Samar K. Das^[194] and others research groups^[195] through tuning the MOFs channel towards the hydrophilicity has explored a wide range of MOFs for proton conduction applications. Biradha's group has reported a Li-MOF which showed ionic conductivity in $10^{-5} \text{ S cm}^{-1}$ order magnitude at room temperature.^[196]

1.6.6. Magnetism

Magnetism is one among many attributions of MOFs where the networks can be decorated by magnetic moments carriers like paramagnetic metals and organic ligands. Anti-ferromagnet^[197], ferromagnet^[198], ferrimagnet^[199], long-range ordered, short-range ordered, metamagnet, single-molecule magnet^[200], single-ion magnet^[201] and single-chain magnet^[202] are found in this field of magnetic MOFs/CPs. Exchange of interaction between the magnetic moment carriers is needed for magnetization at a certain distance within a range that is feasible in the MOFs. Molecular based magnets (MBMs) and single-chain magnets (SCMs) of CPs

have been developed by keeping these phenomena. For MBMs, a strong interaction between the chains of CPs is required and for SCMs, the ratio of intra and interchain value should be high for slow relaxation of magnetization. Mohamedally Kurmoo has given a critical review on “magnetic MOFs”. He discussed the diversity of magnetic exchange interaction between the various magnetic moment carriers such as dimer to oligomers of infinite chains containing Co-CPs.^[203] In one of the examples, temperature dependent magnetic susceptibility fluctuates with the structural environment. Toledo et al. have reported paramagnetic CP of Co(II) with a combination of cobalt(II) acetylacetonate and 4'-(4-carboxyphenyl)-3,2':6',3''-terpyridine. The ferromagnetic behaviour of this 2D CP resulted in a magnetic moment of 3.76 B.M. near to the spin only value of 3.87B.M. At lower temperatures, a sharp decrease of $\chi_m T$ (χ_m is the molar susceptibility of per Co(II)) was observed due to the inter-cluster antiferromagnetic interaction. This complex observation of magnetism is due to the orbital contribution of the octahedral crystal field and axially distortion of octahedron environment of Co(II).^[204]

1.7. Aim of the present study

MOFs/CPs have undergone overwhelming development, not only for their fascinating structures or topological networks but also for their multi-functional properties including gas adsorption, ion exchange, catalysis, optical devices, molecular magnetism, photoluminescence, drug delivery. Pyridyl based coordination polymers were mainly under the category of 1st generation CPs. The use of carboxylate-based CPs resulted in a wide range of 2nd generation CPs. The design and synthesis of 3rd generation CPs are still in their infancy.

Objective of present thesis is to make use of crystal engineering technique for developing the design strategy through the non-covalent interactions which could change the molecular confirmation with electronic delocalization in molecular packing and tune the emissive properties of ligands such as aggregation induced emission and aggregation caused quenching. Further, the purpose of this thesis is to synthesize bis(aryl) heteroatom spacer containing linkers based on imine (C=N), amide (HN-C=O) and sulfonamide (HN-S(=O)₂) functional groups in crystalline form which can also co-ordinate with metal ions and form infinite 1D, 2D, and 3D molecular network through their assembling of non-covalent interactions. The second purpose is to explore multifunctional properties of CPs/MOFs in various fields such as cation exchange, guest removal, guest adsorption, photocatalysis, conductivity, magnetism, and catalysis. The observed luminescent properties of linkers are correlated with their crystal packing in a solid

state. The phenomena of ligation are very selective among the various metal ions which are applied in real-time application. The flexible alkylene chain length can control the chelation with metal ions. The variation in position of pyridyl nitrogen affords either discrete complexes (2-pyridyl) or CPs/MOFs (3/4-pyridyl).

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