# Chapter 1

# General Introduction

## 1.1 Coordination polymers

Coordination Polymers (CPs) are polymers with high-molecular-weight materials are organized by replicating subunits joined by covalent bonds. Coordination polymers are network of metal ions (M) and linkers (L) (also called as organic ligand) in endless systems where normal repeating units connected with coordination bonds and supplementary weak chemical bonds can enlarge "infinitely" into one, two or three dimensions (1D, 2D or 3D, respectively) through some covalent M-L bonding (Fig. 1).

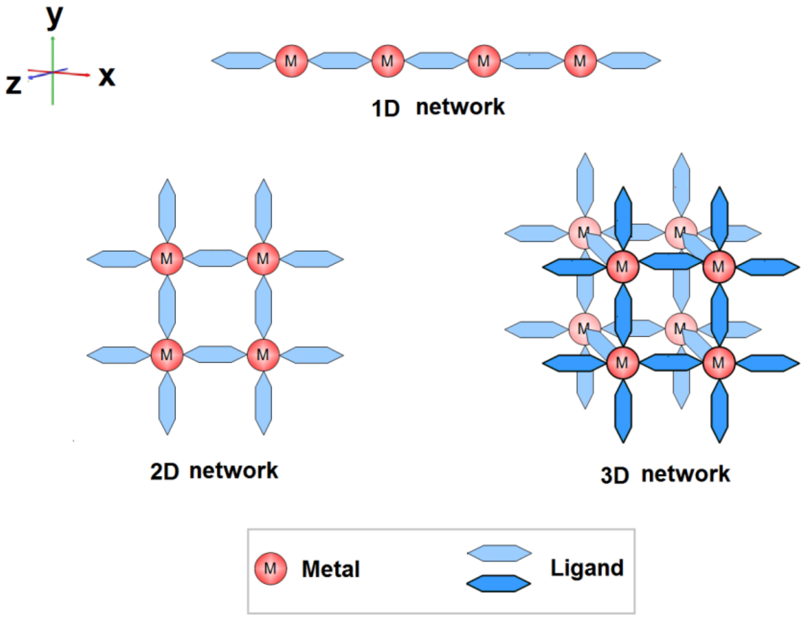


**Fig. 1** Formation of 1D, 2D and 3D network

In case of organized structures such coordination polymers are also designated as metal organic coordination framework. The particular organization of the species in CPs normally stays in the solid state. In solution state, the organizing blocks act together via interactions (covalent) and weaker forces like hydrogen bonds, π-π stacking, van der Waals interactions to produce miniature molecular units. Finally, CP is formed by the self-assembly method through interactions. Naturally the products formed as solid are insoluble and may change upon dissolution. X-ray crystallographic techniques fix the constitution of CPs and categorization in solution signifies the certainty of oligomeric fragments.

Coordination bonds in CPs are built through the donation of the ligand (Lewis base) lone pair of electron to the metal cation (Lewis acid). Again, electrostatic attraction among the positively charged (metals ion/ions) and negatively charged or polarized (donor atom/atoms) centers of the ligand. In such interactions the energy assessment is more or less 50 kJ mol$^{-1}$. For reasonable hydrogen bonds the energy of D-H…A interaction differs around 15-40 kJ mol$^{-1}$ (D-H : the proton donor to A). The distance of H…A is around 1.5-2.2 Å for strong O-H…O/N hydrogen bonds having ∠DHA of around 140-180°. The distance of 2-3 Å with ∠DHA 120-180° is observed for weak interactions. Significantly, π-π interactions are vital for the creation of CPs. Face-to-face and edge-to-face (C-H…π) orientations engross aromatic interactions. All the above-mentioned interactions are collective result of various factors like van der Walls interactions, electrostatic repulsion, etc. The stacking of aromatic rings lessens the repulsion and maximizes attractions. In case of face-to-face interactions, 3.4-3.8 Å is the centroid-to-centroid distance. The π-π interaction energy is around 5-10 kJ mol$^{-1}$.[1-3]

Intensive study of network structures has been done on CPs, especially, compounds having backbone raised from metal cations as connectors and ligands as linkers.[4–31] The term, “coordination polymers” came into sight in near the beginning 1960s, and it fore mostly reviewed in 1964.[32]

## 1.2 Synthesis principles

**1.2.1 Ideology:** Two central components are there for coordination polymers i) connectors and ii) linkers, which indicate the main skeleton of coordination polymer. Moreover, the auxiliary components are blocking/capping ligands, nonbonding guests/templates, anions and molecules. However, the effectiveness of linkers and connectors are directed via the number and arrangement of their sites of binding which exactly denote the coordination numbers along with the geometries of coordination. Metal ions are repeatedly applied as adaptable connectors during the preparation of CPs. The coordination numbers of a metal ion can vary between 2 to 7 which is tuned by the metal ion, additionally, the oxidation state (of metal ion) creates variety of geometries like linear, square-planar, tetrahedral, square-pyramidal, trigonal-bipyramidal, octahedral, trigonal-prismatic, pentagonal-bipyramidal, and also the distorted structures analogous. [33] Besides, linkers manage to gift an extensive diversity of connecting sites which control the binding potency and directionality (Fig. 2) straightforwardly. The least and simplest of every linkers [33] are halides like F, Cl, Br, and I. Instances of CPs with cationic organic ligands are very few in the literature of their little affinity for cationic metal ions Conversely, cationic ligands derived from N-aryl pyridinium and viologen were effectively justified.[34–36]

### 1.2.2 Bonding interactions:

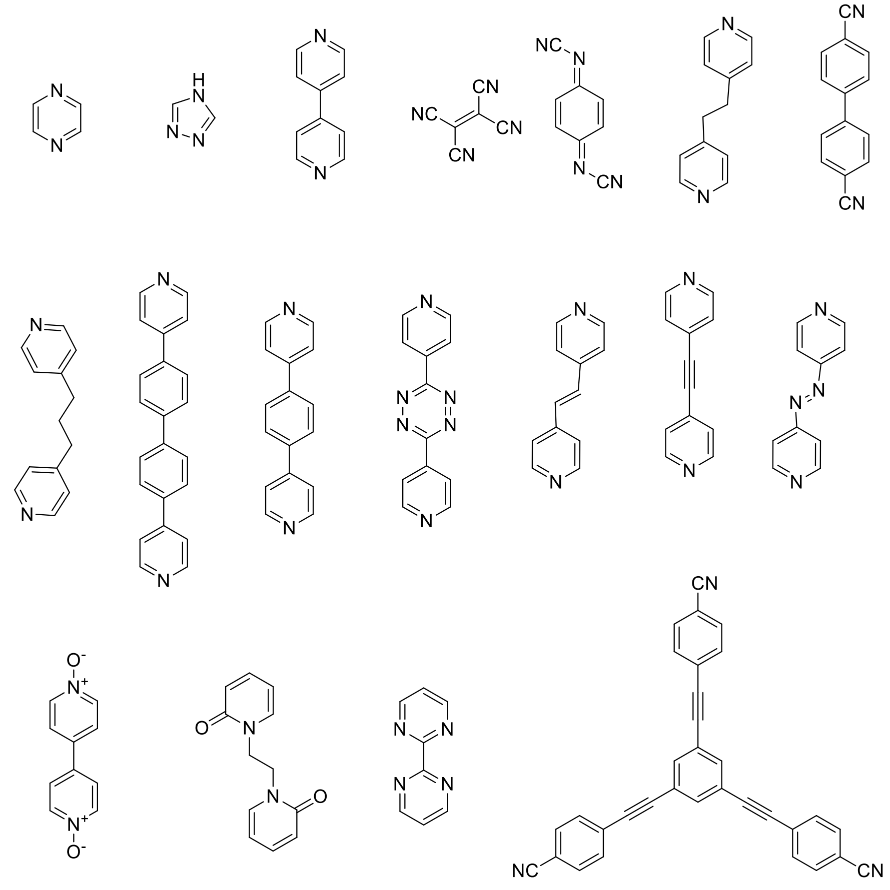
Commonly, four types of bonding interactions provide the framework geometry of CPs which is given in Figure 3. They are, (a) only coordination bond (CB), (b) coordination bond + hydrogen bond (CB+HB), (c) coordination bond + extra interactions (metal–metal bond (MB), π-π (PP), CH– π (HP)), and (d) coordination bond + combination of interactions (for example, HB+PP, HB+MB, or MB+PP). The enhance in the contribution of the coordination bond influences the potency of 3D motifs. HB, PP and HP the excess weak bonds often influence the aggregation of the 1D and 2D motifs to furnish 3D networks. The 3D motifs may interrelate with each other by weak interactions (e.g. interpenetration geometry) as mentioned earlier. A variety of 1D linear M–L (L= bipyridine ligands) CPs are coupled via hydrogen bonds that are formed between ligands and solvent (coordinated) to make 2D rectangular grids, every of them is associated via π-π interactions among the ligands of the pyridine moieties (type d: CB+HB+PP).[33, 37–42]

### a. Inorganic ligands

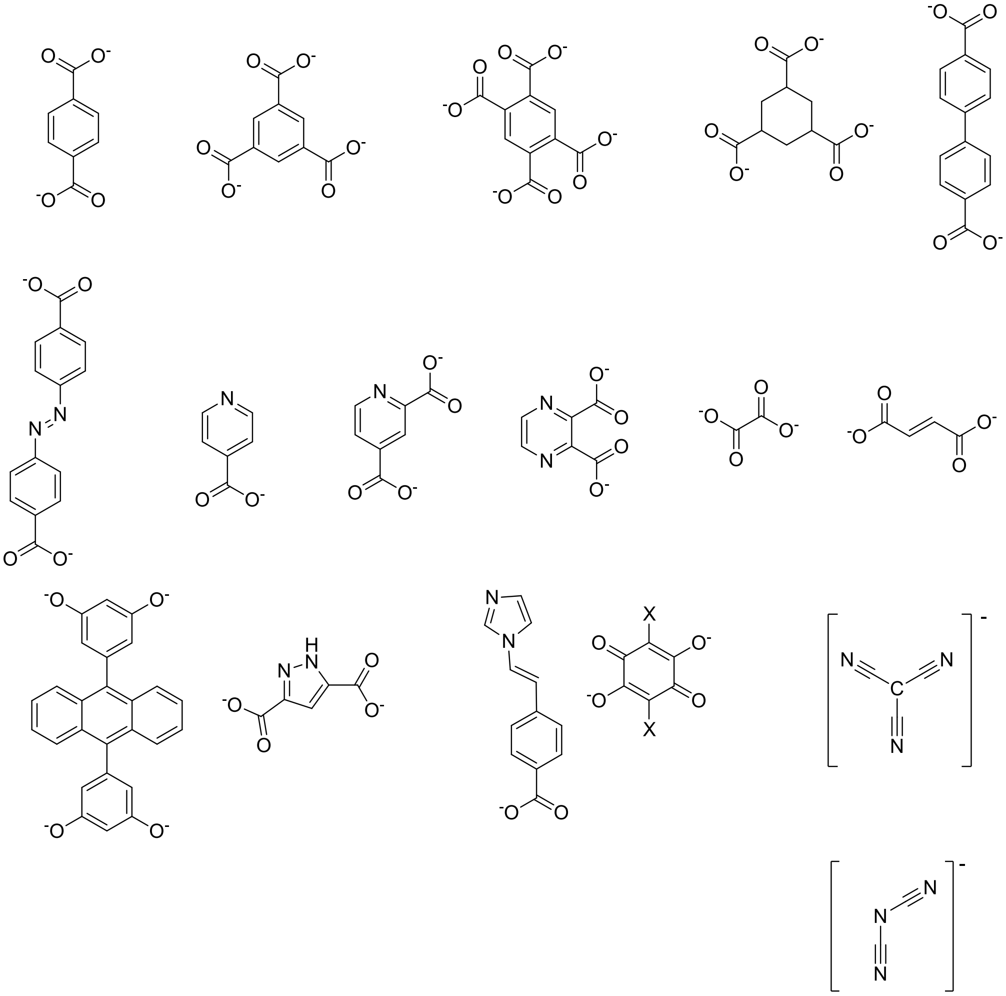
**Halides** F, Cl, Br, I **Cyanometallates** $[M(CN)_X]^{n-}$

CN- $SCN^-$

### b. Neutral organic ligands



**c. Anionic organic ligands**



**d. Cationic organic ligands**

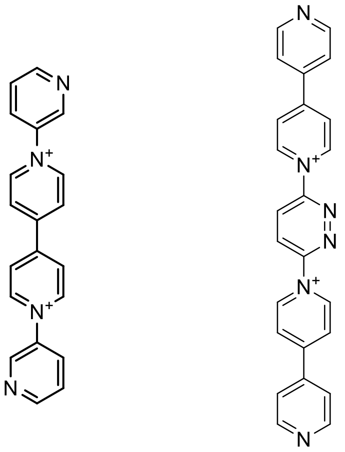


**Fig. 2** Some representative linkers for coordination polymers

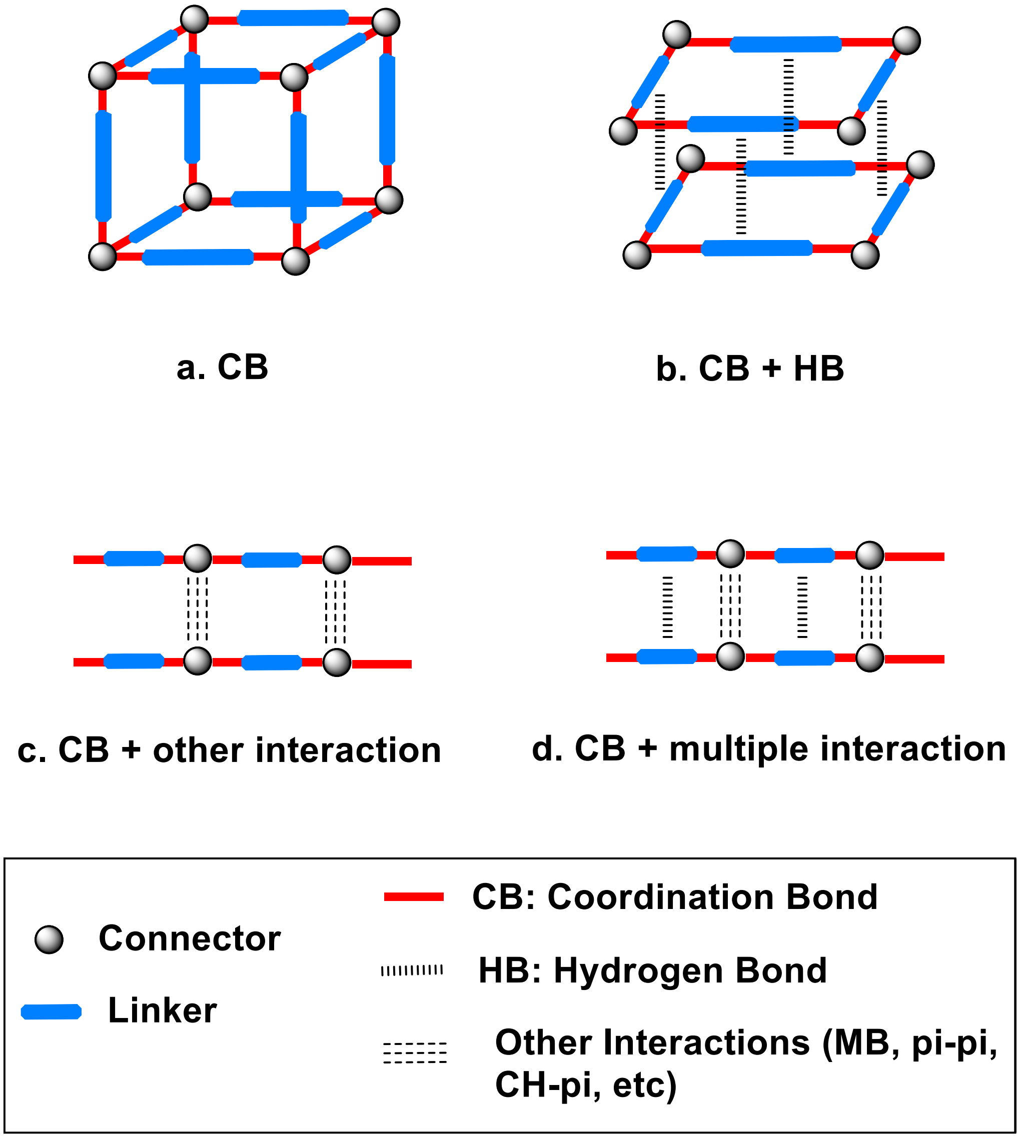


**Fig. 3** Arrangement of interactions contributing in coordination polymers

## 1.3 Synthetic methods :

One of the challenging tasks of this research is to attain suitable single crystals for detailed crystallographic analysis. Once synthesis is done, most of such coordination polymers not able to get dissolved in water. That's why crystallization is barely a choice.

In order to synthesize coordination polymers [43] several synthetic methods have been exploited. Such approaches are (1) diffusion of reactants into the polymeric matrix in a slow manner, (2) gas phase diffusion, (3) solvent evaporation at ambient/reduced temperature, (4) precipitation/recrystallisation from solvent mixture, (5) cooling by controlling the temperature and (6) synthesis by hydrothermal method.

Coordination polymers are synthesized using common wet chemistry that is normally practiced in a synthetic inorganic chemistry laboratory where ligand(s) and metal salt(s) are permitted to react in a solvent either at an superior temperature or at room temperature. In the synthetic procedure the reaction temperature is a key parameters.

### 1.3.1. Hydro(solvo)thermal methods:

In hydro(solvo)thermal synthesis single crystals were obtained by the combining organic ligands with metal salts under solvothermal conditions. Zeolite synthesis are originally done in Hydrothermal methods [44]. Not only this but a recent expansion of this method is functional to the synthesize of wide-ranging materials, including the polyoxoalkoxometalates.[45] Hydrothermal reactions, utilize the self-assembly of the material synthesized from soluble precursors in the temperature variation of 120 - 260 0C under autogenous pressure. [46] High boiling polar solvents like water, acetonitrile, dialkyl formamides, dimethyl sulfoxide, are applied to mix the reactants. Credit must be given to consider that the main parameters when conducting solvothermal MOF synthesis are the pH of the solution, the concentrations of ligand and metal salt, temperature, solubility of the reactants (in solvent). Under such circumstances the reduction of viscosity enhances the method of diffusion, so that growth of crystals from solution is favored.[47]

### 1.3.2. Sonochemical Reaction and Synthesis:

The appliances of ultrasound for the synthesis of CPs are regular now a day and the processes and reactions are popularly called Sonochemistry. In sonochemistry molecules pass through a reaction under ultrasound irradiation of around 20 kHz–10 MHz. [48]. This is finely a top– down approach to the producion of coordination polymers [49]. The ultrasound with high intensity is useful to produce the new materials.

## 1.4 Dimensionality of coordination polymers:

Based on some explicit features of structure and composition the classification of CP is done. The most significant classification is considered as dimensionality. In it we find a number of one-dimensional (1D), two-dimensional (2D) or three-dimensional (3D) structures having fascinating structural features via coordination bonding, aromatic p-p stacking interactions, hydrogen bonding and van der Waals forces.[50-53,17,54-56] One dimensional structure enhances in a straight line (along the x axis); a two dimensional structure enhances in a plane (x and y axes); and a three dimensional structure enhances in three directions (x, y, and z axes).[57] Now-a-days all these variants have attracted wide attention.

Many a variety of success stories has been highlighted encompassing different aspects of CP family from structural along with application some typical latest works are being highlighted to have a glance on the recent stasus of this research area.

### 1.4.1. 1D Coordination polymers

1D Coordination polymers When the one-dimensional metal ion pattern are connected with ligand molecules (two) in an infinite alternate way, they form several chain like geometry such as linear, zigzag, double chains, ladder-like etc. along with several structural variety like fish-bone, helix etc.[58-66] The report of Razaei et. al. highlights that a 1D Zn(II) - trimesic acid coordination polymer works as anti-breast cancer drug carrier if the 1D network is stabilized by hydrogen bond[68] Liu et. al. recently published a lanthanide-transition metal heterometallic Dy-

Zn coordination polymer showing molecular magnetism having magnetic bistability and magnetic relaxation, popularly known as single-molecule magnet having prospective application in the field of information storage, quantum information processing etc.[68] The effort of Sasnovskaya et. al [69] has projected the single chain magnet behavior where the root of the single chain magnet behavior is the 1D Mn(II) coordination polymer. Literature also reported so many attractive 1D coordination polymer. Several interesting 1D coordination polymers has been published in the literature.[70,71-81] Song et. al. reported a zinc-based one-dimensional (1D) coordination polymer has been synthesized and characterized by spectroscopic and physicochemical methods, single-crystal X-ray diffraction, and thermogravimetric analysis. [72] (Fig. 4).

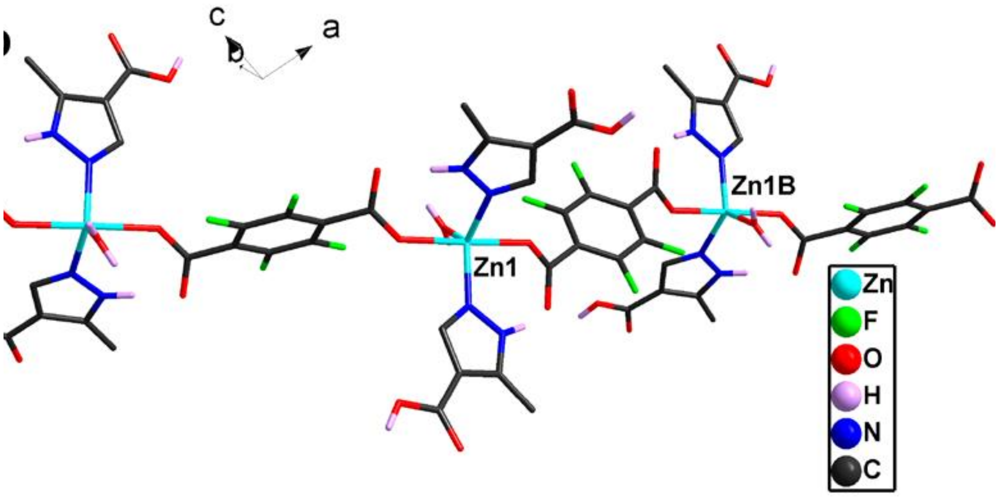


**Fig. 4**. Zn(II) 1D chain

### 1.4.2 2D Coordination polymers:

Cucos et. al. reported Co(II) CP where cobalt(II) ions connected [CoII4] helicates to form a 2D CP where the ac magnetic quantity revealed the incidence of slow magnetization relaxation due to the uncorrelated and single cobalt(II) ions, that were thinned in a diamagnetic environment of {CoII4} moieties.[80] J.P. Lang group reported a cadmium(II) CP as a luminescent multi-responsive sensor for mercuric ($Hg^{2+}$), chromate ($CrO_4^{2-}$) and dichromate ($Cr_2O_7^{2-}$) ions in aqueous medium by the method of luminescence quenching.[81] Rodríguez-Diéguez et. al. reported 2D CP where dynamic ac susceptibility study disclose an exclusive single-ion-magnets (SIMs) among the few instances of reported CPs showing that behaviour. [82] An exceptional 2D series of hetero bi-metallic $Fe^{II}$-$Hg^{II}$ coordination polymers (Fig. 5) with two spin-crossover (SCO) was reported by Zhang et. al. [83]. Several 2D CPs were present in the literature. [84-93]

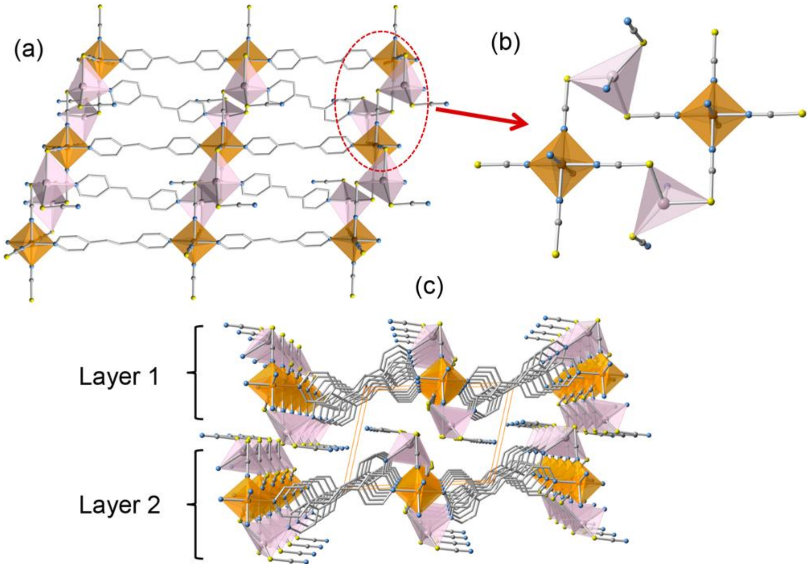


**Fig. 5**. (a) Fragment of a layer displaying the $[Fe(\mu\text{-tvp})]_n^{2n+}$ chains connected through $\{[Hg^{II}(SCN)_3]_2(\mu\text{-L})\}^{2-}$ units. (b) View down the [001] direction of the connection between two chains (note that this connection contains another relevant inversion center). (c) Stack of two consecutive layers. Coordination centers: $[FeN_6]$ (orange), $[HgS_3N]$ (pink).

### 1.4.3 3D Coordination polymers

3D Coordination polymers Very recently, a chiral cobalt(II) based CP with the topology of 3D hyperkagome´ is published [94] where the aqua molecules that were coordinated to a crystallographically pair symmetric cobalt(II) ions are discreetly in two steps on heating/cooling. This was supported by the conversion of single-crystal-to-single-crystal (SCSC). Li et. al reported Pb-based coordination polymers which possess through elevated thermal stabilities, the favored adsorption of $CO_2$ over $N_2$ and excellent activities of photocatalytic for degradation of dye through visible light irradiation.[95] A water-stable lanthanide CP was reported, [96] which has a luminescent sensor with multi-responsive character that can offer higher sensitivity and lower limits of detection for $Fe^{3+}$, Cr(VI) or 4-nitrophenol in water medium. A semiconducting 3D mixed valenced iron-fluoranilate CP was reported by Murase et. al. [97] where the octahedral metal ions were connected via fluoranilate ligands forming the 3D network. (Fig. 6) The existence of pores in the structure helps an opportunity for introducing electron donors or acceptors as guests that may modulate the electronic along with the magnetic property of the network. A variety of 3D CPs were published in the literature. [98-108]

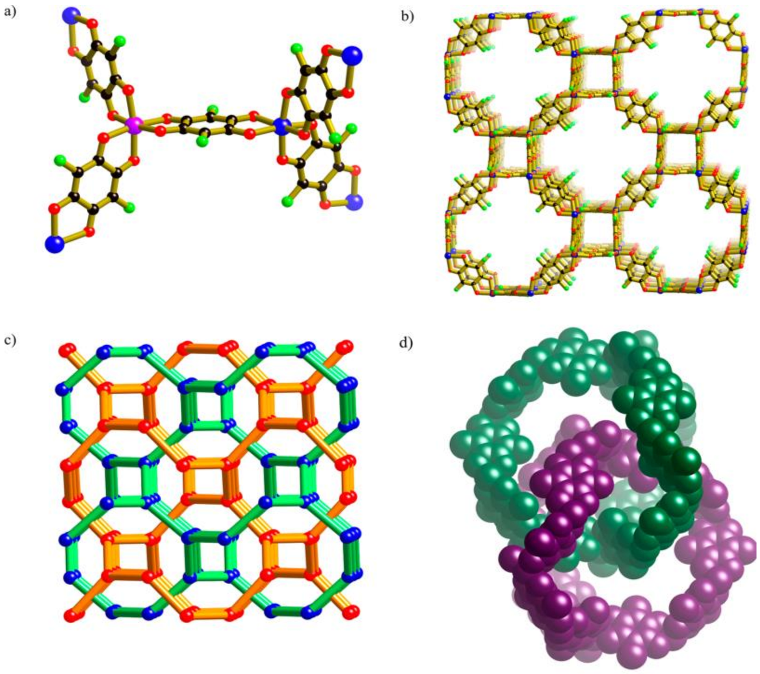


**Fig.6**. Structure of the CP showing (a) the coordination environments of the Fe centers, C black, O red, F green, Fe1 blue, Fe2 pink; Fe2 is located on a crystallographic threefold axis. (b) One of two (10,3)-a networks. (c) Schematic representation of the two independent (10,3)-a nets; spheres represent Fe centers (nodes), and connections represent bridging fan anions. (d) Space-filling representation of the two anionic networks (green and purple).