Conclusion

Chapter 2 of the thesis describe the synthesis, characterization, and luminescence study of two complexes: $[Pb_3(idiac)_3(phen)_2(H_2O)].2(H_2O)$ (**1**) and $[Pb(ndc)]_n$ (**2**). The lead (II) atoms to exhibit a highly distorted square bipyramid geometry (ψ-octahedron) atom with the lone pair occupying one of the bipyramid axial vertices.Pb1 ion is chelated by the phen and by the tridentate idiac ligand, of which the carboxylate oxygen O (1b), behaving as a bridging donor, bounds the central lead Pb(2). On the other hand Pb2 is chelated by the tridentate idiac anion through the central N and the oxygen donors from the carboxylic groups, and in addition by an aqua ligand and the oxygen (O(1b) at x, y-1, z) from the carboxylate of the indiac chelating Pb1. Both the metal centers are five coordinated with close comparable Pb-N and Pb-O bond distances involving the iminodiacetato ligand.

The three nuclear building block gives rise to a 2D coordination network developing in the ab-plane. The layers have the phen rings pendant at both sides and are packed to form a 3D architecture where interdigitatedphenantroline ligands give rise to strong π – π interactions . The centroid-to-centroid distances between the rings of the chelating aromatic ligands are of 3.565(5) and 3.571(4) Å.

In Complex **2** the metal atom exhibits a hemidirected disposition of O-donors [35] and has a disphenoidaltrigonalbipyramidal geometry. The $[Pb(carboxylate)2]_n$ polymeric chains through the naphthalene-dicarboxylato give rise to a 3D architecture , where the NDC ligand adopts a bis(bidentate-bridging) coordination mode where every NDC ligand bridges four Pb(II) cations. The crystal packing does not evidenced any significant π – π interaction, being the shorter distance between the naphthalene rings of 4.5 Å, but rather C-H...π-ring interactions, where the H…ring distance is of 2.89(8) / 2.92(6) Å and C-H. Ring centroid angle of 142(5)and 119(6)° are measured.

Luminescence studies for 1-2 are also explored in this chapter**.** The blue shifted emission in complex **1** may be assigned as π*–π and π*–n charge transfer transition of the o-phen ligand and complex **2** may originate from the intraligand transition of naphthalenedicarboxylate.

Chapter3 of thesis deals with the synthesis, characterization and luminescence study of coordination polymers of Zn(II) and Cd(II) with 5-nitroisophthalic acid, 5-sulfoisophthalate, 1,4-benzenediacrylic acid and bipyridine i.e $\{[Zn(bipy)(NIPH)].1.5H_2O\}_n$ (**3**), $\{[Cd_2(bipy)_2(NIPH)_2].2H_2O\}_n$ (**4**) and $\{[Cd_2(bipy)_4(BDAC)(NO_3)](NO_3).6H_2O\}_n$(**5**). The crystal structure of compound **3** reveals a zig-zag coordination running along axis *c*, chain built by Zn(bipy) units connected by the 5-nitro-isophthalate anions (NIPH) through the carboxylic groups. The coordination geometry presents a highly distorted trigonalbipyramidal where O2' and N2 donors are located at axial positions (N (2)-Zn-O(2') bond angle = 154.05(8)°) .

In CP **4,** two crystallographic independent cadmium ions Cd1 and Cd2 have a hexa and hepta coordination number, respectively, the coordination sphere is sketched. In CP **4** displays a 1-D ladder-like chain where each distinct cadmium ion forms an array running parallel to crystallographic axis *a*. The Cd(bipy) moieties are bridged by NIPH anions through carboxylic groups acting as chelating groups. These carboxylic groups O3/O4 and O7/O8 are slightly out of plane from the aromatic rings, forming a dihedral angle of 14.4 and 19.8° with it. The lattice water molecule O1w binds O2 and O10 through H-bonds and strengthens the double chain. The crystal packing evidences the ribbons slightly interacting by π–π stacking of N4 bipy rings.

The crystal packing of compound **5** shows 1-D channels occupied by uncoordinated nitrate anions and lattice water molecules that connect the coordination chains through H-bonds to give rise to a 3D supramolecular network. CPs **3** and **5** exhibit similar bathochromic shifts (red shift) and CP **4** shows the blue shifted emission band with H_2NIP and H_2BDAC ligands respectively. Since both Zn(II) and Cd(II) are d^{10} systems, it is really difficult for these to undergo oxidation or reduction process. The spectral behavior of these complexes is neither due to metal-to-ligand nor ligand-to-metal charge transfer transition. Hence, metal perturbed intraligand π–π* charge transfer transition is responsible for the emission behavior of the reported complexes.

Chapter 4 describe the synthesis and characterisation of Mn(II) coordination polymer of formula $[Mn_3(phen)_2(phdac)_3].2H_2O$ (**6**), $[Mn(4,4'\text{-bipy})(H_2O)_4](cbprop)$ (**7**) and $[Mn(2,2'\text{-bipy})(4\text{-nph})(H_2O)_2]_2$ (**8**). The complex **6** and **7** are synthesized hydrothermally by reacting Mn $(OAc)_2{\cdot}4H_2O$ with 1,4-phenylene diacetic acid and 3-(4-carboxyphenyl)propionic acid respectively but complex **8** is synthesized reflux condition by reacting with Mn $(OAc)_2{\cdot}4H_2O$ and 4-nitrophthalic acid. In CP **6**, it forms a 2D coordination polymer parallel to the (111) crystallographic planes. The crystal packing shows trinuclear manganese (II) entities featuring two Mn(phen) moieties that sandwich another manganese ion by means of six bridging carboxylate groups in a centrosymmetric fashion. The crystal packing is a 2D coordination polymer of (4,4) topology where the trinuclear units represent the nodes and the edges are formed by a pair of phdac and by a single phdacanion, the latter positioned on a center of symmetry. The layers are interdigitated so that facing phen pyridine rings interact through π-π interactions (centroid-to-centroid distance of 3.7438(1) Å). In addition lattice water molecules bridge carboxylate oxygen O3 and O6 of different layers by means of weak H-bonds, thus forming a 3D architecture.

The structural determination of the CP **7** reveals $Mn(H_2O)_4$units bridged by 4,4´-bipyridine ligands with the occurrence of 1D coordination polymeric chains. In the chain the metal exhibits a slightly distorted octahedral geometry, where the metal coordination sphere is completed by four water molecules. 3D architecture is thus created by the described H-bond scheme and in addition by weak π-π interactions between the 4-carboxyphenylpropionate ring and pyridine ring N, as evident from Fig. 4.12.

In CP 8 intra-molecular O-H···O hydrogen bonds between the aqua ligands and uncoordinated carboxylate O atoms reinforce the whole structure. In addition the water molecules link the binuclear complexes to form supra-molecular chains propagating parallel to [100] direction. The spectral behaviour of these complexes is neither due to metal-to-ligand nor ligand-to-metal charge transfer transition. Hence the emission behaviour of **6** and **8** are due to the metal perturbed intra ligand ***π****–***π*** charge transfer transition for **6** and ***π****–***π*** and ***π**-n** charge transfer transitions for **8**.

Chapter 5 of thesis deals with the synthesis, characterization and luminescence study of 2D and 1D coordination polymers of Ag(I) ions with 1,4-pheneylene diacetic acid, 5-Sulfosalicylic acid and N-donor coligands *i.e.*, $[Ag_2(bpp)_2(Phdac)].5H_2O$ (**9**) and $[Ag_2(bpp)(HSSal)]$ (**10**). CP **9** is a 2-D layer coordination polymer constructed from 1,4-pheneylene diacetic acid and 4,4’-trimethylene dipyridine ligands. The Ag atom is coordinated by two carboxylate oxygen atoms from the 1,4-pheneylene diacetate anion and two nitrogen atoms from two 4,4’-trimethylene dipyridine ligands in a distorted tetrahedral geometry. The 1D polymeric chain which propagates along . The solvent water molecule O1 at (x, y, z) acts as donor to the carboxylate oxygen atom O4 in the molecule at (1-x, y, 1-z), thus interconnects the parallel polymeric chains to build a 2D layer assembly in **9**. The C15 atom of the 4,4’-trimethylene dipyridine ligand in the molecule acts as donor to the carboxylate oxygen atom O4 in the molecule, thus generating a 3D supramolecular framework in **9**; the parallel and central projection of the 3D architecture .

In CP **10** is also a 2-D coordination polymer constructed from 5-Sulfosalicylic acid and 4,4’-trimethylene dipyridine ligands. The asymmetric unit contains two Ag(II) ions with different coordination environments, in which Ag(1) is triply coordinated while Ag(2) is four-coordinated with distorted tetrahedral geometry. The pyridine ring carbon atom C12 in the molecule act as hydrogen bond donor to the aryl ring (C1–C6) in the molecule , so generating a 2D layer network in (1 0 1) plane . Interestingly, both the metal ions Ag(1) and Ag(2) are in contact with the centroids of the pyridine rings through Ag···π interactions . The Ag (2) ion with the centroid of the pyridine ring, leads the molecules to build a unique layered network in the (0 1 1) plane . Complex **9** is slightly red shifted with respect to bpp ligand. Complex **10** is red shifted with respect to 5-Sulfosalicylic acid (H_3SSA) and blue shifted with respect to 4, 4’-trimethylene dipyridine (bpp) ligand. As Ag(I) ion is a d^{10} system so it is very difficult for this metal to get oxidized or reduced. Such emission behavior of **9** and **10** may be assigned to metal perturbed intra-ligand charge transfer transition.

Chapter 6 describethe synthesis, characterization and thermal study of two Pb(II) coordination polymers: **$[Pb(ind)_2(H_2O)]_n$** (**11**) and **$[Pb(dbsf)(bipy)]_n$** (**12**). In CP **11**, of formulation $[Pb(ind)_2(H_2O)]n$, revealed for this a 1-D chain-like coordination polymer. The lead atom is chelated by two indan-2-carboxylato groups and by two oxygens, which come from symmetry related different ligands. The coordination sphere is completed by a water molecule .

In CP **12**, the lead(II) atom is pentacoordinated, being double chelated by the carboxylic groups from symmetry related dbsf anions and further bound by a bipy nitrogen donor. The hemidirected coordination geometry. The TGA reveals that the complexes **11** and **12** are stable up to 66°C and 245°C respectively.