Abstract

The chemistry of the coordination polymers (CPs) has in recent years advanced extensively, affording various architectures, which are constructed from a variety of molecular building blocks with different interactions between them. Taking advantage of the structural flexibility of organic ligands, various coordination spheres of metal ions, or the strength of supramolecular interactions, variety of coordination polymers could be synthesized having potential applications in diverse areas

Chapter 1 of the thesis contains introduction which contains a brief review of CPs including the various bonding interactions involved in CPs. The synthesis methodologies like solvothermal synthesis, sonochemical synthesis were discussed. From structural point of view, various type of CPs like 1D, 2D and 3D coordination polymers and their applications were briefly discussed.

Chapter 2 of the thesis describe the synthesis, characterization, and luminescence study of two new lead(II) coordination polymers of composition $[Pb_3(idiac)_3(phen)_2(H_2O)].2(H_2O)$ (**1**) and $[Pb(ndc)]_n$ (**2**). In CP **1** layers having phen rings at both the sides were packed to form the 3D structure. Strong $\pi - \pi$ interactions stabilized the system through interdigitated phen ligands. In CP **2** the $[Pb(carboxylate)_2]_n$ polymeric chains were formed through the naphthalene-dicarboxylato to form 3D architecture. Luminescence study of both the CPs was done.

Chapter 3 of thesis deals with the synthesis, characterization and luminescence study of coordination polymers of Zn(II) and Cd(II) having compositions **{**$[Zn(bipy)(NIPH)].1.5H_2O\}_n$ (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**). In solid state, all the complexes expanded their dimensionality to 3D by means of π – π interactions and hydrogen bonds produced by lattice water molecules. The fluorescence study signify intraligand π – π* charge transfer.

Chapter 4 describes 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** were synthesized hydrothermally but complex **8** was synthesized under reflux condition. CP **6** forms 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 phda canion, the latter positioned on a center of symmetry. The layers are interdigitated and the phen pyridine rings interact through π-π interactions. Lattice water molecules bridge carboxylate oxygens of different layers via weak H-bonds, forming a 3D architecture. In CP **7** the $Mn(H_2O)_4$ units were bridged by 4,4´-bipyridine ligands forming 1D coordination polymeric chains. 3D architecture is formed by the H-bond. Additionally, weak π-π interactions are identified between the 4-carboxyphenylpropionate ring and pyridine ring. In CP **8** intra-molecular O-H···O hydrogen bonds between the aqua ligands and uncoordinated carboxylate O atoms reinforce the whole structure. The spectral behavior of these CPs is neither due to metal-to-ligand nor ligand-to-metal charge transfer transition. The emission behavior of **6** and **8** were 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 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. Initially formed 1D polymeric chain formed with which propagates along (0 0 1) direction. The solvent water molecule acts as donor to the carboxylate oxygen atom interconnects the parallel polymeric chains to build a 2D layer assembly which finally formd a 3D supramolecular framework in **9.** CP **10** is also a 2-D coordination polymer constructed from 5-Sulfosalicylic acid and 4,4'-trimethylene dipyridine ligands. Here two Ag(I)-metal ions are in contact with the centroids of the pyridine rings through Ag···π interactions. Emission behavior of **9** and **10** may be assigned to metal perturbed intra-ligand charge transfer transition.

Chapter 6 describe the synthesis, characterization and thermal study of two Pb(II) coordination polymers: [Pb(ind)$_2$(H_2O)]$_n$ (**11**) and [Pb(dbsf)(bipy)]$_n$ (**12**). CP **11** is a 1-D chain-like coordination polymer. The lead atom is chelated by two indane-2-carboxylato groups and by two oxygens, which come from symmetry related different ind 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 is evident in the structure. The TGA reveals that the CPs **10** and **12** are stable up to 66°C and 245°C respectively.