ABSTRACT

Synthesis of metal complexes with chelating ligands specially Schiff base is an important field of research in Chemistry. Coordination complexes comprising transition metal ions and various ligands have received paramount interests to synthesis coordination chemists due to their interesting structural features and diverse functionalities. Transition metal-based coordination compounds have wide range of application in Biology, Magnetic Materials, Photo-electronic device, Therapeutic agents and so on. The design of synthetic analogues for the active sites of different metallo-enzymes makes a significant advancement in Bio-mimicking Chemistry with novel mechanistic insights of the catalytic cycles.

Chapter I: In this chapter introduces the design, foundation and applications of the coordination compounds based on synthetic and commercially available ligands. This chapter deals with the objectives and applications of the present work in the present context of scientific development.

Chapter II: This chapter comprises the synthesis, X-ray crystallography, spectroscopic characterization and phosphoester cleavage activity of a linkage isomer, bis(2,2′-dipyridylamine)dithiocyanato(*k*-S)nickel(II), $[\mathrm{Ni}(\mathbf{L}^1)_2(k\text{-SCN})_2]$ (**1**) of a previously reported Ni(II) complex, $[\mathrm{Ni}(\mathbf{L}^1)_2(k\text{-NCS})_2]$ [$\mathbf{L}^1$ = 2,2′-dipyridylamine; SCN = thiocyanate]. X-ray diffraction analysis of the nickel(II) complex reveals that nickel(II) compound crystallizes in a monoclinic system with $P2_1/c$ space group. The nickel(II) ion exists in tetragonal coordination geometry where the square plane consists of two units of dpa ligands. Two thiocyanate ions coordinate at axial position to the Ni(II) centre in this centrosymmetric structure and satisfies the cationic charges of Ni(II) ion. The phosphoesterase cleavage efficiency of the Ni(II) complex has been examined in aqueous-methanolic medium using disodium (4-nitrophenyl)phosphate hexahydrate (PNPP) as a standard substrate. The mechanistic cycle is explicated by computational calculations and ESI mass spectral analysis of PNPP in presence of Ni(II) complex.

Chapter III: Here highlights the synthesis, physicochemical and morphological characterization, supramolecular interactions and aggregation-induced blue emission of a newly developed Schiff base, 1,2-bis(phenyl(pyridin-2-yl)methylene)hydrazine ($\mathbf{L}^2$).

The photophysical behaviour of the Schiff base is studied in both monomeric and aggregated forms. FESEM images exhibit a large number of aggregated islands of the monomeric **L²** particles in the solid state. These short-ranged dispersive forces account for isoenergetic and isotropic C–H···π and π···π interactions, thus playing a significant role in aggregation behaviour of **L²**. The total dispersive energy involved in the cluster of molecules is estimated to be -192.4kJ/mol.

Chapter IV: Chapter IV summarizes the synthesis, structural characterization and phenoxazinone synthase-like activity of two structurally similar copper(II) complexes developed with a benzimidazole functionalized Schiff base ($\mathbf{L^3}$). The ligand, $\mathbf{L^3}$ is designed and synthesized in high yield by the reaction of p-methoxy benzaldehyde with o-phenylenediamine. The reaction of $\mathbf{L^3}$ with $CuCl_2$ and $Cu(NO_3)_2$ leads to the formation of two isostructural complexes, $[Cu(\mathbf{L^3})_2Cl_2]_2$ (**2**) and $[Cu(\mathbf{L^3})_2(NO_3)_2]_2$ (**3**). An attempt has been made to understand the role of coordinated co-ligands on the catalytic oxidation of 2-aminophenol (2-AP) to 2-amino-3H-phenoxazine-3-one (2-APX) in methanol. The presence of coordinated nitrate to Cu(II) ions imparts a more labile character to complex **3** and the catalytic efficiency (k_{cat}/K_M) for complex **3** (1.50×10^7) was determined almost double compare to that of complex **2** (8.78×10^6). Electrochemical and EPR spectral analysis of the reaction mixture confirm the presence of active $2\text{-AP}^-/2\text{-AP}^{\bullet-}$ redox species in the course of catalytic oxidation and suggest the radical driven oxidative coupling of 2-AP in an aerobic environment.

Chapter V: In this chapter presents the synthesis, structural characterization and phenoxazinone synthase activity of a new phenoxido-bridged dicopper(II)-Schiff base complex, $[Cu_2(\mathbf{L^4})_3]ClO_4$ (**4**), [$\mathbf{L^4}$ = (Z)-2-methoxy-6-(((2-methoxyphenyl)imino) methyl)phenol]. X-ray structure of the Cu(II) complex reveals that each of the two Cu(II) centres in **4** adopts different coordination geometries (distorted octahedral and distorted square planar) and phenoxido bridges couple two Cu(II) centres to form a dinuclear copper complex with Cu···Cu distance 3.182 Å. The dicopper(II) complex catalyzes the aerobic oxidation of 2-aminophenol (2-AP) to aminophenoxazinone species in acetonitrile with good turnover number, 78.14 h^{-1}. Electro-chemical, electrospray ionization mass spectrometry, EPR analysis and computational calculations of **4** in presence of 2-AP ensure the radical-driven catalytic oxidation of 2-AP.

Chapter VI: This chapter reports a peculiar characteristic of a polydentate Schiff base towards zinc(II) ion in the presence of pseudohalides (thiocyanate and azide) and the charge transport properties of the zinc complexes mediated devices in the solid state. The designed polydentate chelator, [**L^4** = (Z)-2-methoxy-6-(((2-methoxy phenyl)imino)methyl)phenol)] has been synthesized by coupling of *o*-anisidine and *o*-vanillin in ethanol under reflux. Crystal engineering approach, Hirshfeld surface and energy framework analysis of the complexes delineated the dominant contribution of H···S, H···N hydrogen bonding and C−H···π interactions for a structural assortment of the compounds. Further, the complexes have been employed to construct devices to explore the charge transport properties in dark and shower photons. The complex **6** exhibited better charge transport properties relative to complex **5**, as evident from high DC conductivity measurement values and relaxation times caused by optical phonon activation in dark and photo conditions.

Chapter VII: Finally, the future scope of the research work has been delineated in this chapter.