

ABSTRACT

Design, synthesis and characterization of Schiff bases and their complexes with transition metals is a recurring theme of coordination chemistry research. Schiff base complexes containing transition metal ions have been studied in great detail for their various crystallographic features, enzymatic reactions, steric effects, structure–redox relationships, mesomorphic characteristics, catalysis, photophysical and magnetic properties, NLO activity and their important role in the understanding of the coordination chemistry of transition metal ions.

In view of the diverse applications of metal Schiff base complexes, the present Ph.D. thesis titled “**Synthesis, Mesomorphic and Photoluminescence Study of Strategically designed Schiff base ligands and their Complexes with some Transition Metal ions**” describes synthesis, characterization and structural assessment of strategically functionalized Schiff base ligands with multiple donor sites and their transition metal complexes. The newly synthesized compounds were explored for their mesomorphic and photophysical properties. Energy optimized structure of the compounds have been ascertained with the aid of density functional theory calculations employing Gaussian 09/DMoL3 program at B3LYP /BLYP level.

The content of the entire thesis is distributed over six chapters.

CHAPTER 1

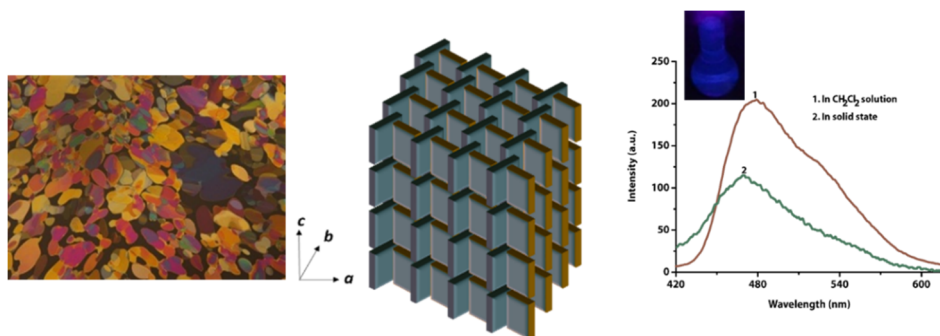
Chapter 1 presents a brief discussion pertaining to Schiff base ligands and their metal complexes drawing references from contemporary literature. Structure and property of some reported Schiff base metal complexes related to the work embodied in the present thesis is discussed in the subsequent sections. Thereafter, a short description on general applications of Schiff base complexes, emphasizing mainly on the catalytic, biological, liquid crystallinity and photophysical aspects are presented. A very short and general introduction about liquid crystals and the various mesophases is also covered in this chapter.

CHAPTER 2

A description of chemicals, solvents, and details of the instrumental techniques used for physical studies is presented in **Chapter 2**.

CHAPTER 3

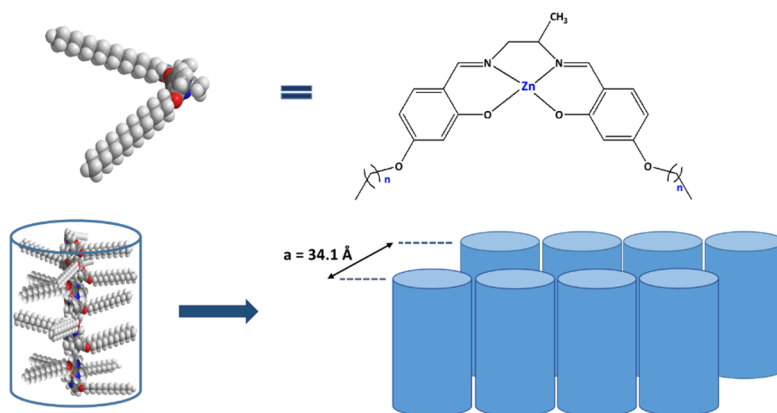
Synthesis and characterization of a series of four-coordinate d^{10} -metal complexes of the type $[ML_2]$ $\{M = \text{Zn, Cd, Hg}; L = 4\text{-nitro-2-}((\text{octadecylimino})\text{methyl})\text{phenol}\}$, incorporating a new N-alkylated bidentate [N,O]-donor salicylaldimine Schiff base ligand forms the subject matter of discussion in **Chapter 3**. The ligand is non-mesomorphic and non-luminescent. The Zn(II) and Cd(II) complexes, however, display highly ordered mesophases. An orthogonal symmetry with a ‘herringbone’ array for the zinc complex and a primitive triclinic symmetry ($p1$) for the cadmium complex, respectively, has been proposed on the basis of variable temperature powder X-ray diffraction study. The complexes emit blue light at room temperature, both in solution and solid state. The complex of Hg(II), though luminescent, is non-mesomorphic and decomposes prior to melting.



CHAPTER 4

Chapter 4 deals with the synthesis, characterization and systematic investigation of the mesomorphic and photophysical properties of a new series of photoluminescent Zn(II) complexes $[\text{ZnL}]$, $\text{H}_2\text{L} = [\text{N,N}'\text{-bis-(4-n-alkoxysalicylidene)-1,2-diaminopropane}]$ ($n = 12, 14$ and 16) derived from asymmetric ‘salen’ type Schiff base ligands. Though the ligands are non-mesomorphic, coordination to zinc(II) ion induces liquid crystalline behaviour.

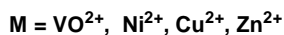
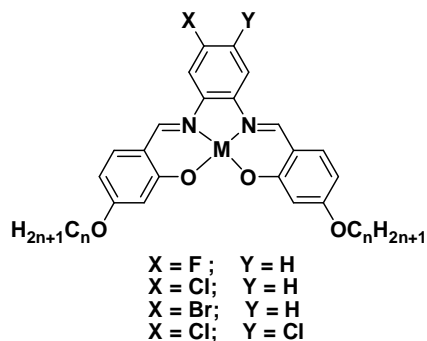
The complexes exhibit a lamello-columnar phase (Col_h), as characterized by a variable temperature powder X-ray diffraction (XRD) study. Intense blue emissions are observed for the complexes at room temperature in solution, in the solid state and in the mesophase. Besides, the complexes exhibit interesting aggregation behaviour in dilute solution of solvents, driven by the nature of coordinating species. While de-aggregation to monomer occurs in coordinating solvents due to axial coordination to Zn(II), aggregates are formed in the solution of non-coordinating solvents. DFT and Time-dependent DFT (TD-DFT) spectral correlative study carried out on a representative complex allows considerable insight into the geometry and electronic properties of the complexes.



CHAPTER 5

In **Chapter 5**, synthesis of three new series of monosubstituted and a series of disubstituted ‘salphen’ type Schiff base ligands bearing different halogen substituents at the spacer and their corresponding VO(IV), Ni(II), Cu(II) and Zn(II) complexes is discussed. Effect of the spacer group substitution on the mesomorphic and photophysical properties of the ligands and the corresponding metal complexes has been studied at length. The role of the metal ion on the mesomorphism and photophysical behaviour of the complexes has also been explored. Mono-substituted ligands are all mesomorphic. Phases shown by these ligands are oblique columnar ($p1$), rectangular columnar ($p2mm$) and hexagonal columnar ($p6mm$), respectively, former two being stable down to room temperature. Besides, these ligands are also photoluminescent and emit blue and green light respectively, in solution and in the

solid state. The photoluminescence property of the fluoro and chloro substituted ligands is preserved in the mesophase as well. Quite opposite to the monosubstituted ones just mentioned, vicinal dichloro substituted (-Cl,Cl) salphen ligands, are non-mesomorphic. However, these ligands are also photoluminescent and emit in the blue-green region of visible spectrum. Amongst the oxovanadium(IV) complexes of the respective mono and di-halogenated salphen ligands, both mono-fluoro and chloro substituted ones are mesomorphic, displaying rectangular columnar phase($p2mm$), while complexes of mono bromo- and dichloro-substituted ligands are not, which decompose at temperatures greater than 270°C . Ni(II) complexes of mono and di-halogenated (-Cl,Cl) ligands are all mesomorphic and display oblique columnar phase($p1$) and/or rectangular columnar phase ($p2mm$), respectively. Besides, the mono-halogenated Ni(II) derivatives display weak emission in the blue region of the visible spectrum. The dichloro substituted analogues are however, non-emissive. The Cu(II) complexes of all the ligand series are non-mesomorphic, and decompose prior to melting. The Zn(II) complexes of these ligands are all mesomorphic, displaying rectangular columnar phases of $p2gg$, $p2mm$ and $p2mg$ symmetry, mesophase of dichloro substituted complexes being stable down to room temperature, thus affording room temperature mesomorphism. These complexes are all photoluminescent and emit in the green region both in the solution, solid state and mesophase (for dichloro substituted Zn(II) complexes only). In addition, the Zn(II) complexes exhibit interesting aggregation behaviour in solvents of different coordinating abilities. While H-type aggregates are formed in non-coordinating solvents, polar coordinating solvents are marked by the presence of monomers. Optimized electronic structure of selected representatives of the ligands and the complexes has been ascertained by density functional calculations.



CHAPTER 6

An overall summary highlighting the salient findings of the research work discussed in **Chapter 3-5** is incorporated at the end of the thesis. The future scope of studies has also been projected in this chapter.

References cited in the text have been separately compiled at the end of each of the chapters. A list of research publications emanating from the thesis and conference/workshops attended is also appended along with the copies of published/accepted papers.