ABSTRACT

In view of the escalating diverse interests attached to the Schiff base and its transition metal complexes particularly in the development of coordination chemistry, physico-chemical properties, catalytic transformations, bioactivities, antimicrobial activities, the present Ph.D. thesis entitled **"Synthesis, Photoluminescence and Mesogenic Properties of Some d- and f-block Metal Schiff Base Complexes"** concerns the synthesis of newer functionalised multidentate Schiff base ligands from strategically selected aldehydes with appropriate amines and complexation with d- and f-block transition metals. The experimental investigations including photophysical, mesogenic, magnetic and electrochemical properties of the synthesized compounds are the primary goal of the present thesis. DFT/TDDFT studies using DMol3/B3LYP program were carried out to obtain the optimized geometry of the complexes.

The content of entire thesis is distributed over seven chapters.

Chapter 1:

Chapter 1 portrays an introductory overview of Schiff base ligands and their metal complexes drawing references from contemporary literature thus explaining the motive of undertaking this particular work. A general introduction about the basics of liquid crystals, different types of mesophases is covered in this chapter. Significant properties and application of Schiff base ligands and their metal complexes in the context of liquid crystallinity, photoluminescence, catalytic and biological activity is discussed in the chapter.

Chapter 2:

A description of experimental methods, chemicals and materials, and details of the equipment used for physical measurements are described in Chapter 2.

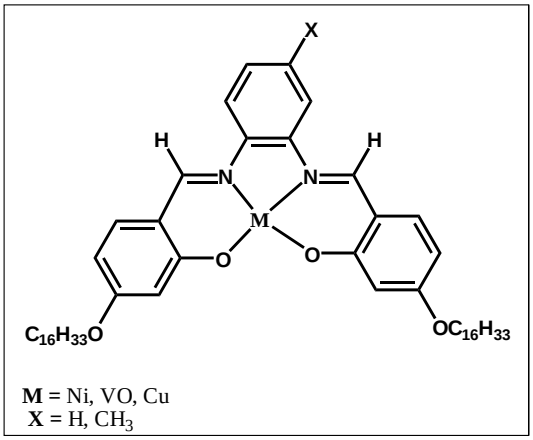
Chapter 3:

In Chapter 3 synthesis and characterisation, systematic investigation of mesomorphic and photophysical properties of salicylaldimine based Schiff bases and their VO(IV)/Cu(II)

metal complexes have been described. A series of new oxovanadium(IV) Schiff-base complexes bearing long as well as short alkoxy tail on both side of aromatic ring are all found to be thermally quite stable and exhibit smectic mesomorphism. Two series of oxovanadium(IV) and copper(II) salicylaldimine complexes bearing polar substituent on aromatic rings have been successfully synthesised. The ligands are found to exhibit smectic/nematic mesomorphism. However, the nitro-substituent compound with a C_4 tail lacks any mesomorphism. None of the oxovanadium complexes are found to be mesogenic. Interestingly, the copper complexes except the nitro-substituted one (C_4 tail) are mesogenic and showed smectic A phase. At 330 nm excitation, the ligands showed green emission in the solid state (~516-559 nm) at room temperature.

Chapter 4:

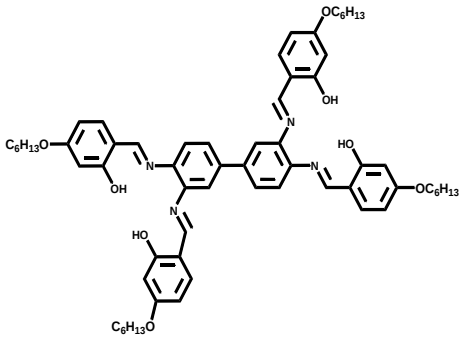
Chapter 4 incorporates the synthesis and characterisation of salophen-based Schiff base metal complexes. Detailed discussion on liquid crystalline properties which is ascertained using polarised optical microscopy, differential scanning calorimetry and powder X-ray diffraction technique as well as self-organized assembly of the molecules in the mesophase is done in this chapter. A new series of Ni(II)–salophen complexes (Ni-16opd/Ni-16mpd) bearing differently substituted aromatic spacer (opd: orthophenylene diamine and mpd: methyl substituted orthophenylene diamine) all showed rectangular columnar mesomorphism. An interesting phase behaviour exhibiting two types of rectangular columnar phases (Col_{r1} to Col_{r2}) was observed for the vanadyl complexes, the former (Col_{r1}) being stable down to room temperature. The copper complexes with methyl (CH_3) or no substituent on the aromatic spacer showed rectangular columnar (Col_r) mesophase and rectangular plastic columnar (Col_{rp}) phase, respectively. Influence of spacer group substituent on mesomorphism in metal complexes of 'salen' type Schiff bases is also discussed in this chapter. A discussion on DFT study has been made which allows considerable insight into the nature and electronic structures of transition metal complexes.



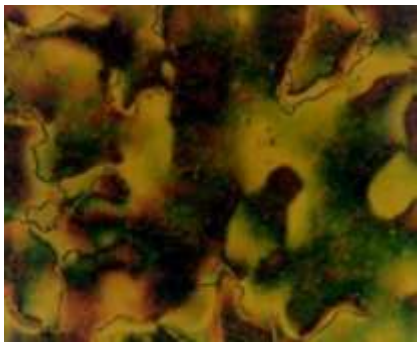
M = Ni, VO, Cu
X = H, CH_3

Chapter 5:

Chapter 5 includes synthesis, characterisation, the mesogenic and photophysical properties of dinuclear Schiff base metal complexes. Novel photoluminescent salicylaldimine ligands condensed from 3′, 3′, 4′, 4′-tetraminobiphenyl and 4-substituted long/short alkoxy salicylaldehyde possessing two sets of tetradentate [N_2O_2] showed monotropic nematic mesomorphism (C_6 alkoxy chain length) whereas the ligand with alkoxy tail of carbon chain length 12 showed enantiotropic SmC phase. The zinc(II) complexes are non-mesogenic and show very interesting photoluminescent properties. Dinuclear copper(II) and zinc(II) complexes synthesized from ONO donor tridentate Schiff base ligand exhibited SmA phase for Cu(II) and a rectangular or oblique columnar mesophase is conjectured for Zn(II) complex respectively. The strategy adopted herein can be effectively employed to access a variety of newer bimetallic systems with tunable molecular construction motifs leading to smart multifunctional materials.



Compartmental Schiff base ligand (C_6 alkoxy tail) with [N_4O_4] donor site

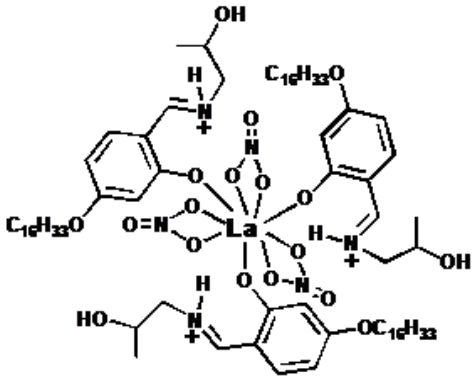


Nematic phase of ligand

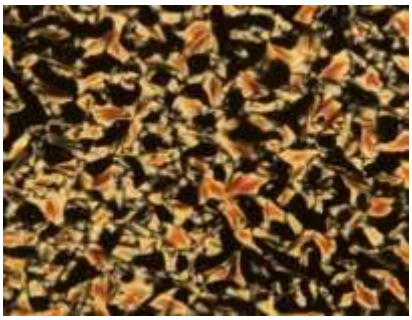
Cu(II) and Zn(II) complexes of ONO donor Schiff base ligand

Chapter 6:

In chapter 6 synthesis and characterisation of series of f-block metal complexes accessed from ONO donor Schiff base ligand with long alkoxy arm has been described. Liquid crystalline behaviour and intense photoluminescent properties of the lanthanum complexes of the type $[Ln(LH)_3(NO_3)_3]$, (Ln = La, Pr, Sm, Gd, Dy, Tb, Yb) have been discussed in detail. The lanthanide complexes pass through a smectic A mesophase before clearing to the isotropic liquid. The ligands are blue light emitters with broad emission maxima at ~438 nm while the lanthanide complexes show intense emission in the visible range at ~450–645 nm.



Structure of Lanthanum complex



Smectic A phase of Lanthanum complex

Chapter 7:

An overall conclusion reflecting the salient findings of the work is included at the end. A brief idea on future scope of studies has also been projected in this chapter.

References have been summarized at the end of each chapter. Finally, a list of research publications emanating from the research and conferences / workshops attended is appended along with the copies of published papers.