

CHAPTER 7
CONCLUSION

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Schiff base and its transition metal complexes has undergone a great proliferation in recent years particularly in the development of coordination chemistry, physico-chemical properties, catalytic transformations, bioactivities, metal-containing liquid crystals along with photoluminescence property with highlights on their potential applications such as displays, solar cells, active components for image and data treatment and storage etc. With the recognition of the promising applications of Schiff base transition metal complexes, synthesis, characterisation, structural assessment of some d- and f- block metal complexes with Schiff base ligands and study of their liquidcrystallinity and photoluminescence constitute the main theme of the present Ph.D. research program.

A series of salicylaldimine-based copper(II) and oxovanadium(IV) complexes of the type $[ML_2]$ ($M=Cu$ and VO , $L = N,N'$ -bis-(4-X-amino phenyl (4'-n-alkoxy)-salicylaldiminato), $n=4, 6$; $X = Cl, NO_2$) and a series of new oxovanadium(IV) Schiff-base complexes of the type $[VO(L)_2]$, [$L = N$ -(4-n-alkoxysalicylaldimine)-4'-dodecyloxyaniline, $n = 6, 8, 16, \text{ and } 18$] have been synthesized. The ligands with polar end groups (Cl/NO_2) 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 $>200^\circ C$. A cyclic voltammetry study revealed a quasireversible one-electron response for all the complexes. Variable temperature magnetic susceptibility studies suggested occurrence of isolated spin centres with hardly any exchange interaction. The $\nu_{V=O}$ band at $\sim 980\text{cm}^{-1}$ also suggested the lack of any discernible . . . $V=O$. . . $V=O$. . . interaction. At 330 nm excitation, salicylaldimine-

based polar Schiff base ligands showed green emission in the solid state (~516-559 nm) at room temperature.

Oxovanadium(IV) complexes $[VO(L)_2]$ bearing long as well as short alkoxy tail on both side of aromatic ring has been demonstrated. All the compounds are found to exhibit smectic mesomorphism. No definitive trends were noted as a function of carbon chain lengths of alkoxy tails both for the ligands and complexes. Based on spectral and DFT studies, a tentative five-coordinate square pyramidal structure for vanadium, and a square planar structure for copper complexes have been proposed.

Salophen based hemi-disc shaped complexes of Ni(II)/Cu(II)/VO(IV) elements bearing long alkoxy substituent in 4-position of the side aromatic ring and central substituted/unsubstituted aromatic diamine spacer groups have been successfully synthesized, mesomorphism as well as photophysical properties were investigated. Nickel(II) complexes exhibited monotropic/enantiotropic phase transition showing rectangular columnar mesophases (Col_r). At room temperature with 330 nm excitation, the nickel complexes showed blue emission both in the solid state and in solution. An interesting phase behaviour exhibiting two types of rectangular columnar phases (Col_{r1} to Col_{r2}) was observed for the vanadyl complexes. Cu-salophen complexes showed Col_r/Col_{rp} phase behaviour. An antiparallel dimeric association of half-disc shaped molecule for the complexes forming a disc-like arrangement in the mesophase is proposed on the basis of powder X-ray diffraction study.

Synthesis, characterization, the mesogenic and photophysical properties of dinuclear Schiff base metal complexes have been described. The zinc(II) complexes described in this chapter show very interesting photoluminescent properties with high emission quantum yield. 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. The tetra-coordinated $[N_4O_4]$ donor compartmental Schiff base ligands showed nematic/smecticA phase whereas their zinc(II) complexes are non-mesogenic showing very interesting photoluminescent properties. Copper and zinc complexes of ONO donor tridentate Schiff base ligand

exhibited SmA phase for copper and a rectangular or oblique columnar mesophase is conjectured for zinc complex respectively.

A series of new mononuclear lanthanide(III)-salicylaldimine complexes of the type $[\text{Ln}(\text{LH})_3(\text{NO}_3)_3]$ (Ln = La, Pr, Sm, Gd, Tb, Dy, and Yb) have been synthesized and characterized. Schiff base ligand occurs in zwitterionic form with the phenolic-H shifted to imine-N, thus coordinate to the metal ion via the negatively charged phenolic oxygen only; no binding occurs between the lanthanide ion and the imine nitrogen. The lanthanide complexes pass through smecticA mesophase before clearing to the isotropic liquid. The ligands are blue light emitters with broad emission maxima at ~438nm while the lanthanide complexes show intense emission in the visible range at ~450-645nm.

Based on the work documented in this thesis, certain areas, amongst others, which have scope for future exploration, are;

1. Synthesis of mixed d-f metal complexes.
2. NLO and sensory activity of some selected compounds.
3. Reactivity of the coordinatively unsaturated metal complexes with neutral and anionic donors to access newer complexes.