

**CHAPTER 1**  
**GENERAL INTRODUCTION**

# CHAPTER 1

## GENERAL INTRODUCTION

---

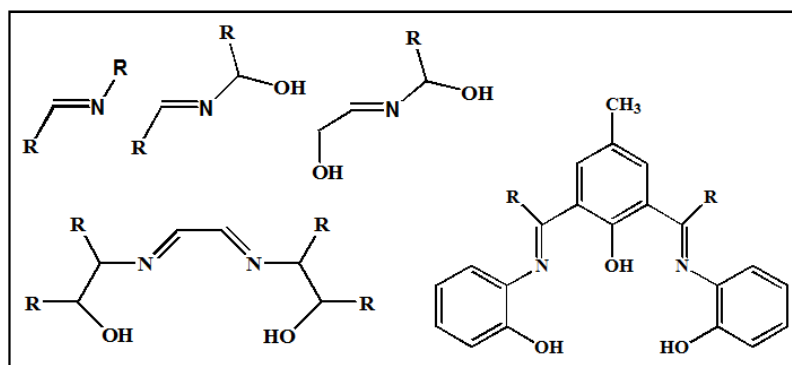
### 1.1 Schiff base:

Schiff base was first reported by Hugo Schiff in 1864 can be prepared by condensing carbonyl compounds and amines in different conditions and in different solvents with the elimination of water molecules.<sup>1</sup> The basic skeleton of Schiff base is  $RR''C=NR'$  where usually R is an aryl group, R'' is a hydrogen atom or alkyl or aryl group and R' is either an alkyl or aromatic group. Aryl substituted Schiff bases are more readily synthesized and substantially more stable due to effective conjugation, while those which contain alkyl substituents are relatively unstable and polymerizable.<sup>2</sup> Schiff bases are considered as a class with wide structural versatility because they can have a variety of different substituents and can be unbridged or N, N'-bridged type. Most commonly, Schiff bases have NO, N<sub>2</sub>O, NO<sub>2</sub> or N<sub>2</sub>O<sub>2</sub>-donor atoms but the oxygen atom(s) can also be substituted by sulphur, nitrogen, or selenium atoms.<sup>3-7</sup> In this study our attention was drawn mainly to the salen, salophen and bi-, tri-dentate salicylaldimine types. Exploring strategies for the synthesis of various functionalised Schiff base and their use as ligands in metal complexation is a recurring theme of current research. Bearing the excellent electron-donor group (C=N imino group), they can form various complexes with a wide range of metals including main group, transition and lanthanide metal ions. The ease of preparation and flexibility in varying the chemical environment of Schiff base ligands renders them an efficient tool in coordination chemistry. Schiff bases have been intensively used as synthetic intermediates and as ligands for coordinating transition and inner transition metal ions and recently also for coordinating anions.<sup>8,9</sup> Redox properties, solubility, spin state magnetism can be modulated through structure-function relationship. There has been a resurgence of interest in synthesis and characterisation of well-designed Schiff base due to their flexible coordination donor sites, diverse structures and properties generating a variety of stereochemistries and a wide range of bonding interactions. With the recognition of Schiff base as "privileged ligand" and its metal complexes as potential applicants for catalysis, pharmacology, liquid crystallinity,

photoluminescence, non-linear optical activity, the research involving synthesis, structural assessment of newer multidentate functionalised Schiff base ligands and their complexes of some d and f-block transition metals have acquired immense significance.

## 1.2 Schiff base metal complexes:

The Schiff base ligands exert profound influence on the activity of the metal centre. The extensive coordination ability of Schiff base with a wide range of metals including main group metals, transition metals, and lanthanide ions is due to the presence of azomethine linkage. Schiff base ligands have a tendency to donate the lone pair of electrons present on the  $sp^2$  hybridized nitrogen atom of the azomethine moiety ( $-CH=N-$ ). The presence of an electron donor group (acidic group like a phenolic OH, SH, etc.) close to the azomethine group increases the coordinating ability of the lone pair of electrons, thereby increasing the stability of the metal complexes. The stability of Schiff base complex depends upon the strength of carbon-nitrogen bond, the basicity of amino group and steric factors. Schiff base metal complexes have occupied a central place in the development of coordination chemistry after the work of Jørgensen and Werner in mid-nineteenth century.<sup>10</sup> However, concrete and rapid advances in the field of Schiff base metal complexes became evident after the preparative work of Pfeiffer and his co-workers<sup>11</sup> reported a series of complexes derived from Schiff bases of salicylaldehyde and its substituted analogues. According to the number of donor atoms, Schiff bases are classified as uni-, bi-, tri- or polydentate ligands as shown in **Fig.1**.



**Fig.1:** Some typical examples of Schiff bases of different denticity.

Schiff base ligands form stable mononuclear and polynuclear metal complexes through the O,O; O,N,N; O,N,S and O,N,O donor sequences of the ligand moiety.<sup>3,12,13</sup> These complexes can be obtained by condensation of a diamine with a salicylaldehyde derivative, followed by complexation with a metal ion. In relation to the kind of diamine, it is possible to distinguish two classes of complexes: the “*salen*” species, if the diamine is aliphatic and the “*salphen*” or “*salophen*” species in the case of aromatic diamines. Schiff base ligands of salen and salophen type form four coordinate chelate complexes through two phenolate anions (O-donors) and two imine nitrogen atoms and usually adopt square-planar, tetrahedral, distorted tetrahedral or distorted trigonal pyramidal around the metal centre.<sup>14</sup> The salicylaldimine type Schiff base ligand formed is well recognised as a good promesogenic unit as the azomethine linkage is stabilised by intramolecular hydrogen bonding in addition to being a good donor site for coordination with metals.<sup>15</sup>

In fact, the large amount of commercial amines, aldehydes and the various synthetic routes of their functionalization allow the achievement of a larger number of ligands and then metal complexes with properties easily fine-tunable. The type and the coordination geometry of the metal centre are crucial in determining the properties of the Schiff base complexes.

### **1.3 Structure and properties of some Schiff base metal complexes:**

In the following section, chemistry of Schiff base complexes of metals we chose to work with as a part of the present Ph.D research program are briefly discussed.

#### **1.3.1 Vanadium Schiff base complex chemistry:**

Vanadium(IV) is the most stable oxidation state under ordinary conditions and majority of vanadium(IV) compounds contain the  $\text{VO}^{2+}$  unit (oxovanadium(IV) or vanadyl ion) which can persist through a variety of reactions and in all physical states. The  $\text{VO}^{2+}$  ion forms stable anionic, cationic and neutral complexes with several types of ligands and has one coordination position occupied by the vanadyl oxygen. A wide variety of oxovanadium(IV) complexes have been prepared and characterized.<sup>16-18</sup> Square pyramidal geometry has been well established for oxovanadium(IV) complex with the oxygen at the apical position and the vanadium atom lying above the plane

defined by the donor atoms of the equatorial ligands. Oxovanadium(IV)-Schiff base complexes have received significant attention due to their interesting physicochemical properties, bioactivities and catalytic functions in organic and inorganic transformations.<sup>19,20</sup> Most oxovanadium(IV) complexes attain monomeric square-pyramidal coordination geometry or linear chain structures ( $\bullet\bullet\bullet\text{V}=\text{O}\bullet\bullet\bullet\text{V}=\text{O}\bullet\bullet\bullet$ ) with distorted octahedral coordination with a tetradentate Schiff base ligands. Vanadium(V) complexes with tridentate Schiff base ligand demonstrate a significant trigonal–bipyramidal distortion of the square pyramidal geometry.<sup>21</sup>

### **1.3.2 Nickel Schiff base complex chemistry:**

Nickel(II) coordination complexes of Schiff bases have received intense attention because of intriguing variety of coordination architectures, varying from octahedral to square planar including five-coordinate and tetrahedral coordination modes. Tetra coordinated nickel(II) complexes attain diamagnetic planar geometry whereas paramagnetic tetrahedral configuration is enforced by the sterically hindered bulky substituents of the ligand fragment surrounding the metal ion. Formation of both high- and low-spin square pyramidal or the trigonal bipyramidal geometry around the five-coordinated nickel(II) complexes are reasonably common. The six-coordinate octahedral geometry around the metal centre is prevalent in aqua and ammine nickel(II) complexes.<sup>22,23</sup>

### **1.3.3 Copper Schiff base complex chemistry:**

Copper-Schiff base complexes adopt square-planar and square-pyramidal coordination by dimerization.<sup>24, 25</sup> Due to Jahn-Teller distortion, copper(II) ion also adopt distorted octahedral and tetrahedral configuration to remove degeneracy in valence level orbitals. The distortion is usually seen as axial elongation consistent with the lability and geometric flexibility of the complex. Therefore, typical copper(II) complexes have square planar or square pyramidal geometries with weakly associated ligands in the axial position but some form trigonal bipyramidal geometry as well.

#### 1.3.4 Zinc Schiff base complex chemistry:

Zinc(II) Schiff-base complexes are not as abundant as that reported for the copper and nickel derivatives. Among the other first row transition metal series zinc(II) ion has  $d^{10}$  electronic configuration and are diamagnetic in nature. The stereochemistries of these species are determined by considerations of electrostatic forces, covalent bonding forces and the size of the metal ion.<sup>26</sup> Zinc(II) can easily be 4-,5-,or 6-coordinated with the former two being the most common. Due to metal-ligand bond distance and repulsive energy, four coordinated zinc complexes attain tetrahedral geometry in preference to planar configuration. A peculiarity of zinc(II) Schiff base complexes is the tendency of the metal ion to expand its coordination sphere through the axial coordination with neutral donors, such as alcohols, carbonyls, nitrogen-based donor Lewis bases, or in their absence can be stabilised through intermolecular  $Zn\cdots O$  axial coordination involving Lewis basic atoms of the ligand framework.<sup>27</sup> These features allow such complexes to be relevant in the fields of supramolecular assemblies, nano-structured materials and sensing.<sup>28</sup>

#### 1.3.5 Lanthanide Schiff base complex chemistry:

Lanthanides have very rich and challenging coordination chemistry characterized by high coordination numbers and flexible coordination geometries depending on factors such as ionic radius, the nature of counter anions and the metal-to-ligand ratio.<sup>29</sup> Coordination numbers of lanthanide complexes range from six to twelve, eight and nine being the most common coordination numbers. Lanthanides complexes with coordination number 6 are coordinatively unsaturated and can expand their coordination sphere by adduct formation with neutral molecules. Lanthanides are weak Lewis acids and preferably coordinate to hard Lewis bases mostly with oxygen donors and, to a lesser extent, nitrogen donors. A special feature of the Schiff's base complexes with lanthanides is that the Schiff bases coordinate as neutral ligands to the lanthanum atom. However, the oxygen atoms of the phenolic -OH group are deprotonated and the hydrogen atoms move to the nitrogen atom of the imine moiety of the Schiff base ligand. In this way, a zwitterionic structure ( $-C=N^+-H---O^-$ ) is formed i.e. negative charge on the oxygen atom and positive charge on the imine nitrogen atom.<sup>30</sup>

Extensive studies on Schiff base metal complexes continue not only due to interesting coordination geometries, structural versatility of ligand spheres, but also because of their varied industrial application, catalytic and biological activity.<sup>31-33</sup>

#### **1.4 Applications:**

While elaborating on applications of metal-Schiff base complexes we intend to restrict the discussion to liquid crystal, photoluminescence, catalytic and biological applications only. In the present Ph.D. research we, however, explored the liquid crystal and photoluminescence properties of the synthesized complexes.

##### **1.4.1 Liquid Crystal:**

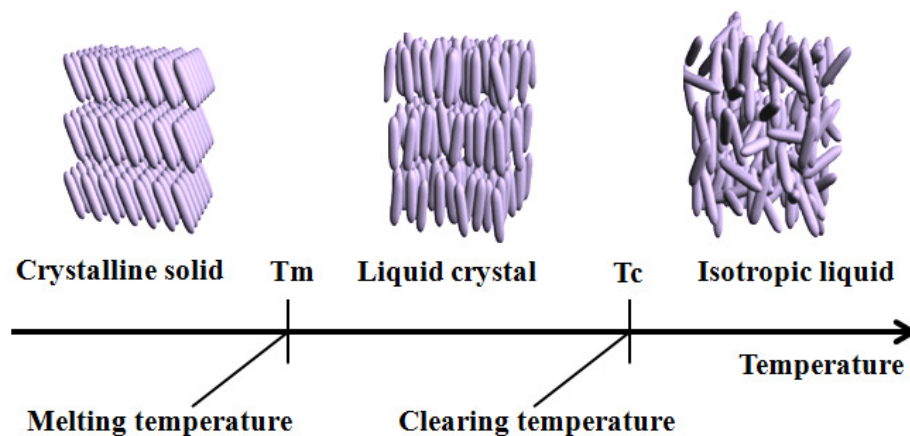
The phase of matter existing between the classical condensed anisotropic solid and isotropic liquid is called liquid crystal phase. The liquid crystal state represents an intermediate situation and possesses properties reminiscent of crystalline and liquid phase. The properties of liquid crystal phases include the exhibition of positional order in one or two dimensions, optical anisotropy associated with crystals and fluidity of an isotropic liquid. The term “liquid crystal” refers to substances that exhibit intermediate phases, called mesophases, between the crystalline and liquid phases. These mesophases are distinct from the crystalline and isotropic liquid phases in that they exhibit partial long-range order in one or more dimensions, but are also fluid.<sup>34,35</sup> Liquid crystallinity was first observed by a botanist Friedrich Reinitzer in 1888 who noticed a reversible colour change during multiple heating and cooling cycles of cholesterol derivatives.<sup>36</sup> In addition, he observed that these compounds exhibited a peculiar melting behaviour—melt from solid to a cloudy liquid with increasing temperature finally turning to a clear liquid. Reinitzer consulted his observations with Otto Lehmann, the inventor of the hot stage polarising microscope and jointly proposed the phenomenon *Flüssige Kristalle* (liquid crystals).<sup>37</sup> In 1906, a review article by Daniel Vorländer first stated the origin of crystalline-liquid state results from a molecular structure and anisotropy of the molecule.<sup>38</sup> Later George Friedel, a French crystallographer introduced new terminology “mesomorphism” for the liquid crystalline behaviour. A compound with properties similar to liquid crystals is *mesogenic* and its behaviour denotes *mesomorphism*. The liquid state is

conventionally termed as *isotropic*. The *melting point* represents the temperature when a solid goes into a mesophase, whereas the *clearing point* is the temperature at which the mesophase becomes an isotropic liquid. When a mesophase appears both on heating and cooling, it is called an *enantiotropic* mesophase. When a mesophase only appears on cooling from the isotropic liquid, it is termed *monotropic*. The liquid crystal state is stabilized by geometric anisotropy, interaction anisotropy and micro-segregation of the molecules which form the phases.<sup>39</sup>

It may be appropriate here to discuss briefly as to how liquid crystals are classified. Considering that only thermotropic liquid crystals are dealt with in the present thesis, discussion on this class is stressed in the following section.

**Thermotropic liquid crystal:**

When the compound passes through a solid, liquid and liquid crystal state as a primary function of temperature and in the absence of solvent, the liquid crystal behaviour is termed thermotropic.<sup>40,41</sup> The liquid crystallinity of thermotropic LC appears only in a particular temperature range, as schematically shown in **Fig.2**.



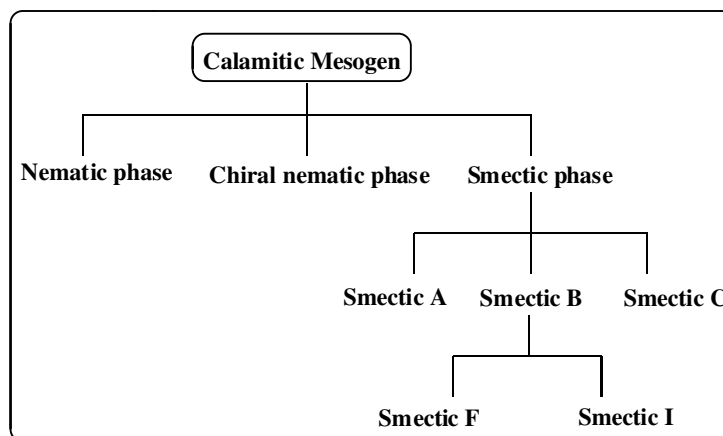
**Fig. 2:** Thermotropic liquid crystalline transition.

Based on the shape of the mesogenic molecules, thermotropic liquid crystals are classified into three main groups: (a) calamitic (rod-like); (b) discotic (disc-like) and (c) bent core (banana-like).

**Mesophases formed by calamitic molecules:**

Calamitic mesogens are broadly divided into two classes - the nematic and smectic phases (**Fig.3**)





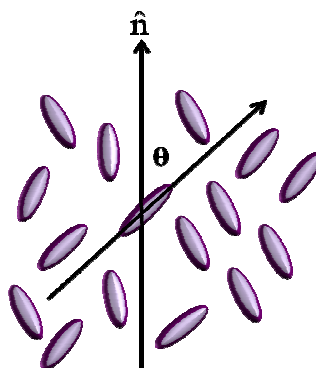
**Fig. 3:** Classification of calamitic mesogen.

### Nematic phase:

Compounds exhibiting a nematic phase have the highest fluidity with least order and viscosity of all the other existing mesophases. The *nematic* (N) phase has no positional order, but only orientational order. The word nematic comes from the Greek word *nematos* meaning thread-like—this arises from the observed optical texture of the phase between crossed polarizers.<sup>41</sup> The average orientation of the molecules (**Fig. 4**) along their long molecular axes within the phase is defined by the director  $\mathbf{n}$ . The degree of orientational order within the phase is expressed by the parameter  $S$  (eqn. i), where  $\theta$  is the average angle between the molecular long axis and the director.

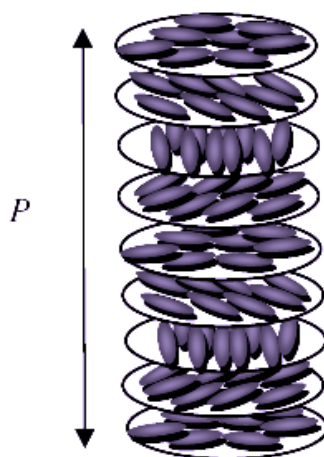
$$S = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle \quad (\text{i})$$

Typically for a nematic phase, the value of order parameter,  $S$  lies between 0.4 and 0.7.<sup>40</sup>



**Fig. 4:** Molecular order in nematic liquid crystal.

The chiral version of the nematic phase is abbreviated as  $N^*$ . Chiral nematic phase is observed when a nematic phase is shown by a pure enantiomer or by a mixture of enantiomers with one in excess or by a racemic or non-chiral compound doped with 5–10% chiral material.<sup>40-42</sup> The chiral nematic phase was the first liquid crystal phase to be studied, named after the cholesteryl derivatives investigated by Reinitzer and is historically called as the cholesteric phase.<sup>42</sup> Chiral nematic phase forms a helical structure with a pitch length  $P$ , which is a  $2\pi$  radian rotation of the director  $\mathbf{n}$  (a full rotation), and  $P/2$  becomes the periodicity due to the equivalence of  $\mathbf{n}$  and  $-\mathbf{n}$  (**Fig. 5**).

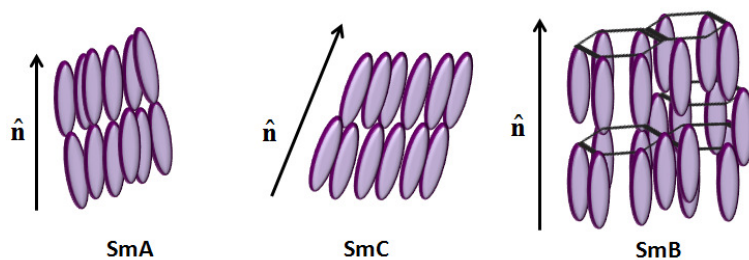


**Fig. 5:** Schematic representation of the molecular ordering in the chiral nematic phase. (Source: ref.34)

### **Smectic phases:**

The *Smectic phase* (Sm) is characterized by orientational correlations and partial translational order of the molecules into layers or planes. The word “*smectic*” is derived from the Greek word for soap. Smectic phases (Sm) occur when the thermal energy is enough to overcome the Vander Waals attractive forces between the ends of the rod-like molecules and so positional order of each layer may be lost.<sup>43</sup> As a result, smectic layers slide freely over one another which give rise to fluidity to the system with higher viscosity than nematics. Several types of smectic phases exist (**Fig.3**). Two of the most common of which are the *smectic A* (SmA) and *smectic C* (SmC) phases. The *smectic A* phase is the most disordered smectic phase with the director

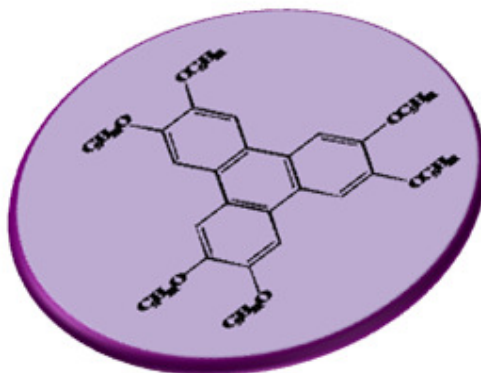
perpendicular to the layer plane (**Fig.6**). In the *smectic C* (SmC) phase, long axes of molecules are tilted by a certain angle with the layer plane (**Fig.6**). When molecules adopt a hexagonal ordering within the smectic layers the *smectic B* (SmB) phase is obtained. The *smectic B* phase is an orthogonal hexatic phase (**Fig.6**), whereas the *smectic I* and *smectic F* phases are tilted variations. Thus, the *smectic I* (SmI) phase may be regarded as SmB phase which is tilted toward a vertex of the hexagonal net while the *smectic F* (SmF) phase is tilted towards the edge of the hexagonal net. SmC, SmF and SmI phases can also exist as chiral modifications (SmC\*, SmF\* and SmI\*). Soft crystal phases (B, E, G, H, J and K) are characterized by the appearance of inter-layer correlations. They exhibit long-range positional order in three dimensions.



**Fig. 6:** Molecular ordering in smectic phases.

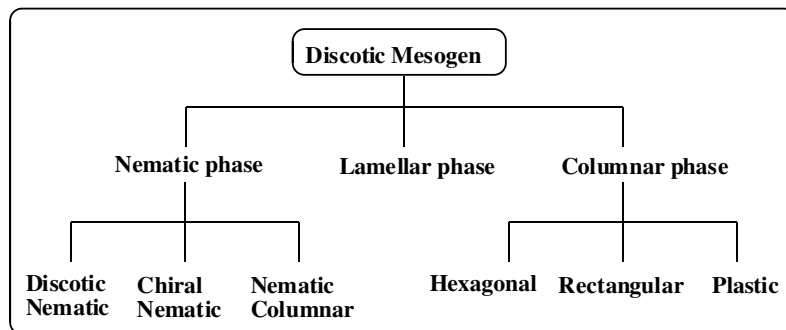
#### Mesophases formed by discotic molecules:

Discotic mesogens carrying the abbreviation “D” generally consist of flat, rigid (usually polycyclic aromatic) cores surrounded by long alkyl chains which stack one on top of each other in a columnar fashion (**Fig.7**).



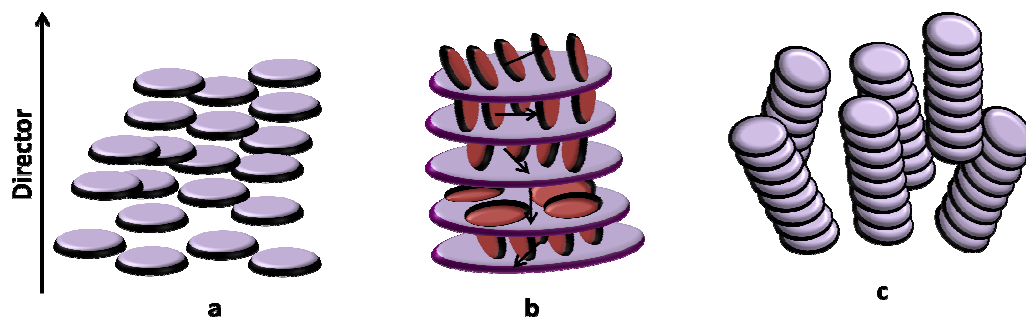
**Fig. 7:** General molecular structure of a disc-like liquid crystal.

Discotic liquid crystals, first discovered by Chandrasekhar<sup>44</sup> quickly followed up by a variety of other groups have attracted considerable attention over the years regarding their potential applications.<sup>45</sup> The spontaneous self-organization behaviour of disc-like (discotic) moieties probably due to intense  $\pi$ - $\pi$  interactions of polyaromatic cores. The core-core separation in a columnar mesophase is usually of the order of  $3.5\text{\AA}$  so that there is considerable overlap of  $\pi$ -orbitals leading to high charge-carrier mobilities which offer possibilities of their application in organic electronic devices, light emitting diodes, photovoltaic solar cells, field-effect transistors etc.<sup>44,46</sup> Mesomorphism exhibited by discotic molecules (**Fig.8**) are primarily of three types: nematic, columnar and lamellar.



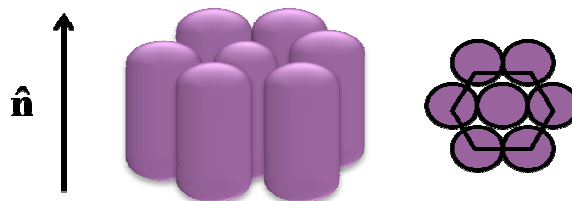
**Fig. 8:** Classification of discotic mesogen.

The nematic phases of disc-shaped molecules can be subdivided into three types: (a) discotic nematic (b) chiral nematic and (c) nematic columnar. The *discotic nematic* ( $N_D$ ) phase is the least ordered and consequently least viscous phase formed by disc-like molecules. The molecules in this phase are established by the short molecular axis and stay more or less parallel, having orientational order but no long-range positional order (**Fig.9a**). Like chiral calamitic nematic or cholesteric phase, discotic *chiral nematic* mesophase,  $N_D^*$  also exists. This mesophase occurs in mixtures of discotic nematic and mesomorphic or non-mesomorphic chiral dopants as well as in pure chiral discotic molecules.<sup>46, 47</sup> The helical structure of chiral discotic nematic phase is schematically shown in **Fig.9b**. The *nematic columnar* ( $N_{Col}$ ) phase is characterized by a columnar stacking of the molecules displaying a positional short-range and an orientational long-range order (**Fig.9c**). However, these columns are randomly distributed and do not form two-dimensional lattice structures.<sup>46</sup>



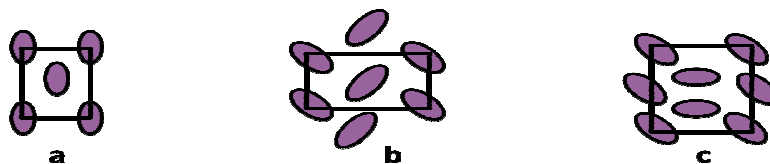
**Fig. 9:** a) Discotic nematic phase; b) Chiral nematic phase; c) Nematic columnar phase.

Columnar phase of discotic molecules are classified depending on the order in the molecular stacking in the columns and symmetry of the two-dimensional inter-columnar lattice. Most common is the least ordered uniaxial *hexagonal columnar mesophase* ( $Col_h$ ) shown in **Fig.10**.



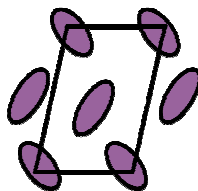
**Fig. 10:** Molecular ordering in hexagonal columnar phase.

The planar space group of a  $Col_h$  mesophase is  $P6mm$  and sometimes the intracolumnar stacking order or disorder is denoted as  $Col_{ho}$  and  $Col_{hd}$ , respectively.<sup>46,47</sup> The *columnar rectangular phase* is characterized by rectangular packing of molecular biaxial columns consisting aromatic cores surrounded by the disordered aliphatic chains tilted with regard to the stacking axis. Three different planar space groups  $c2mm$ ,  $p2gg$ ,  $p2mm$  exist for rectangular ordering of the columns illustrated in **Fig.11**.



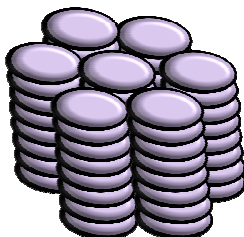
**Fig. 11:** Top view of the molecular ordering in the rectangular columnar phase  
a) Space group  $c2mm$ ; b) Space group  $p2gg$ ; c) Space group  $p2mm$

A rarely observed columnar phase due to molecules with strong core-core interactions along the column in tilt fashion is the *oblique columnar phase* ( $\text{Col}_{\text{ob}}$ ) with primitive space group  $p1$  shown in **Fig.12**.



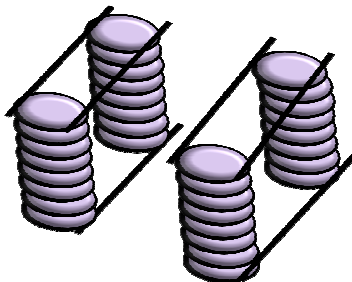
**Fig. 12:** Top view of the molecular ordering in the oblique columnar phase.

Occurrence of *columnar plastic phase*, denoted as  $\text{Col}_p$ , has been identified recently in discotic liquid crystals. The plastic phase (**Fig.13**) is characterized by three-dimensional crystal-like order with restricted motional freedom of discs around the columnar axis.<sup>48</sup>



**Fig. 13:** Molecular ordering in plastic columnar phase.

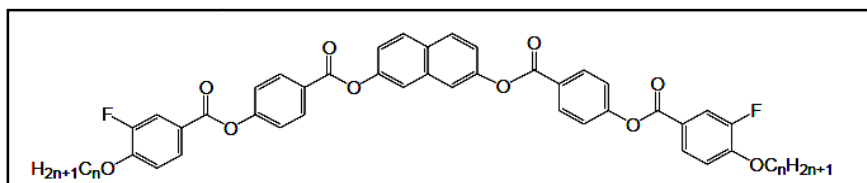
In the *columnar lamellar phase* or *lamello columnar phase* ( $\text{Col}_L$ ), columns of stacked discotic molecules are arranged in layers<sup>49, 50</sup> but the columns in different layers are devoid of any positional symmetry and the columns within layers can slide as illustrated in **Fig.14**.



**Fig. 14:** Molecular ordering in lamello columnar phase.

### Mesophases formed by bent core (banana-like) molecules:

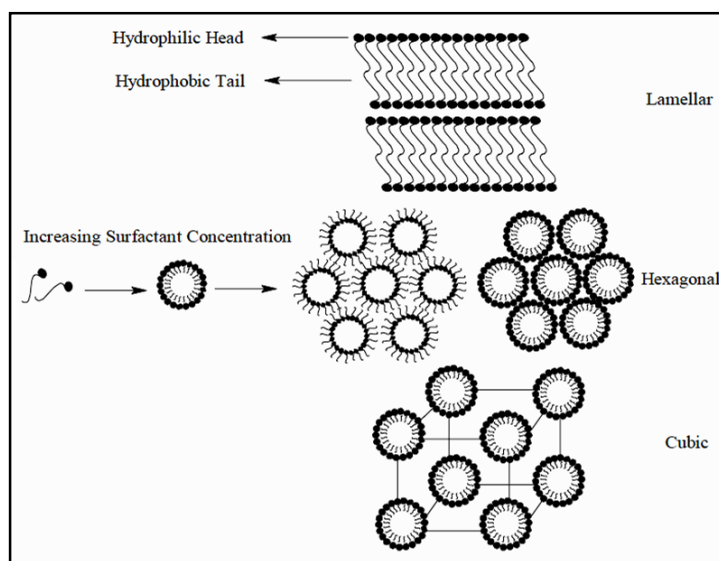
In the mid-90's banana-shaped liquid crystals or bent-core liquid crystals breathed new life into the field (**Fig.15**). This sort of material is an active field of research in both mesogenic materials and supramolecular chemistry.<sup>51</sup> Vorländer was first to synthesize several bent-core liquid crystals in 1929 and reported their mesogenic properties.<sup>52</sup> Since the pioneering results by Niori *et al*, extensive research has been carried out on these bent-core liquid crystals, and the results have allowed us to appreciate a new kind of truly fascinating materials.<sup>53</sup> This apparently naive structural modification of a rod-like molecule gives rise to some radically new mesophases which were initially denominated as B phases<sup>54</sup> and numbered chronologically (B<sub>1</sub>, B<sub>2</sub>, B<sub>3</sub>, etc.). The occurrence of novel and intriguing polar mesophases, the induction of supramolecular chirality using achiral molecules and the noticeable optical, ferroelectric and antiferroelectric responses of these materials are, among others aspects that are now well documented.<sup>55</sup> The search for biaxiality in BCLCs has been split into two main areas: the bent-shaped molecules themselves and their linear covalent coupling with a rod-like unit to form a non-symmetrical dimer in order to enhance the shape biaxiality of the rod-like mesogen. Of these approaches, the research into hybrid rodlike and bent-core liquid crystalline dimers to give biaxial phases has attracted the most attention. Research on hybrid rod-like and bent-core liquid crystalline dimers have captured attention for the interesting biaxial phase sequences.<sup>56</sup> The size and type of mesogenic units, the parity and nature of the spacer as well as linkage groups have proven to be crucial in the properties of the dimeric systems. A different series of bent-core coupled with cholesterol derivatives, cyanobiphenyl or azobenzene-derived calamitic units exhibiting fascinating mesophases, photoreactivity and electrical property of the dimers have been reported.<sup>51-56</sup>



**Fig. 15:** General structure of bent-core (banana-shaped) liquid crystals

### Lyotropic liquid crystal:

Though this does not fall under the scope of the present work yet it would not be out of place here to touch upon briefly about the lyotropic mesogen. These are formed depending on the concentration of the mesogen in an appropriate solvent.<sup>57</sup> One of the historic examples of lyotropic liquid crystal is myelin in water which exhibited birefringence in a microscopic study reported in 1854.<sup>58</sup> Anisotropy in lyotropics arises from the arrangement of molecules into spheres, rods or discs called micelles when hydrophobic head groups and hydrophilic tails, both which interact differently with the solvent. Usually lyotropic liquid crystal forms lamellar, cubic and hexagonal mesophases illustrated in **Fig.16**.



**Fig. 16:** Structure of lyotropic liquid crystal.

Metal-based lyotropic liquid crystals though rarely been studied but offers the opportunity to design surfactants with unusual shapes and geometries with induced catalysis, magnetism and redox behavioural aspects.<sup>59,60</sup>

A ferrocene-containing carbohydrate surfactant exhibiting both thermotropic and lyotropic liquid-crystalline phase behaviour has been reported by Donnio *et al.*<sup>60</sup>

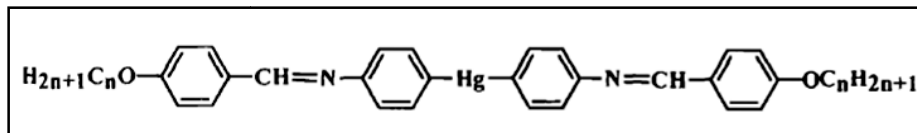
Later on, Galyametdinov *et al.* reported lyotropic mesomorphism of rare-earth trisalkylsulphates in the water–ethylene glycol system. In ethylene glycol, a normal hexagonal phase and a cubic phase could be detected, whereas in water a normal hexagonal phase and a lamellar phase were found.<sup>61</sup>



**Metallomesogen:**

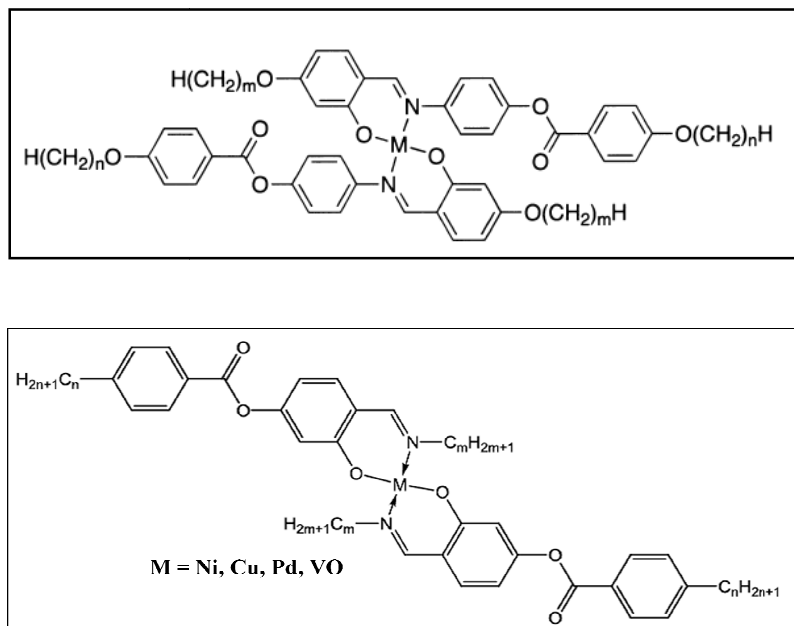
Metal centred organic liquid crystals with different functionalities and induced non-conventional shapes and unique properties are called metallomesogens.<sup>62</sup> The continued extension of liquid crystal science to additional technologies requires new types of mesomorphic materials that integrate novel structural elements and physical properties. The introduction of metal centres can bring valuable physical properties to liquid crystalline materials (colour, polarisability, redox behaviour, magnetism, nonlinear optical behaviour, electric properties, etc.) and can potentially expand technological applications of liquid crystals. Furthermore, metals offer multiple structural possibilities for novel molecular architectures, including linear, square planar, trigonal, tetrahedral, octahedral, and square pyramidal and lantern structures which are unobtainable in pure organic compounds and which in turn may lead to new types of molecular organisations or mesophases.<sup>63,64</sup> Metal complexes derived from Schiff-base ligands feature amongst the earliest and most widely studied class of metallomesogens.<sup>62-64</sup> The advantages of incorporating the imine functionality lie in the diverse range of potential structures and their ease of preparation. Consequently, this versatile functionality has produced metallomesogens of thermotropic liquid crystals<sup>62, 65</sup>, surfactants<sup>66</sup>, polycatenar mesogens<sup>67</sup>, polymers<sup>68</sup>, luminescent materials<sup>69</sup>, magnetic materials<sup>70</sup>, ferrocene<sup>71</sup>, chiral complexes<sup>72</sup> and metallohelicates.<sup>73</sup> The design of the ligands that are employed in a metallomesogen is fundamental in determining whether or not the complex forms mesophases. The principal elements to consider are the size and shape of the core (calamitic or discotic) and the length, positioning and number of the tails. The metal is typically incorporated into the core of the mesogen with an anisotropic, rigid organic framework surrounding it. From a structural perspective, this can mean that the metal's (including s-, p-, d- and even f-block elements) coordination geometry provides much of the required structural anisotropy in the core and<sup>74-76</sup> opens up the possibilities of the incorporation of new physical properties into the liquid crystals. Calamitic metallomesogens must incorporate a long, rigid, core in order to form mesophases.<sup>62</sup> As such, metals that naturally form linear complexes or trans-substituted square planar complexes are ideal for incorporation into calamitic metallomesogens. The first thermotropic metal-containing liquid crystals were

reported by Vorländer in 1910.<sup>77</sup> He observed that the alkali-metal carboxylates,  $R(\text{CH}_2)_n\text{COONa}$ , formed classical lamellar phases characteristic of soap. Later in 1923, Schiff base-mercury mesogens (**Fig. 17**) exhibiting smectic phase were first examined by Vorländer representing the earliest known example of metallomesogens.<sup>78</sup>



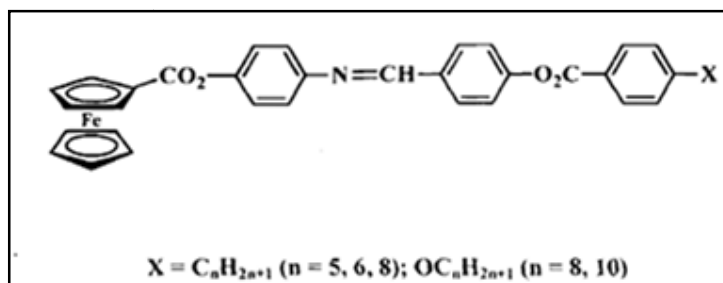
**Fig. 17:** Schiff base-mercury mesogens

Of particular interest are the salicylaldimine complexes, examples of which are shown in **Fig.18**. The salicylaldimine moiety used to bind the metal is both anisotropic and it allows for easy derivitization to larger, more complex core architectures. A number of reported examples of well-established metal–salicylaldimine mesogens were described in a review by Hoshino.<sup>15</sup>



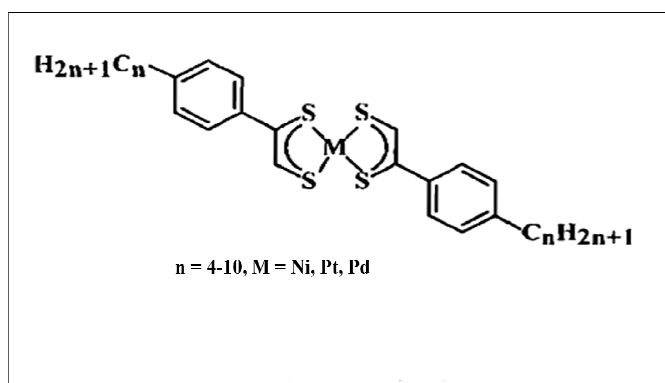
**Fig. 18:** The archetypical salicylaldimine complexes

Smectic ferrocenyl Schiff bases (**Fig.19**) synthesized by Malthete and Billard in 1976 were the first well characterized organotransition metallomesogens.<sup>79</sup>



**Fig. 19:** Smectic ferrocenyl Schiff bases

The first systematic study of d-block metallomesogens was carried out by Giroud and Muller-Westerhoff in 1977 on dithiolene complexes (**Fig.20**) of Ni(II), Pd(II) and Pt(II) showing nematic and smectic phases.<sup>80</sup>

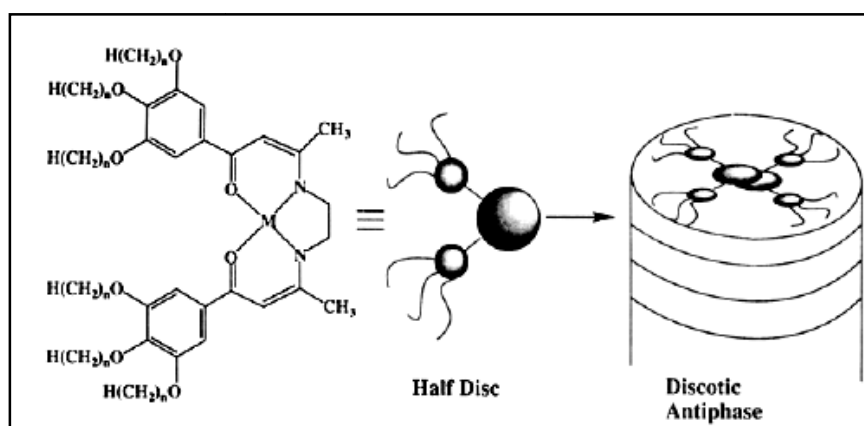


**Fig. 20:** Dithiolene metallomesogen

Ovchinnikov and coworkers were the first to report the calamitic bis-N-(4-substituted) salicylaldiminato copper (II) and nickel (II) complexes with aliphatic spacer which exhibit lamellar smectic mesomorphism.<sup>81</sup>

A typical discotic liquid crystal has a central rigid, disc shaped core with substitution of flexible alkyl chains at the periphery. Incorporation of a metal with a non-anisotropic coordination geometry into such a core can be achieved more easily than in the calamitic case through the use of large chelating ligands, however many discotic metallomesogens do incorporate metals with square planar geometries. These complexes often use the square planar geometry of the metal as a basis to form the flat disc shape needed. Square planar metal complexes are particularly important building blocks for new materials since the open axial coordination sites allow for inter-

metallic communication via direct metal-metal or ligand-mediated interactions. Examples of these are the  $\beta$ -diketonate<sup>82</sup>, phthalocyanine<sup>83</sup>, and porphyrin-based discotic metallomesogens.<sup>84</sup> The first mesogenic complex based on  $\beta$ -diketonates was bis(1 octyloxyphenyl-1,3-butanedionato) palladium(II) prepared in 1977.<sup>85</sup> A series of structurally related  $\beta$ -diketonates complexes reported by Ohta *et.al* exhibiting columnar mesomorphism.<sup>86</sup> Swager *et al.* developed half-disc shaped square-planar 1, 3-diketonate Schiff base complexes of Cu, Ni and Pd ions (**Fig.21**) which assemble to form antiparallel discotic hexagonal columnar phase.<sup>87</sup>

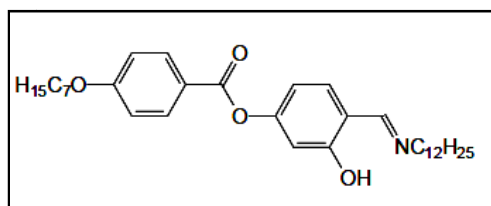


**Fig. 21:** Assembly of the diketonate Schiff base complexes into a discotic antiphase superstructure. (Source: ref.87)

Tetradentate Schiff bases (*salen/salophen* type ligands) have been also used as ligands to produce interesting liquid-crystalline transition metal complexes.<sup>16, 88-91</sup> The Co(II), Ni(II), Cu(II), VO(IV) salen complexes with 5-substituted alkoxy or alkyl chains of the aromatic rings usually generate linear rod-like (1D) liquid crystal structures and show smecticA mesophases at higher temperature.<sup>88-91</sup> A series of transition metal (II)-salen complexes containing 4-substituted long alkoxy chains of aromatic rings showed lamello-columnar phase with high thermal stability.<sup>92</sup> Espinet *et al.* reported liquid crystalline hemi discotic-and polycatenar-like metallomesogens based on salen manganese(III) complexes affording columnar (hexagonal/rectangular mesophases by self-assembling of dimer aggregates.<sup>93</sup> Our group have reported analogous series of 4-substituted oxovanadium(IV), zinc(II), nickel(II) as well as

copper(II) complexes, using cyclohexane/phenylene diamine spacer exhibiting different type of columnar phase.<sup>94</sup>

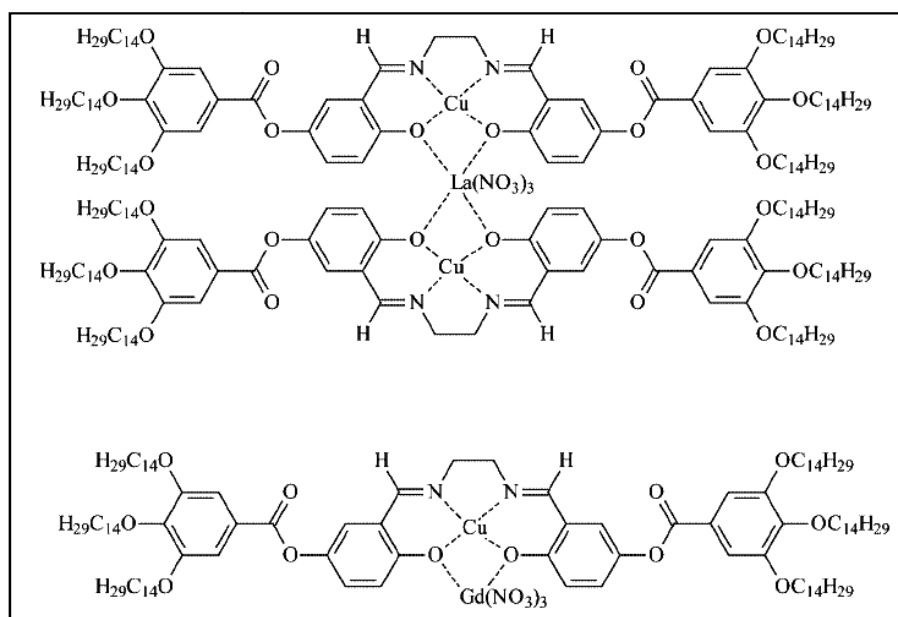
Quite apart from d-block transition metals, the design of lanthanide-containing liquid crystals is a challenge because the trivalent lanthanide ions have higher coordination numbers which seem to be incompatible with the structural anisotropy that is necessary to exhibit liquid crystalline property.<sup>94,95</sup> High magnetic anisotropy and the bright photoluminescence of lanthanides render their study yet more interesting.<sup>95</sup> The first calamitic lanthanide-containing liquid crystals (**Fig.22**) with Schiff base ligand were reported in 1991 by Galyametdinov and co-workers.<sup>96</sup>



**Fig. 22:** Ligand of the first calamitic lanthanide-containing liquid crystal

The ligand, a nematogen, its lanthanide complexes form a highly viscous smectic mesophase, which was later identified as a smectic A phase. Soon after, in 1994, Galyametdinov and co-workers<sup>97</sup> discovered the first liquid crystalline lanthanide complexes with a non-mesomorphic Schiff base ligand where mesomorphism is induced by the lanthanide ion. Further work done by the research groups of Galyametdinov, Bruce, and Binnemans provided more insight into the structure of these Schiff base complexes.<sup>98</sup> Lanthanide complexes exhibiting a hexagonal columnar mesophase were obtained by placing an additional alkoxy chain on the benzoyloxy group.<sup>99</sup> Lanthanide complexes of the Schiff base ligand 4-dodecyloxy-N-hexadecyl-2-hydroxybenzaldimine and with perfluorinated alkyl sulfate counterions showing smecticA mesophase were described.<sup>100</sup> The viscosity of this mesophase is much lower than that of analogous compounds with nitrate or alkyl sulfate counterions which is required for strong magnetic anisotropy.<sup>101,102</sup> Mesogenic lanthanoid metal complexes of a non-mesogenic Schiff-base, N,N'-di-(4-hexadecyloxysalicylidene)-1',8'-diamino-3',6'-dioxaoctane ligand display smecticA/nematic mesophase have been reported.<sup>103</sup>

Nearly all metallic elements of the periodic table have been used to create metallomesogens, but examples of liquid crystals that contain heteronuclear lanthanide or rare-earth ion (f-block) and d-block metal ion are rare. The first examples of mixed f-d metallomesogens (**Fig.23**), a trinuclear copper(II)/lanthanum(III) complex and a dinuclear copper(II)/gadolinium(III) complex with a mesogenic 2,2'-N,N'-bis(salicylidene)ethylenediamine (salen) ligand resulting in a hexagonal columnar phase, reported by Binnemans *et al.*<sup>104</sup>

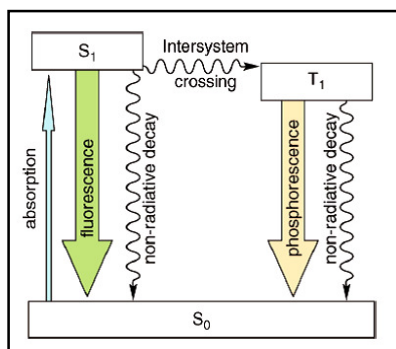


**Fig.23:** A copper(II) complex of a mesogenic 2,2'-N,N'-bis(salicylidene) ethylenediamine (salen) derivative used to form adducts with lanthanide(III) nitrates.(Source: ref.104)

This work was extended further in the sense that the copper(II) was replaced by nickel(II) and that the influence of the chain length on the transition temperatures was investigated.<sup>105</sup> Later on, four mesogenic metal complexes namely, two copper(II) and one nickel(II), and two binuclear copper(II)/lanthanum(III) and nickel(II)/lanthanum(III) complexes with 1,2-diaminobenzene spacer group exhibiting a hexagonal columnar phase (Col<sub>h</sub>) over an extended temperature range were reported.<sup>106</sup>

### 1.4.2 Photoluminescence:

Photoluminescence is the emission of light arising “from direct photoexcitation of the emitting species”.<sup>107</sup> Photoluminescence is formally divided into two categories: **fluorescence** and **phosphorescence** depending on the nature of the excited state (**Fig.24**). Fluorescence is a type of photoluminescence that is generated when in excited singlet states, the electron in the excited orbital is paired (by opposite spin) to the second electron in the ground-state orbital. Consequently, return to the ground state is spin allowed and occurs rapidly by emission of a photon. The emission rates of fluorescence<sup>108</sup> are typically  $10^{-8}$ s, so that a typical fluorescence lifetime is near 10ns ( $10 \times 10^{-9}$ s). Phosphorescence is emission of light from triplet excited states, in which the electron in the excited state has the same spin orientation as the ground-state electron. Transitions to the ground state are forbidden and the emission rates are slow ( $10^{-3}$  to  $10^0$ s), so that phosphorescence lifetimes are typically milliseconds to seconds; however, longer lifetimes are possible. Following exposure to light, the phosphorescence substances glow for several minutes while the excited phosphors slowly return to the ground state. Transition metal–ligand complexes, which contain a metal and one or more organic ligands, display mix singlet–triplet states. These complexes display intermediate lifetimes of hundreds of nanoseconds to several microseconds.<sup>108</sup>



**Fig. 24:** Simplified Perrin-Jablonski diagram showing the difference between fluorescence and phosphorescence.(Source: ref.107)

Photophysical properties of transition metal complexes of organic ligands have received widespread interest because a better understanding of the excited-state properties helps in the design of new molecules as fluorescent probes for sensing and

highly luminescent materials, especially for organic light emitting devices. Compounds with extended  $\pi$ -systems, conjugated polymers, well defined oligomers have become an important class of electronic materials. Complexes of transition and non-transition metals with Schiff base ligands are promising materials for optoelectronic applications due to their outstanding photoluminescent and electroluminescent properties, and the ease of synthesis that readily allows structural modification for optimization of material properties. Metal complexes offer many attractive properties, such as displaying a double role of electron transport and light emission, higher thermal stability, and ease of sublimation. Moreover, an attractive feature of these complexes is the ability to generate a much greater diversity of tunable properties and their color emission by virtue of the coordinated metal centre or by modifying the backbone substituents of ligands.<sup>109</sup> The luminescence properties of Schiff bases are useful for recognizing biochemically relevant details and can be a basis for the development of new highly sensitive analytical methods. Additionally, luminescence properties are important for investigations of photochromism and thermochromism. These facts have motivated a number of works about fluorescent aromatic Schiff bases.<sup>109,110</sup> Photoluminescent materials have attracted much attention in recent years due to their significant expansibility in commercial applications such as optoelectronic devices, sensors, semiconductors, etc. In contrast to organic dyes and polymers,<sup>111</sup> few efficient materials based on chelated metal complexes using Schiff bases such as three-ligand complexes (Alq<sub>3</sub> (q = 8-hydroxyquinoline) and its analogue)<sup>112</sup> and a series of intramolecular azomethine zinc-Schiff base complexes were reported to be effective emitters having good electron transport capability in a two-layer cell structure.<sup>113</sup> A recent paper by Che *et al.* described the utilization of vapour deposited Pt–salen complexes as efficient electrophosphorescent dyes in multilayer organic light emitting diode (OLED) devices with a maximum luminous efficiency.<sup>114</sup> Recent startling interest for lanthanide luminescence is stimulated by the continuously expanding need for luminescent materials meeting the stringent requirements of telecommunication, lighting, electroluminescent devices, (bio-) analytical sensors and bio-imaging set-ups.<sup>115,116</sup>

The development of compounds showing both luminescence and liquid crystallinity comprise a relatively new field of endeavour due to their promising applications in



OLEDs, information storage, sensors, photovoltaic devices, thin-film transistors and enhanced contrast displays.<sup>117</sup> The first example of blue emissive one-ring salicylaldehyde type Schiff base ligands exhibiting smectic mesomorphism was reported from our group.<sup>118</sup> Numerous Schiff base transition metal complexes of  $d^{10}$  transition metal such as  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Cu^+$ ,  $Ag^+$  and  $Au^+$  etc. have been reported and showed luminescent properties.<sup>65,119-123</sup> The first examples of d-block metallomesogens luminescent in the liquid crystal phase were the smectogenic rodlike gold(I) isocyanide complexes described by Espinet and co-workers.<sup>65</sup> A series of luminescent square planar platinum(II) salen complexes containing 4-substituted alkoxy chains of aromatic rings have been reported.<sup>124</sup> The lanthanidomesogen also have enjoyed lot of interests owing to unusual geometries and novel properties such as spin crossover, ferroelectricity, photorefractivity, non-linear optical properties, large magnetic anisotropy and luminescence.<sup>117,125</sup>

### 1.4.3 Catalysis:

Schiff base complexes have been a field of academic and industrial interest to analyze the catalytic activity of various metal complexes. A very significant aspect of metal Schiff base complexes is their role in catalytic activities like oxygenation, hydrolysis, electro-reduction and decomposition.<sup>126</sup> Four coordinated cobalt(II) Schiff base chelate complexes show catalytic activity in oxygenation of alkene.<sup>127</sup> Recent studies show Schiff base complexes of iron(II) exhibit catalytic activity towards electro-reduction of oxygen<sup>128</sup> and iron (III) as efficient catalyst for oxidation of sulphides to sulfoxides by urea hydrogen peroxide.<sup>129</sup> Some polymer bound Schiff base metal complexes show catalytic activity on decomposition of hydrogen peroxide and oxidation of ascorbic acid.<sup>130</sup> The high thermal and moisture stabilities of many Schiff base complexes were useful attributes for their application as catalysts in reactions involving at high temperature. The Heck reaction, an industrially useful process to synthesize fine chemicals and pharmaceutical, was successfully catalyzed using Schiff base complexes.<sup>131,132</sup> Dinuclear Schiff base complexes of copper(II) ions were used successfully in hydroxylation of phenol.<sup>133</sup> Although Ni(Salen) complexes have not found many applications in catalysis, their planar coordination geometry constitutes an interesting platform to coordinate other metals. The Schiff bases are able to act as a

metallacrown and an interesting structure containing different metals can result. Ni(Salen) bearing another metal can behave as a bifunctional catalyst, as prepared by Kozłowski.<sup>134</sup> Alkynylation has attracted considerable interest in recent years, as propargylic alcohols are valuable synthetic precursors. The undeveloped addition of alkynyl zinc reagents to ketones can be realized using Zn(Salen) as a catalyst, leading to new perspectives in the formation of quaternary stereocenters.<sup>135</sup> An interesting application of lanthanide Schiff base complexes in catalysis has been recently reported.<sup>136</sup>

#### 1.4.4 Biological activity:

Schiff base complexes have grown to be among the most widely explored coordination compounds in the past few years, since they are becoming increasingly important as biochemical, analytical and antimicrobial reagents. The Schiff base complexes exhibit important properties such as anti-inflammatory activity, antibiotic activity, antimicrobial activity and antitumour activity.<sup>137</sup> The biological activity of the Schiff bases has been attributed to their coordination ability with suitable metal ions allowing successful synthesis of homo and hetero-metallic complexes with varied stereochemistry. Some of the Schiff base complexes serve as biomimetic model for oxygen carrier systems.<sup>138</sup> Tridentate Schiff base and their metal complexes show antibacterial activities against *B.subtilis*, *E.coli*, *S.aureus* and *B.pumpilis*.<sup>139-141</sup> Schiff base derived from furylglyoxal and p-toluidine show potent antibacterial activities against *Escherichia coli*, *Staphylococcus*, *Bacillus subtilis* and *Proteus Vulgaris*.<sup>142</sup> Anti-HIV activity, antibacterial activity is possessed by Isatin derived Schiff bases.<sup>143,144</sup> Thiazole, benzothiazole and triazole Schiff bases complexes with copper, ruthenium, oxovanadium possess effective antifungal activities.<sup>145-147</sup> Literature search reveals that large number of Schiff base complexes are excellent DNA cleavage reagents. Co(III) Schiff base-DNA adducts are a versatile class of specific and potent tools for studying zinc finger domain proteins with potential applications in anticancer therapeutics.<sup>148</sup> A new chiral V(V) Schiff base complex as potential agents capable of interacting at the specific site of DNA and protein for their use as artificial nucleases and proteases have been reported.<sup>149</sup> The oxidative nature of metallo-salen (metal complexes of bis(salicylidene)ethylenediamine) complexes have attracted biological

chemists to utilize this feature in development of novel DNA/RNA modifiers and biomolecular probes.<sup>150</sup>

### **1.5 Objectives:**

In view of the recognition of potential applications of Schiff base and their metal complexes particularly in the context of liquid crystallinity, photoluminescence, catalytic transformations and biological activities as highlighted in the aforementioned discussion, the principal objectives of the present research program are as follows:-

1. To devise synthetic strategy for the synthesis of newer functionalised multidentate Schiff base ligands from the condensation of strategically selected aldehydes or ketones with appropriate amines.
2. Complexation with d- and f-block transition metals and isolation in solid state.
3. Identification, characterisation and structural assessment of the compounds by a combination of physico-chemical techniques.
4. Investigation of liquid crystallinity and photoluminescence property of some selected compounds.
5. To carry out DFT/TDDFT studies using DMol3/B3LYP program to determine the optimized geometry of the compounds.

## References:

1. Schiff, H.; *Ann. Suppl.* **1864**, 3, 343.
2. Hine, J.; Yeh, C.Y. *J. Am. Chem. Soc.* **1967**, 89, 2669.
3. Cozzi, P. G. *Chem. Soc. Rev.* **2004**, 33, 410.
4. Kumar, P. M. V.; Radhakrishnan, P. K. *Inorg. Chim. Acta.* **2011**, 375, 84.
5. Sui, Y.; Li, D-Pi.; Li, C-H.; Zhou, X-H.; Wu, T.; You, X-Z. *Inorg. Chem.* **2010**, 49, 1286.
6. Amirasr, M.; Bagheri, M.; Farrokhpour, H.; Schenk, K. J.; Mereiter, K.; Ford, P.C. *Polyhedron* **2014**, 7, 11.
7. Dutta, P. Kr.; Asatkar, A. K.; Zade, S. S.; Panda, S. *Dalton Trans.* **2014**, 43, 1736.
8. Uzarevic, K.; Dilovic, I.; Matkovic-Calogovic, D.; Sisak, D.; Cindric, M.; *Angew. Chem. Int. Ed.* **2008**, 47, 7022.
9. Vigato, P. A.; Tamburini, S. *Coord. Chem. Rev.* **2004**, 248, 1717.
10. Jorgensen, C. K. *Acta Chem. Scand.* **1957**, 11, 73.
11. Pfeiffer, P.; Buchholz, E.; Baver, O. *J. Prakt. Chem.* **1931**, 129, 163.
12. McGarrigle, E. M.; Gilheany, D. G. *Chem. Rev.* **2005**, 105, 1563.
13. Atwood, D. A.; Harvey, M. J. *Chem. Rev.* **2001**, 101, 37.
14. Whiteoak, C. J., Salassa G.; Kleij, A.W. *Chem. Soc. Rev.* **2012**, 41, 622.
15. Hoshino, N. *Coord. Chem. Rev.* **1998**, 174, 77.
16. Rahchamani, J.; Behzad, M.; Bezaatpour, A.; Jahed, V.; Dutkiewicz, G.; Kubicki, M.; Salehi, M. *Polyhedron* **2011**, 30, 2611.
17. Monfared, H. H.; Bikas, R.; Mayer, P. *Inorg. Chim. Acta* **2010**, 363, 2574.
18. Grivani, G.; Bruno, G.; Rudbari, H. A.; Khalaji, A. D.; Pourteimouri, P. *Inorg. Chem. Commun.* **2012**, 18, 15.
19. Abe, Y.; Iyoda, A.; Seto, K.; Moriguchi, A.; Yokoyama, H. *Eur. J. Inorg. Chem.* **2008**, 2148.
20. Ohta, A.; Yamamoto, Y.; Kamihata, H.; Lee, Y. H.; Ichikawa, F.; Ohta, K.; Abe, Y.; Hoshino, N.; Kojima, M.; Hayami, S. *Inorg. Chem. Commun.* **2012**, 16, 89.
21. Romanowski, G.; Wera, M. *Polyhedron* **2010**, 29, 2747.
22. Saccon, L.; Nannelli, P.; Cxmpigli, U. *Inorg. Chem.* **1965**, 4, 818.

23. Raman, N.; Ravichandran, S.; Thangaraja, C. *J. Chem. Sci.* **2004**, *116*, 215.
24. Ahmad, J. U.; Raisanen, M. T.; Nieger, M.; Sundberg, M. R.; Figiel, P. J.; Leskela, M.; Repo, T. *Polyhedron* **2012**, *38*, 205.
25. Pradeep, C. P.; Zacharias, P. S.; Das, S. K. *J. Chem. Sci.*, **2005**, *117*, 133.
26. Cotton F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; John Wiley & Sons, 5<sup>th</sup> edition: New York, **1988**.
27. Kleij, A. W. *Dalton Trans.* **2009**, 4635.
28. Consiglio, G.; Failla, S.; Finocchiaro, P.; Oliveri, I. P.; Di Bella S. *Dalton Trans.*, **2012**, *41*, 387.
29. Setyawati, I. A.; Liu, S.; Rettig S. J.; Orvig, C. *Inorg. Chem.* **2000**, *39*, 496.
30. Binnemans, K. *Inorganic Chemistry Highlights II*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, **2004**.
31. Kawi S.; Gates, B. C. *Clusters and Colloids: From Theory to Applications*; Wiley-VCH: Weinheim, **1994**, *4*, 298.
32. Bunzli J. C. G.; Piguet, C. *Chem. Rev.* **2002**, *102*, 1897.
33. González-Lorenzo, M.; Platas-Iglesias, C.; Avecilla, F.; Geraldes, C. F. G. C.; Imbert, D.; Bunzli, J-C. G.; de Blas, A.; Rodríguez-Blas, T. *Inorg. Chem.* **2003**, *42*, 6946.
34. Demus, D.; Goodby, J.; Gray, G. W.; Spiess, H. W.; Vill, V. *Handbook of Liquid Crystals*; Wiley-VCH: Weinheim, **1998**.
35. Collings, P. J. *Liquid Crystals: Nature's Delicate Phase of Matter*; Princeton University Press: Princeton, **1990**.
36. Reinitzer, F. *Monatsh. Chem.* **1888**, *9*, 421.
37. Lehmann, O. *Z. Phys. Chem.* **1889**, *4*, 462.
38. Vorlander, D.; *Kristallinisch-flussige Substanzen*; Enke, Stuttgart, Germany, **1905**.
39. Collings, P. J.; Patel, S. J. *Handbook of Liquid Crystal Research*; Oxford University Press: Oxford, **1997**.
40. Demus, D.; Goodby, J. W.; Gray, G. W.; Spiess, H.-W.; Vill, *Handbook of Liquid Crystals. Volume 2A: Low Molecular Weight Liquid Crystals I*; Wiley-VCH: Weinheim, **1998**.
41. Dierking, I. *Textures of Liquid Crystals*; Wiley-VCH: Weinheim, **2003**.

42. Kitzerow, H. S.; Bahr, C. *Chirality in Liquid Crystal*; Springer: New York, **2001**.
43. Gray, G. W.; Goodby, J. W. *Smectic Liquid Crystals: Textures and Structures*; Leonard Hill: London, **1984**.
44. Chandrasekhar, S.; Sadashiva, B. K.; Suresh, K. A. *Pramana* **1977**, 9, 471.
45. Chandrasekhar, S. *Liquid Crystals*; 2<sup>nd</sup> edition, Cambridge University Press: **1992**.
46. Kumar, S. *Chem. Soc. Rev.* **2006**, 35, 83.
47. Bisoyi, H. K.; Kumar, S. *Chem. Soc. Rev.* **2010**, 39, 264.
48. Glusen, B.; Heitz, W.; Kettner, A.; Wendroff, J. H. *Liq. Cryst.* **1996**, 20, 627.
49. Mery, S.; Haristoy, D.; Nicoud, J. F.; Guillon, D.; Diele, S.; Monobe, H.; Shimizu, Y. *J. Mater. Chem.* **2002**, 12, 37.
50. Ziessel, R.; Douce, L.; El-ghayoury, A.; Harriman, A.; Skoulios, A. *Angew. Chem. Int. Ed.* **2000**, 39, 1489.
51. Etxebarria J.; Ros, M. B. *J. Mater. Chem.* **2008**, 18, 2919.
52. Vorländer, D. *Ber. Dtsch. Chem. Ges.* **1929**, 62, 2831.
53. Niori, T.; Sekine, T.; Watanabe, J.; Furukawa T.; Takezoe, H. *J. Mater. Chem.* **1996**, 6, 1231.
54. Takezoe, H.; Takanishi, Y. *Jpn. J. Appl. Phys.* **2006**, 45, 597.
55. Gimeno, N.; Ros, M. B.; Serrano, J. L.; de la Fuente, M. R. *Angew. Chem. Int. Ed.* **2004**, 43, 5235.
56. Sebastian, N.; Gimeno, N.; Vergara, J.; Lopez, O. D.; Serrano, J. L.; Folcia, C. L.; de la Fuente M. R.; Ros, M. B. *J. Mater. Chem. C* **2014**, 2, 4027.
57. Myers, D. *Surfaces, Interfaces, and Colloids: Principles and Applications*; VCH Publ.: New York, **1991**.
58. Virchow, R. *Archiv für pathologische Anatomie und Physiologie und für klinische Medicin.* **1854**, 6, 572.
59. Usoltseva, N.; Espinet, P.; Buey J.; Serrano, J. L. *J. Mater. Chem.* **1997**, 7, 215.
60. Donnio, B.; Seddon, J. M.; Deschenaux, R. *Organometallics* **2000**, 19, 3077.
61. Galyametdinov, Y. G.; Jervis, H. B.; Bruce, D. W.; Binnemans, K. *Liq. Cryst.* **2001**, 28, 1877.

62. Date, R. W.; Iglesias, E. F.; Rowe, K. E.; Elliott, J. M.; Bruce D. W. *Dalton Trans.* **2003**, 1914.
63. Serrano, J. L. *Metallomesogens: Synthesis, Properties and Applications*; Wiley-VCH: Weinheim, **1996**.
64. Gimenez, R.; Lydon, D. P.; Serrano, J. L. *Curr. Opin. Solid State Mater. Sci.* **2002**, *6*, 527.
65. Espinet, P.; Esteruela, M. A.; Ore, L. A.; Serrano, J. L.; Sola, E. *Coord. Chem. Rev.* **1992**, *17*, 215.
66. Donnio, B. *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 371.
67. Lai, C. K.; Chang, C. H.; Tsai, C. H. *J. Mater. Chem.* **1998**, *8*, 599.
68. Oriol, L.; Serrano, J. L. *Angew. Chem., Int. Ed.*, **2005**, *44*, 6618.
69. Yang, Y.; Driesen, K.; Nockemann, P.; Van Hecke, K.; Van Meervelt, L.; Binnemans, K. *Chem. Mater.* **2006**, *18*, 3698.
70. Binnemans, K.; Gorller-Walrand, C. *Chem. Rev.* **2002**, *102*, 2303.
71. Seshadri T.; Haupt, H. J.; Jurgen, H. *Chem. Commun.* **1998**, 735.
72. Saccomando, D. J.; Black, C.; Cave, G. W. V.; Lydon D. P.; Rourke, J. P. *J. Organomet. Chem.* **2000**, *601*, 305.
73. Ziessel, R. *Coord. Chem. Rev.* **2001**, *195*, 216.
74. Tschierske, C. *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 69.
75. Giroud-Godquin, A. M.; Maitlis, P. M. *Angew. Chem., Int. Ed.* **1991**, *30*, 375.
76. Donnio, B.; Guillon, D.; Deschenaux, R.; Bruce, D. W. *Metallomesogens. In Comprehensive Coordination Chemistry II*; Elsevier, Oxford: United Kingdom, **2003**.
77. Vorlander, D. *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 3120.
78. Vorlander, D. *Z. Phys., Chem. Stoichiomet. Verwandtschaftsl.* **1923**, *105*, 211.
79. Malthete, J.; Billard, J. *Mol. Cryst. Liq. Cryst.* **1976**, *34*, 117.
80. (a) Giroud, A. M.; Muller-Westerhoff, U. T. *Mol. Cryst. Liq. Cryst.* **1977**, *41*, 11. (b) Giroud, A. M. *Ann. Phys.* **1978**, *3*, 147. (c) Giroud, A. M.; Nazzal, A.; Muller-Westerhoff, U. T. *Mol. Cryst. Liq. Cryst.* **1980**, *56*, 225. (d) Muller-Westerhoff, U. T.; Nazzal, A.; Cox, R. J.; Giroud, A. M. *Mol. Cryst. Liq. Cryst.* **1980**, *56*, 249.

81. Ovchinnikov, I. V.; Galyametdinov, Y. G.; Ivanova, G. I.; Yagfarova, L. M. *Dokl. Akad. Nauk. SSSR* **1984**, 276, 126.
82. Zheng, H.; Lai, C. K.; Swager, T. M. *Chem. Mater.* **1995**, 7, 2252
83. Ford, W. T.; Sumner, L.; Zhu, W.; Chang, Y. H.; Um, P. J.; Choi, K. H.; Heiney, P. A.; Maliszewskyj, N. C. *New J. Chem.* **1994**, 18, 495.
84. Sun, E-J.; Sun, Z-Y.; Yuan, M.; Wang, D.; Shi, T-S. *Dyes and Pigments* **2009**, 81, 124.
85. Bulkin, B. J.; Rose, R. K.; Santoro, A. *Mol. Cryst. Liq. Cryst.* **1977**, 43, 53.
86. (a) Ohta, K.; Jiang, G. J.; Yokoyama, M.; Kusabayashi, S.; Mikawa, H. *Mol. Cryst. Liq. Cryst.* **1981**, 66, 283. (b) Ohta, K.; Jiang, G. J.; Yokoyama, M.; Kusabayashi, S.; Mikawa, H. *Mol. Cryst. Liq. Cryst.* **1981**, 69, 131. (c) Ohta, K.; Yokoyama, M.; Mikawa, H. *Mol. Cryst. Liq. Cryst.* **1981**, 73, 205. (d) Ohta, K.; Yokoyama, M.; Kusabayashi, S.; Mikawa, H. *J. Chem. Soc., Chem. Commun.* **1980**, 392.
87. Zheng, H.; Lai, C. K.; Swager, T. M. *Chem. Mater.* **1994**, 6, 2252.
88. Aiello, L.; Ghedini, M.; La Deda, M.; Pucci, D.; Francesconi, O. *Eur. J. Inorg. Chem.* **1999**, 1367.
89. Paschke, R.; Balkow, D.; Sinn, E. *Inorg. Chem.* **2002**, 41, 1949.
90. Serrette, A.; Swager, T. M. *J. Am. Chem. Soc.* **1993**, 115, 8879.
91. Ohta, K.; Morizumi, Y.; Fujimoto, T.; Yamamoto, I.; Miyamura, K.; Gohshi, Y. *Mol. Cryst. Liq. Cryst.* **1992**, 214, 161.
92. (a) Abe, Y.; Akao, H.; Yoshida, Y.; Takashima, H.; Tanase, T.; Mukai, Ohta, H. K. *Inorganica Chimica Acta* **2006**, 359, 3147. (b) Abe, Y.; Nakazima, N.; Tanase, T.; Katano, S.; Mukai, H.; Ohta, K. *Mol. Cryst. Liq. Cryst.* **2007**, 466, 129. (c) Abe, Y.; Takagi, Y.; Nakamura, M.; Takeuchi, T.; Tanase, T.; Yokokawa, M.; Mukai, H.; Megumi, T.; Hachisuga, A.; Ohta, K. *Inorganica Chimica Acta* **2012**, 392, 254.
93. Chico, R.; Dominguez, C.; Donnio, B.; Coco, S.; Espinet, P. *Dalton Trans.* **2011**, 40, 5977.
94. (a) Bhattacharjee, C. R.; Das, G.; Mondal, P. *Eur. J. Inorg. Chem.*, **2011**, 5390. (b) Bhattacharjee, C. R.; Das, G.; Mondal, P.; Prasad, S. K.; Rao, D. S. S. *Eur. J. Inorg. Chem.*, **2011**, 1418. (c) Bhattacharjee, C. R.; Das, G.;



- Mondal, P.; Prasad, S. K.; Rao, D. S. S. *Inorg. Chem. Commun.*, **2011**, *14*, 606. (d) Bhattacharjee, C. R.; Das, G.; Mondal, P.; Prasad, S. K.; Rao, D. S. S. *Liq. Cryst.*, **2011**, *38*, 615. (e) Bhattacharjee, C. R.; Das, G.; Mondal, P. *Liq. Cryst.*, **2011**, *38*, 441. Bhattacharjee, C. R.; Das, G.; Mondal, P. Rao, N. V. S. *Polyhedron* **2010**, *29*, 3089.
95. Binnemans, K.; Deun, R. V.; Görrler-Walrand, C.; Haase, W.; Bruce, D. W.; Malykhina, L.; Galyametdinov, Y. G. *Mater. Sci. Eng. C* **2001**, *18*, 247.
96. Galyametdinov, Y. G.; Ivanova, G. I.; Ovchinnikov, I. V. *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1991**, *40*, 1109.
97. Galyametdinov Y. G.; Ivanova G. I.; Prosvirin A. V.; Kadkin O. *Russ. Chem. Bull.* **1994**, *43*, 938.
98. (a) Binnemans, K.; Bruce, D.; Collinson S. R.; Van Deun, R.; Galyametdinov, Y. G.; Martin, F. *Philos. Trans. R. Soc. London A* **1999**, *357*, 3063. (b). Binnemans, K.; Galyametdinov, Y. G.; Van Deun, R.; Bruce, D. W.; Collinson, S. R.; Polishchuk, A. P.; Bikchantaev, I.; Haase, W.; Prosvirin, A. V.; Tinchurina, L.; Litvinov, I.; Gubajdullin, A.; Rakhmatullin, A.; Uytterhoeven, K.; Van Meervelt, L. *J. Am. Chem. Soc.* **2000**, *122*, 4335.
99. Martin, F.; Collinson, S. R.; Bruce, D. W. *Liq. Cryst.* **2000**, *27*, 859.
100. Galyametdinov, Y. G.; Haase, W.; Malykhina, L.; Prosvirin, A.; Bikchantaev, I.; Rakhmatullin, A.; Binnemans, K. *Chem. Eur. J.* **2001**, *7*, 99.
101. Binnemans, K.; Galyametdinov, Y. G.; Collinson, S. R.; Bruce, D. W. *J. Mater. Chem.* **1998**, *8*, 1551.
102. Galyametdinov, Y. G.; Ivanova, G. I.; Ovchinnikov, I. V.; Binnemans, Bruce, K. D.W. *Russ. Chem. Bull.* **1999**, *48*, 385.
103. Kumari, S.; Singh, A. K.; Rao, T. R. *Mater. Sci. Eng. C* **2009**, *29*, 2454.
104. Binnemans, K.; Lodewyckx, K.; Donnio, B.; Guillon, D. *Chem. Eur. J.* **2002**, *8*, 1101.
105. Binnemans, K.; Lodewyckx, K. *Supramol. Chem.* **2003**, *15*, 485.
106. Binnemans, K.; Lodewyckx, K.; Donnio, B.; Guillon, D. *Eur. J. Inorg. Chem.* **2005**, 1506.
107. Valeur, B.; Berberan-Santos, M. N. *J. Chem. Educ.* **2011**, *88*, 731.

108. Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; 3<sup>rd</sup> edition, Springer: Singapore, **2006**.
109. Morishige, K. *Anal. Chim. Acta*, **1980**, *121*, 301.
110. Kownacki, K.; Mordzinski, A.; Wilbrandt, R.; Grabowska, A. *Chem. Phys. Lett.* **1994**, *227*, 270.
111. Sheats, J. R.; Antoniadis, H.; Hueschen, M.; Leonard, W.; Miller, J.; Moon, R.; Roitman D.; Stocking, A. *Science* **1996**, *273*, 884.
112. Van Slyke, S. A. *Patent Application, US* **1992**, *151*, 629.
113. Hamada, Y.; Sano, T.; Shibata K.; Kuroki, K. *Jpn. J. Appl. Phys.* **1995**, *34*, 824.
114. Che, C. M.; Chan, S. C.; Xiang, H. F.; Chan, M. C. W.; Liu, Y.; Wang, Y. *Chem. Commun.* **2004**, 1484.
115. Caravan, P. *Chem. Soc. Rev.* **2006**, *35*, 512.
116. Eliseeva S. V.; Bunzli, J-C. G. *Chem. Soc. Rev.* **2010**, *39*, 189.
117. Binnemans, K. *J. Mater. Chem.* **2009**, *19*, 448.
118. Bhattacharjee, C.R.; Das, G.; Goswami, P.; Mondal, P.; Prasad, S.K.; Rao, D.S.S. *Polyhedron* **2011**, *30*, 1040.
119. Molochko, V. A.; Rukk, N. S. *Russ. J. Coord. Chem.* **2000**, *26*, 829.
120. Pucci, D.; Barberio, G.; Bellusci, A.; Crispini, A.; La Deda, M.; Ghedini, M.; Szerb, E. I. *Eur. J. Inorg. Chem.* **2005**, 2457.
121. Cavero, E.; Uriel, S.; Romero, P.; Serrano, J. L.; Giménez, R. *J. Am. Chem. Soc.* **2007**, *129*, 11608.
122. Kozhevnikov, V. N.; Donnio, B.; Bruce, D.; *Angew. Chem.* **2008**, *120*, 6382.
123. Arias, J.; Bardají, M.; Espinet, P. *Inorg. Chem.* **2008**, *47*, 3559.
124. Abe, Y.; Takagi, Y.; Nakamura, M.; Takeuchi, T.; Tanase, T.; Yokokawa, M.; Mukai, H.; Megumi, T.; Hachisuga, A.; Ohta, K. *Inorg. Chim. Acta* **2012**, *392*, 254.
125. Piguet, C.; Bunzli, J-C. G.; Donnio, B.; Guillon, D. *Chem. Commun.* **2006**, 3755.
126. Gupta, K. C.; Sutar, A. K.; *Coord. Chem. Rev.* **2008**, *252*, 1420.
127. Nishinaga, A.; Yamada, T.; Fujisawa, H.; Ishizaki, K. *J. Mol. Catal.* **1998**, *48*, 24.

128. Costamagna, J.; Vargas, J.; Latorre, R.; Alvarado, A.; Mena, G. *Coord. Chem. Rev.* **1992**, 119.
129. Zhao, Y. D.; Pang, D. W.; Zong, Z.; Cheng, J. K.; Luo, Z. F.; Feng, C. J.; Shen, H. Y.; Zhung, X. C. *Chem. Abstr.* **1998**, 128, 252661.
130. Sreekala, R.; Mohammed, K. K. Y. *Chem. Abstr.* **1999**, 130, 115551.
131. Tsuji, J. *Palladium Reagents and Catalysts*; Wiley: New York, **1996**.
132. Beleskaya, P.; Cheprakove, A.V. *Chem. Rev.* **2000**, 100, 3009.
133. Ligtenbarg, A. G. J.; Beuken, E. K.; Meetsma, A.; Veldman, N.; Smeets, W. J. J.; Spek, A. L.; Feringa, B. L. *Dalton Trans.* **1998**, 263.
134. DiMauro, E. F.; Kozlowski, M. C. *Organometallics* **2002**, 21, 1454.
135. Cozzi, P. G. *Angew. Chem., Int. Ed.*, **2003**, 42, 2895.
136. Skinner, M. E. G.; Tyrrell, B. R.; Ward, B. D.; Mountford, P. J. *Organomet. Chem.* **2002**, 647, 145.
137. Syamal, A.; Maurya, M. R. *Coord. Chem. Rev.*, **1989**, 95, 183.
138. Hester R. E.; Nour, E. M., *J. Raman Spectrosc.* **1981**, 11, 49.
139. Cukurovali, A.; Yilmaz, I.; Ozmen, Z.; Ahmedzade, M. *Trans. Met. Chem.* **2002**, 27, 171.
140. Shlyakov, E. N.; Tomnalik, L. E.; Burdenko, T. A.; Chaika, T. S.; Tsapkov, V. I.; Samus, N. M. *Chem. Abstr.* **1989**, 110, 209211.
141. Kumar, M. J. *Orient. Chem.* **2002**, 18, 559.
142. Saxena C. G.; Shrivastava, S. V. *J. Ind. Chem. Soc.* **1987**, 64, 685.
143. Cukurovali, A.; Yilmaz, I.; Ozmen, Z.; Ahmedzade, M. *Trans. Met. Chem.* **2002**, 27, 171.
144. Pandeya, S. N.; Sriram, D.; Nath, G.; De, C. E. *Farmaco*, **1999**, 54, 624.
145. Das, B.; Mahapatra, P. K.; Panda, P.; Patnaik, J. M. *Indian J. Chem. Soc.* **1984**, 61, 1061.
146. Rao, N. R.; Rao, P. V.; Ganorkar, M. C. *Indian J. chem.* **1987**, 26A, 887.
147. Singh, K.; Barwa, M. S.; Tyagi, P. *Eur. J. Med. Chem.* **2006**, 41, 147.
148. Holmgren R. A.; Meade, T. J. *Mol. Pharmaceutics* **2012**, 9, 325.
149. Khan, N. H.; Pandya, N.; Maity, N. C.; Kumar, M.; Kureshy, R. I.; Abdi, S. H. R.; Mishra, S.; Das, S.; Bajaj, H. C. *Eur. J. Med. Chem.* **2011**, 46, 5074.

150. Ansari, K.I.; Kasiri, S.; Grant, J. D.; Mandal, S. S. *Dalton Trans.* **2009**, 8525.