

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

## GENERAL INTRODUCTION

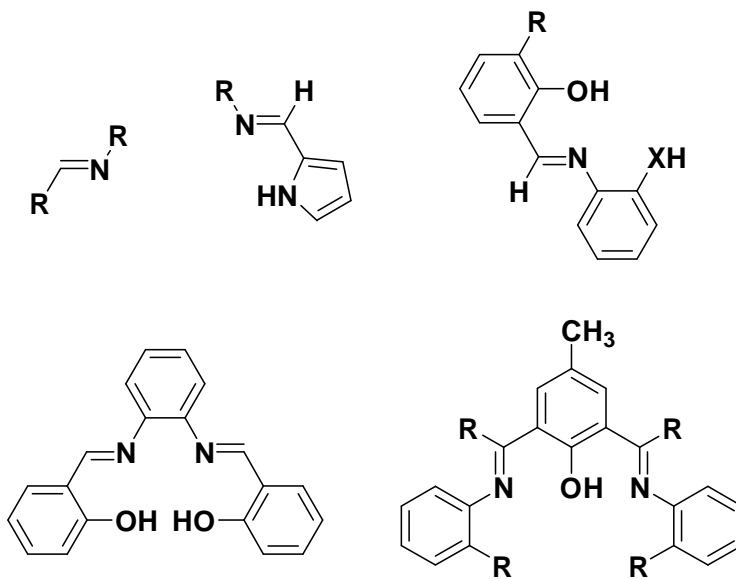
---

Schiff base complexes have been recognized as an important class of coordination compounds with applications in diverse fields ranging from agriculture to optoelectronics,<sup>[1-4]</sup> pharmaceuticals to therapeutics,<sup>[5,6]</sup> polymers to dyes<sup>[7,8]</sup> and drugs to catalysts.<sup>[9-11]</sup> Besides, such compounds currently have also earned a place of interest as liquid-crystalline materials.<sup>[12]</sup> The flexibility in design and the ease of synthesis make Schiff bases versatile ligands with excellent coordinating ability towards a wide range of metal ions in different oxidation states, thereby tuning the overall coordination chemistry of the resulting complexes. The introduction portion is therefore, restricted to a brief discussion on Schiff bases, structure and property of some complexes pertaining to the present thesis. Also presented in this chapter, a discussion on general applications of Schiff base complexes highlighting mainly on the catalytic biological, liquid crystallinity and photophysical applications.

### 1.1. Schiff base

“Schiff base” named after famous German Chemist, Hugo Schiff, are condensation product of amines and carbonyl compounds.<sup>[13]</sup> The basic framework of a Schiff base consists of an azomethine group (-HC=N-). Schiff base can be prepared under different reaction conditions in presence of catalytic amount of acid or base in different solvents. Aliphatic Schiff bases are relatively unstable and prone to polymerization while those derived from aromatic precursors having an effective conjugation are more stable. Schiff bases are in general air stable and can be stored at room temperature without much precautions. However, purification of Schiff bases is a difficult job as degradation may occur during such procedure. Chromatographic separation on silica gel also causes some degree of decomposition through hydrolysis. Purification is therefore accomplished usually by crystallization or by solvent separation techniques.

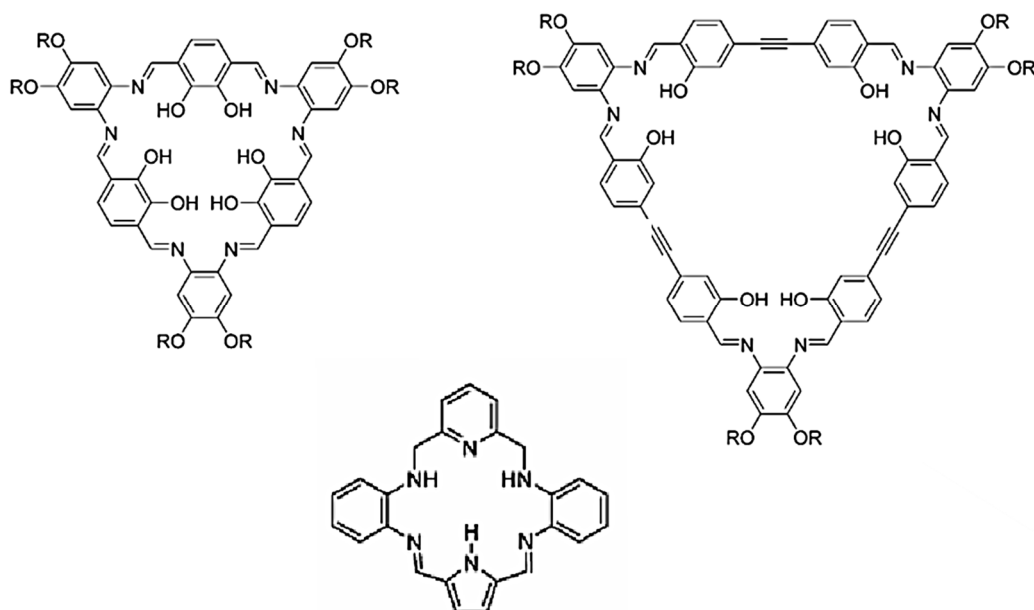
Schiff bases are generally bi-, tri-, tetra- or polydentate ligands binding to metal mainly through the lone pair on the azomethine 'N' in combination with one or more donor atoms close to the azomethine group and linked either to the aldehyde or the amine fragment (**Fig. 1.1**). The combination commonly employed is nitrogen and oxygen, but oxygen can be replaced by sulphur, nitrogen or selenium atoms.<sup>[11,14-16]</sup> Condensation of salicylaldehydes or their derivatives with aliphatic 1,2-diamines results in the formation of an extremely important class of ligands, generally referred to as ‘salen’, while those with aromatic 1,2-diamines leads to the formation of  $\pi$ -conjugated salen systems, often termed as ‘salphen’. Bidentate salicylaldimines are obtained by the reaction of aldehydes with mono-amines.



**Fig. 1.1:** Examples of Schiff bases of varied denticities.

Macrocyclic Schiff base ligands (**Fig. 1.2**) have also drawn considerable research interest as encapsulating ligands finding wide applications in macrocyclic and supramolecular chemistry.<sup>[17,18]</sup> Their multidentate nature results in very high binding constants for many d or f - block metals.<sup>[19,20]</sup> In the present study, the ligand systems chosen are primarily based on bidentate salicylaldimines and tetradentate salen and salphen types. Such ligand systems are considered as ‘privileged ligands’ for their ability to chelate a wide range of metal ions including main group, transition and inner transition metal ions in different

oxidation states.<sup>[17,21]</sup> Also they greatly influence the activity of the metal center in the resulting complexes.

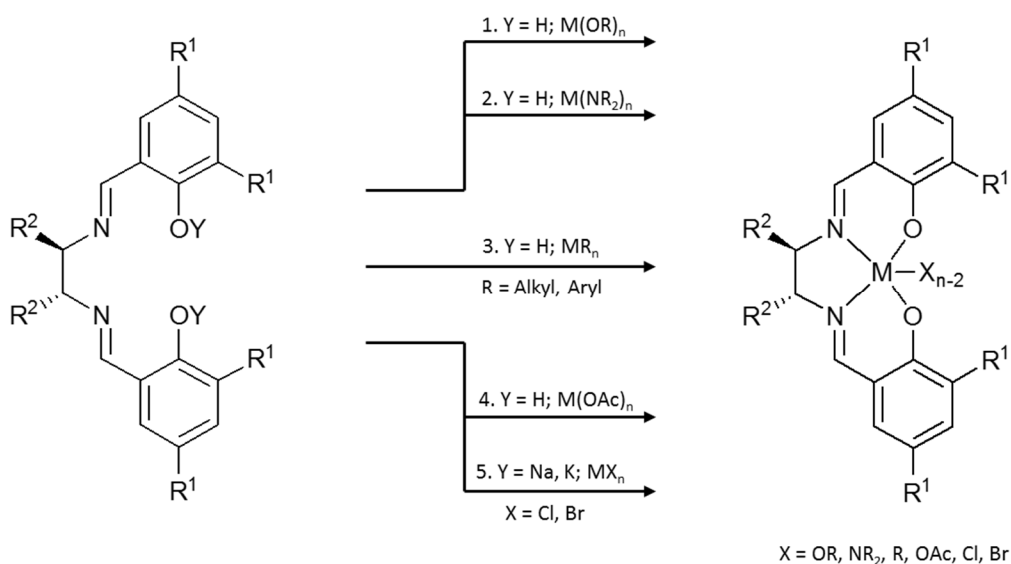


**Fig. 1.2:** Examples of macrocyclic Schiff base ligands.

## 1.2. Metal complexes of Schiff base ligands

Schiff bases serve as useful synthetic intermediates and (or) as ligands and has been extensively employed to coordinate numerous d- and f- block metals in variety of oxidation states and lately for coordinating anions.<sup>[17,21]</sup> Solubility, spin state magnetism and redox properties can be suitably controlled through tuning structure-function relationship. Complexing ability of Schiff base is mainly due to the presence of azomethine linkage. The Schiff base coordinate to metal ions via the lone pair of electrons located on the imine nitrogen atom of the azomethine moiety (-HC=N-). Acidic group like a phenolic OH and SH or any other donor groups, when present in the close proximity of the azomethine group promotes the coordinating ability of the lone pair of electrons enhancing the stability of the metal complexes. Schiff base may act as bidentate: N,O-, tridentate: N,O,O-, N,O,N-, N,O,S-, tetradentate: N,N,O,O-, N,O,O,O-, pentadentate: N,O,O,O,O-, hexadentate: N,N,O,O,S,S-donor ligands, etc.,<sup>[11,22-25]</sup> which can be tailored to yield mononuclear or binuclear complexes or one-dimensional(1D), two-dimensional(2D) and three dimensional (3D) metal-organic frameworks.<sup>[26-30]</sup>

Schiff base metal complexes are generally prepared by carrying out a reaction between the Schiff base and suitable metal precursors such as metal halides, metal alkoxides, metal amides, metal alkyls or metal acetates under appropriate experimental conditions.<sup>[11,31,32]</sup> Five synthesis strategies are generally employed for the preparation of Schiff base metal complexes as outlined by P. G. Cozzi (**Scheme 1**).<sup>[11]</sup>



**Scheme 1.** Preparation of Schiff base complexes. (Ref.: [11])

The early examples of metal Schiff base complexes are over hundred years old,<sup>[33]</sup> even before general procedure for preparation of Schiff base themselves were known. Coordination chemistry of Schiff base metal complexes, however, gained importance after the work of Jørgensen and Werner in the mid-nineteenth century.<sup>[34]</sup> Prior to the work of Jørgensen and Werner, Ettling in 1840, isolated a dark green copper complex from the reaction of cupric acetate, salicylaldehyde and aqueous ammonia.<sup>[35]</sup> Corresponding phenyl and aryl derivatives were synthesized later by Schiff in 1869.<sup>[33,36]</sup> Nevertheless, the systematic study on synthesis of Schiff base metal complexes commenced after Pfeiffer and his co-workers reported a variety of complexes derived from Schiff bases of salicylaldehyde and its substitution products.<sup>[37-40]</sup> Versatility of Schiff base ligands and biological, analytical and industrial applications of their complexes have promoted further

investigations in this area. Therefore, before moving on to the application potential of metal-Schiff base complexes, a brief discussion on the coordination ability of metals is warranted.

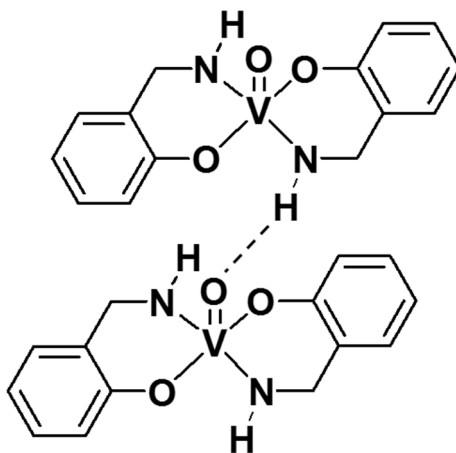
### 1.3. Structure and properties of some Schiff base metal complexes

As the present investigation is based on transition metal complexes of Schiff bases, a brief discussion on the chemistry of Schiff base complexes of the chosen metals is presented in the following section.

#### 1.3.1. Vanadium Schiff base complexes

Vanadium show a wide range of oxidation states ranging from (-I) to (V). While the (II) and (III) states are reducing, the (V) state is slightly oxidizing. The (IV) state is the most stable oxidation state for vanadium and is dominated by the  $\text{VO}^{2+}$  ion, commonly called the vanadyl ion.<sup>[41,42]</sup> This is very stable and exists in a wide range of compounds both as solid and in solution (as the hydrated solution). The characteristics of the coordination chemistry of oxovanadium(IV) complexes is the strong  $\text{V}=\text{O}$  double bond.<sup>[43]</sup> The  $\text{VO}^{2+}$  ion forms complexes predominantly with ligands containing electronegative donor atoms, such as F, Cl, O, or N, though complexes having S-donor atoms are known. The complexes are five coordinate, generally green or blue-green in colour and can be neutral, anionic, or cationic. The geometry around the metal center is mostly square pyramidal and can be related to an octahedron with a vacant coordination site, although some trigonal bipyramidal structures are known.<sup>[41]</sup> In polymeric complexes, the sixth coordination site is either occupied by the vanadyl oxygen of the adjacent molecule<sup>[41,42,44,]</sup> or a hydrogen-bonding interaction can occur (**Fig. 1.3**). In this case, the formation of the binuclear complex enhances the stability so as to withstand reduction to V(III) than related complexes.<sup>[45]</sup> The growing interest on oxovanadium(IV) based Schiff base complexes in past few years is generated by the wide range of biological and catalytic properties.<sup>[46,47]</sup> Many of these complexes are based on ‘salen’ or ‘salphen’ type ligands with N,N,O,O set of donor atoms, formed from reaction between suitably substituted salicylaldehyde and aliphatic or aromatic amines.<sup>[41,44,48-50]</sup> but examples with S donor ligands also exist.<sup>[51]</sup> Oxidovanadium(V) complexes incorporating tridentate Schiff base ligands have also been

investigated for their excellent catalytic activity in various organic transformations.<sup>[52-57]</sup> Metal center in these complexes adopt a five-coordinate square-pyramidal geometry or a distorted six-coordinate octahedral structure.<sup>[52-57]</sup>



**Fig. 1.3:** Hydrogen-bonding interaction in polymeric vanadyl complexes.

### 1.3.2. Nickel Schiff base complexes

Nickel exhibits a range of oxidation states from (-I) to (IV) – the dominant chemistry is of (II) state. The chemistry of nickel in (II) state is quite rich.<sup>[58]</sup> Octahedral and square planar complexes are commonly observed, though several tetrahedral, trigonal bipyramidal and square pyramidal complexes are also known.<sup>[58]</sup> Square planar complexes are diamagnetic and can be visually distinguished from the paramagnetic tetrahedral counterparts due to their characteristic colour. The Ni(II) complexes with Schiff base ligands exhibit a variety of coordination architectures varying from octahedral to square planar including five-coordinate and tetrahedral coordination modes. Nickel(II) complexes with Schiff base ligands act as efficient catalysts in hydrogenation of nitrobenzene,<sup>[59]</sup> epoxidation of olefins,<sup>[60]</sup> oxidation of alcohols into carbonyl compounds<sup>[61]</sup> etc. Moreover, such systems are likely candidates as non-linear optical (NLO) active materials.<sup>[62]</sup>

### 1.3.3. Copper Schiff base complexes

The (II) oxidation state is the most stable and important for copper. The  $\text{Cu}^{2+}$  ion with a  $d^9$  electronic configuration has an unpaired electron. Its compounds are typically coloured due to d-d transition and the compounds are paramagnetic.<sup>[63]</sup> Due to Jahn-Teller distortion, common geometry adopted by Cu(II) complexes are tetrahedral, square planar and octahedral with varying degree of distortions.<sup>[63]</sup> Such complexes show excellent catalytic activity towards different oxidation reactions. There are many reports on the catalytic activity of both mono and multinuclear Cu(II) complexes for oxidation of cycloalkanes, alkenes, benzene, catechol, ascorbic acid etc.<sup>[64-69]</sup> Oxidation of cyclohexane using Cu(II) complexes lures special research interest since its oxidized products are of immense industrial importance.<sup>[70]</sup> Four-coordinate Schiff base Cu(II) complexes exhibit flexible structural features and has been studied at length.<sup>[71,72]</sup> Variation in size and nature of the substituent on the N-imino group of the Schiff base ligand has been correlated with changes in the coordination geometry around the metal center in these complexes.<sup>[71-74]</sup> In some complexes with N-substituted salicylideneimine ligands, structural changes from square planar to tetrahedral coordination has been observed depending on steric and/or electronic effects of the substituents on the imine group of the ligands.<sup>[71,72,75]</sup>

### 1.3.4. Group 12 metals Schiff base complexes

This group comprises of three elements namely- zinc, cadmium and mercury and (II) oxidation state is characteristic of this group. Group 12 di-cations contain a  $d^{10}$ -closed shell electronic configuration and cannot produce d-d spectra.  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$  ions form complexes with N, O and S donor ligands and with halide ions and coordination numbers from 2 to 8 are known. Four coordinate tetrahedral complexes occur largely for Zn(II) and Cd(II), but tetrahedral Hg(II) complexes are also known. Several octahedral, trigonal bipyramidal and square planar complexes have also been reported for these metal ions. Due to metal-ligand bond distance and repulsive energy, four coordinate tetrahedral structures are formed in preference to planar configuration. Square planar geometry is observed in complexes with rigid ligand framework, enforcing planar coordination environment around the metal center.<sup>[76]</sup> Zinc is an essential element in biology, the second most abundant trace metal after iron in biological systems.<sup>[77]</sup> On the contrary, cadmium and mercury are toxic



heavy-metal pollutants and preclude any physiologically beneficial role. Nevertheless, design and synthesis of efficient luminescent chelating Cd(II) and Hg(II) complexes is important for detection of these ions in biological systems.<sup>[78,79]</sup> There has been growing interest in the photophysics of luminescent Zn(II), Cd(II) and Hg(II) coordination complexes in last few years because of their high light emitting efficiency and the possibility of easy tuning of luminescence properties via ligand substitution.<sup>[80-82]</sup> There has been many reports on monomeric and multinuclear Zn(II)/Cd(II) coordination compounds,<sup>[83]</sup> Zn(II) coordination polymers,<sup>[84]</sup> fluorescent detection of Zn(II), Cd(II) and Hg(II) in biological systems,<sup>[78,79,85]</sup> and Zn(II)/Cd(II) coordination complexes as electroluminescent materials applied in OLEDs.<sup>[86,87]</sup> Schiff base complexes of d<sup>10</sup>-metal ions have gained significant attention of researchers due to the flexibility of their stereochemistry and interesting luminescent properties.<sup>[80-82]</sup> Another interesting feature of four coordinate planar Zn(II) Schiff base complexes is that, they are Lewis acidic species and tend to saturate the coordination sphere through the axial coordination with neutral donors, such as alcohols, carbonyls, nitrogen-based donor Lewis bases, or in their absence can be stabilized through intermolecular Zn•••O axial coordination involving Lewis basic atoms of the ligand framework facilitating a variety of aggregate molecular architectures,<sup>[88,89]</sup> supramolecular assemblies<sup>[90,91]</sup> and nanostructures.<sup>[92]</sup>

#### **1.4. Application of metal Schiff base complexes**

In this section, a brief discussion on the applications of metal-Schiff base complexes is attempted, concentrating on the catalytic and biological applications, liquid crystallinity and photoluminescence properties only.

##### **1.4.1. Catalysis**

The demand for cheaper and more efficient systems that can act as catalyst in homogeneous and heterogeneous reactions has grown enormously in recent years. Schiff base complexes display impressive stability and activity, and their readily accessible imine ligands lend themselves as effective catalysts for many asymmetric conversions including (ep)oxidations, epoxide ring-opening reactions, hydrolysis, reduction, decomposition and stereo-selective polymerizations etc.<sup>[93-95]</sup> Structural changes and variation in the type of

Schiff base ligands can bring significant difference in the catalytic activity of the resulting complexes. Schiff base complexes of Co(II)<sup>[96]</sup> and Cr(III)<sup>[97]</sup> are very effective in ring opening of large cycloalkanes with significant enantioselectivity. Schiff base complexes also act as an effective catalyst in the oxidation of hydrocarbons.<sup>[98-102]</sup> Many Schiff base complexes have been effective in reduction of ketones to alcohols<sup>[103]</sup> and alkylation of allylic substrates.<sup>[104-106]</sup> The complexes of chiral salen and binaphthyl have been reported to catalyze Michael addition reaction.<sup>[107]</sup> Schiff base complexes also show catalytic activity in carbonylation of alcohols and alkenes at low pressure to produce  $\alpha$ -arylpropionic acid and their esters,<sup>[108-111]</sup> used as non-steroidal anti-inflammatory drugs. A series of ruthenium Schiff base complexes have been tested for their activity in atom transfer radical polymerization (ATRP) in the presence of trimethylsilyldiazomethane (TMSD) and in ring opening metathesis polymerization (ROMP) of norbornene and cyclooctene.<sup>[112]</sup> The Mn(II)-salen complexes on soluble and insoluble supports were also used as catalysts in various asymmetric epoxidation reactions.<sup>[113,114]</sup> Some polymer bound Schiff base metal complexes have been effective in decomposition of hydrogen peroxide and oxidation of ascorbic acid.<sup>[115]</sup> Palladium(II) complexes of nitrogenous Schiff base ligands exhibit high catalytic activity in Heck reaction.<sup>[116,117]</sup> Cobalt(III)-salen complexes has been catalytically active in the cyclopropanation of styrene with t-butyl diazoacetate and show high trans-selectivity (95%) and enantioselectivity (75% ee).<sup>[118]</sup>

#### 1.4.2. Biological applications

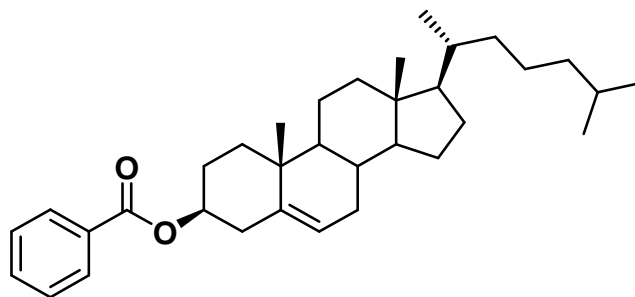
Schiff base complexes have also gained enormous importance as versatile pharmacophores since they exhibit a wide range of biological activities. The hydrogen bond formation between the azomethine nitrogen and the active centers of cell constituents of the targeted cells is believed to be the key to the bio-activity of these complexes.<sup>[119]</sup> Pyrazole-based Schiff bases has been found to be equally as active as standard drug ceftriaxone against microbes such as *P. aeruginosa*, *B. subtilis*, and *E. coli* and most active against *S. aureus*.<sup>[120]</sup> Macrocyclic Schiff bases derived from thiocarbohydrazide has been found to be moderate to strongly active against *K. pneumoniae*, *E. coli*, *S. aureus*, and *S. typhimurium*.<sup>[121]</sup> Co(II), Cu(II), Ni(II), Mn(II) and Cr(III) complexes of Schiff bases derived from 2,6-diacetylpyridine and 2-pyridinecarboxaldehyde with 4-amino-2,3-

dimethyl-1-phenyl-3-pyrazolin-5-one show antibacterial and antifungal activities against *E. coli*, *S. aureus*, *K. pneumoniae*, *M. Smegmatis*, *P. aeruginosa*, *E. cloacae*, *B. megaterium* and *M. luteus*.<sup>[122]</sup> Schiff bases derived from benzocoumarin show *in vitro* antioxidant and *in vivo* antidyslipidemic activity.<sup>[123]</sup> Sydnone based Schiff bases exhibit good anti-inflammatory and analgesic activities.<sup>[124]</sup> Quinolin-2(1H)-one and triazole derived Schiff base ligands and their Cu(II) complexes are potential antifungal and therapeutic agents.<sup>[125,126]</sup> Besides, Schiff base complexes serve as useful reagents for oxidative and hydrolytic cleavage of DNA.<sup>[127]</sup> Cu(II) and Co(II) Schiff base complexes have been largely documented to possess DNA cleavage activity.<sup>[128-131]</sup> Metal(II) amino acid Schiff base complexes are also known to exhibit DNA cleaving activities with calf-thymus DNA (CT-DNA) under aerobic conditions.<sup>[132]</sup>

### 1.4.3. Liquid crystal

‘Liquid crystals’ are a physically distinct state of matter, intermediate between anisotropic crystalline solid and isotropic liquid. They possess some degree of orientational order and sometimes positional order and also possess fluidity of the liquids. As the properties in this state are mid-way between typical solid and liquid, it is often termed as *mesophase* (*mesos* = between) and the compounds that are capable of forming liquid-crystalline phases are referred to as ‘*mesogens*’. The discovery of LCs is credited to Friedrich Reinitzer, when in 1888 he observed double melting behaviour of cholesteryl benzoate (**Fig. 1.4**), one of the several esters of cholesterol-related substances synthesized by him.<sup>[133]</sup> He observed that upon heating, the solid first melted into a cloudy liquid at 145.5 °C and upon further heating, the cloudiness suddenly disappeared at 178.5 °C, and a clear transparent liquid was formed.<sup>[133]</sup> Some unusual colour changes were also observed on cooling. This double melting behaviour was explained by German physicist Otto Lehmann (1855-1922), who first referred them as “soft crystals” and later used the term “crystalline fluids”.<sup>[134]</sup> After detailed examination he suggested that the opaque phase was a homogeneous phase of matter sharing properties of both liquids and solids, and coined the term “*Flüssige Kristalle*” (liquid crystals) in 1889. This term is widely used even today. Further exploration in this field was carried out by German chemist Daniel Vorländer as he and his co-workers synthesized many new liquid crystalline compounds and were the first to

observe more than one LC phase in a single substance.<sup>[135]</sup> He also tried to find an explanation for the relationship between molecular structure and LC properties.<sup>[136]</sup> Later on, in 1922, Georges Freidel published the first classification of LCs into nematic, smectic, and cholesteric.<sup>[137]</sup> He also associated the term ‘mesophase’ to describe the intermediate nature of these phases between the crystal and isotropic liquid states.



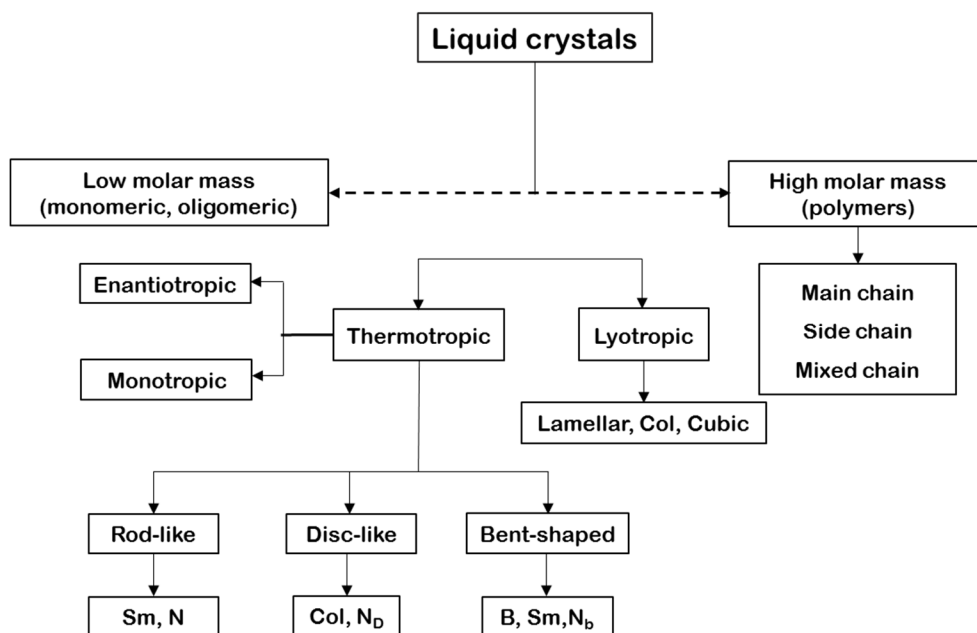
**Fig. 1.4:** Structure of cholesteryl benzoate.

In 1962, George Gray, a British chemist, published a full-length book on molecular structure and properties of LCs.<sup>[138]</sup> In the following decades, numerous new mesogenic compounds were synthesized with different molecular shapes e.g. rod, disc and bent shape etc.

### **Classification of Liquid Crystals**

Liquid crystals are broadly classified into two categories, namely *thermotropic* LCs (mesophase formation is temperature dependent) and *lyotropic* (mesophase formation is solvent or concentration dependent). If both thermotropic and lyotropic liquid crystalline phases are observed in a single substance, then it is called amphotropic LC.<sup>[139]</sup> In addition to this there are also other modes of classification of LCs based on (i) nature of the constituent molecules (organic, inorganic, and organometallic), (ii) molar mass of the constituent molecules, i.e., low molar mass (monomeric and oligomeric) and high molar mass (polymeric) LCs, (iii) overall geometry of the molecules (rod-like, disk-like, banana-like) and (iv) molecular organization in the mesophase (nematic, smectic,

columnar, helical, B phases, etc.).<sup>[140]</sup> A flow chart illustrating the classification of LCs is presented below:



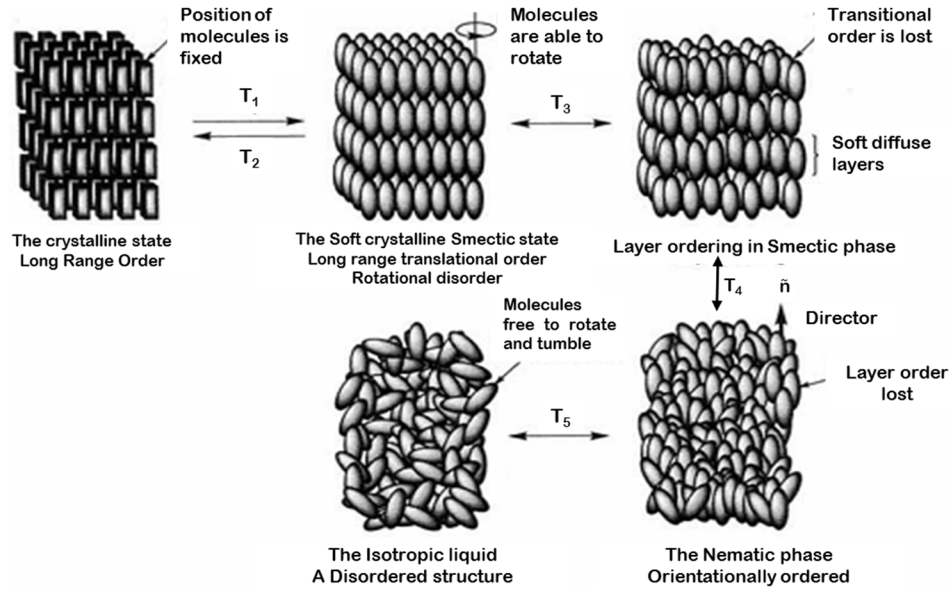
However, considering that the present thesis deals only in thermotropic liquid crystals, discussion on this class is stressed in the following section.

### Thermotropic liquid crystals

When the mesophases are observed on varying the temperature of a pure compound, then the liquid crystals are referred to as thermotropic liquid crystals. The crystals first melt to the mesophase (at the melting point) and then clear to an isotropic liquid at a higher temperature (at the clearing point). If the mesophase appears both on heating and cooling, it is called an *enantiotropic* mesophase, while a mesophase obtained only on cooling the isotropic liquid is termed as *monotropic* mesophase. Structure comprising of a rigid central core (often aromatic) and flexible arms (generally aliphatic chains) is prerequisite for molecules exhibiting thermotropic mesomorphism. Based on the shape of the core of the mesogens, thermotropic LCs are divided into three main categories: (a) calamitic (rod-shaped), (b) bent-core (boomerang or banana-shaped), and (c) discotic (disk-shaped) LCs.

## Mesophases exhibited by calamitic molecules

Calamitic or rod-shaped molecules display mainly two type of mesophases: nematic (from the Greek word *nematos* meaning “thread”) and smectic (from the Greek word *smectos* meaning “soap”).



**Fig. 1.5:** The melting process of a calamitic liquid-crystalline material. (Ref: [141])

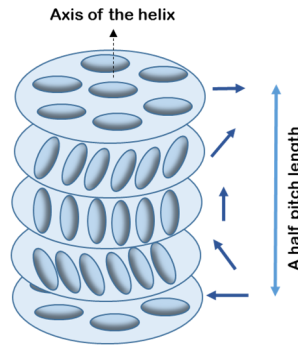
### *Nematic phase:*

The nematic (N) phase is the least ordered mesophase of all the mesophases exhibited by the calamitic molecules closest to the isotropic liquid state. Molecules are orientationally ordered in nematic phase, but do not possess any long range positional order (**Fig. 1.5**). Because of the low molecular order in the nematic phase, this phase has a low viscosity and is very fluid. The rod-like molecules tend to align parallel to each other in this phase with their long molecular axes all pointing on an average towards the same direction, called the director of the phase and denoted by the symbol  $\hat{n}$ .<sup>[142]</sup> The rod-like molecules can rotate freely about their long axes and to some degree about their short axes.

Nematic LCs are extensively used in display devices. Easy alignment and reorientation of the nematogens on application of relatively small electric and magnetic fields serve as a basis for their practical application in LCD devices.

### ***Chiral Nematic phase:***

When the nematic phase possesses chirality, it is called the chiral nematic ( $N^*$ ) phase. This phase was first observed in cholesterol derivatives and hence is also referred to as the *cholesteric phase*.<sup>[143,144]</sup> However, there are many different types of chiral materials having no resemblance to cholesterol, which exhibit the chiral nematic phase. A chiral nematic phase can be generated by a pure enantiomer or by a mixture of enantiomers with one in excess or by adding a small quantity of chiral material (not necessarily liquid crystalline) to a nematic material. In this phase, the director describes a helix through the material with a pitch length  $P$ , which is a  $360^\circ$  rotation of the director  $\vec{n}$  (a full rotation), and  $P/2$  becomes the periodicity due to the equivalence of  $\vec{n}$  and  $-\vec{n}$  (**Fig. 1.6**).

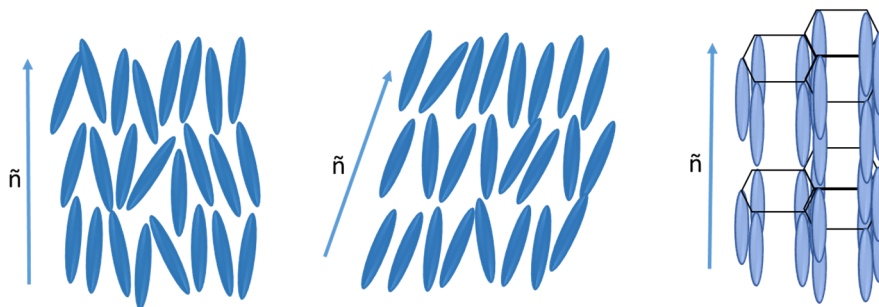


**Fig. 1.6:** Schematic representation of cholesteric phase.

### ***Smectic phase:***

Smectic phases are layered phases which are more ordered than the nematic phase. Smectic phases display certain degree of translational order along with the orientational order found in nematic mesophases. Of the several smectic phases, the two most commonly observed ones are the *smectic A* (SmA) and *smectic C* (SmC) phases (**Fig. 1.7**). The SmA phase is the most disordered type of smectic phase and in it, the long axis of the molecules is orthogonal to the smectic layer plane, and there is no particular positional order within the layers. In SmC phase the molecular organization is similar to that in the SmA phase, except that the director is now tilted at some angle,  $\theta$ , to the layer normal. Chiral versions of this phase have  $C_2$  symmetry in the layers and as such, are ferroelectric- a property which allows their exploitation in display devices.<sup>[145]</sup> Smectic phases are also very fluid and molecules can move freely between the layers. SmB, SmF, and SmI phases are ordered smectic phases in which the molecules possess hexagonal order within the layers. The

$\text{SmB}_{\text{hex}}$  phase is an orthogonal hexatic phase (**Fig. 1.7**), while  $\text{SmF}$  and  $\text{SmI}$  phases are tilted variations in which the molecules are tilted toward the edge and toward the apex of the hexagonal net, respectively. There are also chiral versions of  $\text{SmF}$  and  $\text{SmI}$  phases ( $\text{SmF}^*$  and  $\text{SmI}^*$ ). Smectic B, E, J, G, H, and K are soft crystalline phases which display strong correlation between the preferred positions of the molecules in the different smectic planes and may or may not be tilted.



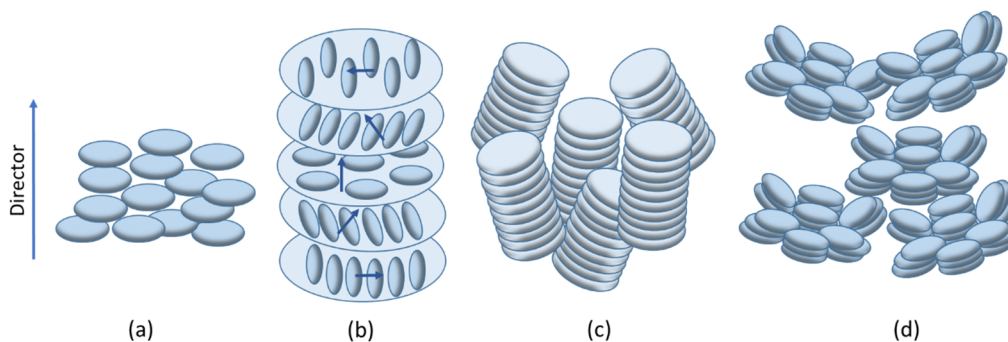
**Fig. 1.7:** Schematic representation of  $\text{SmA}$ (left),  $\text{SmC}$ (middle) and  $\text{SmB}$ (right) phases.

### Mesophases exhibited by disc-shaped molecules

Mesophases of disc-like molecules were first observed in September 1977 by Chandrasekhar et.al at the Raman Research Institute, India.<sup>[146]</sup> They form an entirely new class of LCs where the molecular self-organization in the mesophase is quite different from that in the conventional calamitic molecules. The disk-like molecules spontaneously self-assemble into 1D stacks, which in turn self-organize into various 2D lattices.<sup>[140]</sup> Disc-shaped molecules primarily exhibit three types of mesophases: (1) nematic, (2) smectic, or lamellar and (3) columnar. Disc-shaped molecules extensively exhibit columnar phase followed by the nematic phase, while the lamellar phase is rarely observed. Polymorphism is not common for discotics and most of them exhibit only one type of mesophase, yet few are known to exhibit polymorphism.<sup>[147,148]</sup> Apart from disc-shaped mesogens, polycatenar molecules, dendrimers and bent-core mesogens also exhibit thermotropic columnar phases. Even surfactants aggregating into cylindrical micelles are known since long time to form lyotropic columnar phases.

The nematic phases of disc-shaped molecules can be classified into four types: (a) discotic nematic ( $N_D$ ), (b) chiral nematic ( $N_D^*$ ), (c) nematic columnar ( $N_{\text{Col}}$ ) and (d) nematic lateral ( $N_L$ ).





**Fig. 1.8:** Structure of various nematic phases exhibited by discotic mesogens: (a) discotic nematic, (b) chiral nematic, (c) columnar nematic and (d) nematic lateral.

*Discotic nematic* ( $N_D$ ) phase is the least ordered, least viscous, and more symmetric mesophase among the other nematic phases.<sup>[149]</sup> The preferential direction of the molecules in the discotic nematic phase is established by the short molecular axis and molecules possess full translational and rotational freedom around their short molecular axis (disk normal) and stay more or less parallel (**Fig. 1.8a**).

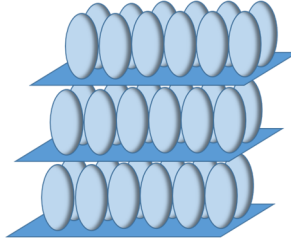
*Chiral nematic* ( $N_D^*$ ) phase is the chiral version of discotic nematic ( $N_D$ ) phase (**Fig. 1.8b**).<sup>[150]</sup> Mixtures of discotic nematic and mesomorphic or non-mesomorphic chiral dopants as well as pure chiral discotic molecules exhibit this mesophase.<sup>[151]</sup>

The *columnar nematic* ( $N_{Col}$ ) phase is characterized by a columnar stacking of the molecules possessing short-range positional and long-range orientational order (**Fig. 1.8c**). The columns behave like supramolecular rods and are randomly distributed with strong lateral interactions. The columns are short and do not form two-dimensional lattice structures.<sup>[152]</sup>

The *nematic lateral* ( $N_L$ ) phase is a recent addition to the nematic phases exhibited by disc-shaped mesogens. In this phase, the disk-shaped molecules aggregate into large superstructures displaying a nematic arrangement (**Fig. 1.8d**).<sup>[153]</sup>

*Smectic* phases of discotic mesogens are observed when there is an unsymmetrical distribution of the peripheral chains or there is a reduced number of peripheral chains around the disc-shaped core. As in the calamitic smectic mesophases, the disks are arranged in layers separated by sub-layers of peripheral chains in the discotic smectic phase (**Fig. 1.9**).<sup>[154]</sup> Molecular rotations about the long molecular axes is hindered in the layers in this phase. This phase is also commonly referred to as *discotic lamellar* ( $D_L$ ) phase.

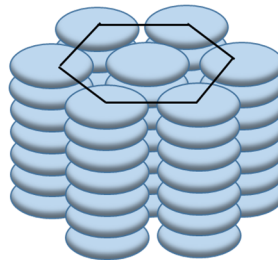
Smectic phases are quite rare in disk-like mesogens as compared to the typical columnar phases.



**Fig. 1.9:** Smectic (discotic lamellar) phase of disc-like mesogens.

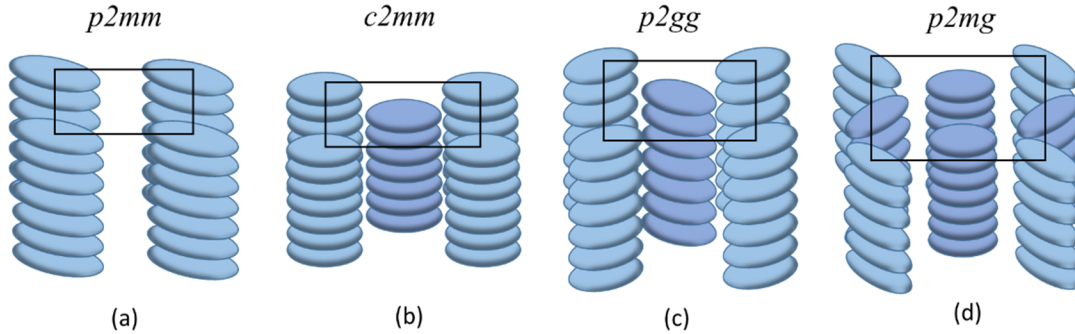
Columnar phase of discotic mesogens is characterized by the periodic stacking of disc-shaped molecules one on top of the other in columns which are then arranged according to the symmetry of various 2D lattices. Periodic stacking of the molecules may be ordered or disordered. Based on the degree of order in the molecular stacking, the orientation of molecules about the columnar axis (orthogonal, tilted, helical, etc.) and symmetry of the 2D lattice, seven types of columnar mesophases are generally encountered, namely: (1) hexagonal columnar phase ( $\text{Col}_h$ ), (2) rectangular columnar phase ( $\text{Col}_r$ ), (3) oblique columnar phase ( $\text{Col}_o$ ), (4) plastic columnar phase ( $\text{Col}_p$ ), (5) columnar helical phase (H), (6) tetragonal columnar phase ( $\text{Col}_t$ ) and (7) lamellar columnar phase ( $\text{Col}_L$ ).

*Hexagonal columnar* ( $\text{Col}_h$ ) phase is the least ordered uniaxial columnar phase among all wherein the columns are arranged at the nodes of a 2D hexagonal lattice. The planar space group of a hexagonal columnar mesophase is  $P6/mmm$ , which is equivalent to  $P6/m2/m$  in the International System (**Fig. 1.10**).<sup>[155]</sup> On the basis of the degree of order in stacking of the cores, hexagonal columnar phases are often denoted as  $\text{Col}_{ho}$  or  $\text{Col}_{hd}$  where “o” and “d” stands for ordered or disordered, respectively.



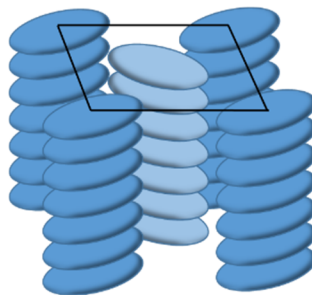
**Fig. 1.10:** Structure of the hexagonal columnar phase.

*Columnar rectangular* ( $\text{Col}_r$ ) phase results from non-cylindrical columnar cores, and their projection onto the lattice plane perpendicular to the columnar axis leading to elliptical, time-averaged, columnar cross-sections.<sup>[156]</sup> Four types of 2D rectangular arrangements of columns are possible for the  $\text{Col}_r$  phases characterized by four different plane groups namely  $c2mm$ ,  $p2gg$ ,  $p2mg$  and  $p2mm$  (**Fig. 1.11**).



**Fig. 1.11:** Structure of different types of rectangular columnar phases.

In the *columnar oblique* ( $\text{Col}_o$ ) phase, the columnar axis is perpendicular to the normal of the lattice plane (**Fig. 1.12**), and the projection of the hard cores onto the lattice plane gives rise to tilted columns.<sup>[155]</sup> The elementary cell is monoclinic. The symmetry of this 2D lattice corresponds to the space group  $P1$ . Examples of columnar oblique mesophases are rare because strong core–core interactions are required.



**Fig. 1.12:** Structure of the oblique columnar phase.

The *plastic columnar* ( $Col_p$ ) phase is characterized by 3D crystal-like order of the center of mass of the molecules (**Fig. 1.13**), while the discs within the columns are able to rotate about the column axis.<sup>[157]</sup> Columnar plastic phase is a recent addition to the mesophases exhibited by discotic mesogens.



**Fig. 1.13:** Structure of the plastic columnar phase. The curved arrow indicates the rotational disorder of the molecules in the columns.

*Columnar helical* (H) phase is characterized by helical stacking of the molecular cores within each column, while the helical period lacks parity with the intermolecular (intracolumnar) spacing (**Fig. 1.14**). This exceptional mesophase structure with helical order has been demonstrated for triphenylene derivatives, namely, hexahexylthiotriphenylene(HHTT)<sup>[158]</sup> and a triphenylene ester derivative.<sup>[159]</sup>



**Fig. 1.14:** Structure of the columnar helical phase.

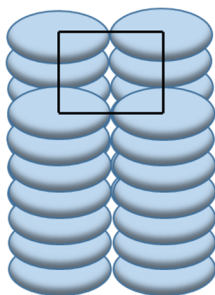
The *Columnar lamellar* ( $Col_L$ ) mesophase consists of a layered structure with columnar organization in which discotic molecules stack to form columns and these columns are then

arranged in layers (**Fig. 1.15**).<sup>[160]</sup> The columns in distinct layers can slide but the columns in different layers do not possess any translational freedom.



**Fig. 1.15:** Structure of the columnar lamellar phase.

The *columnar tetragonal* ( $Col_{tet}$ ) phase is characterized by arrangement of vertically upright columns in a square lattice (**Fig. 1.16**). Columns are aligned in a spontaneous homeotropic fashion as in hexagonal columnar phase.<sup>[161]</sup>

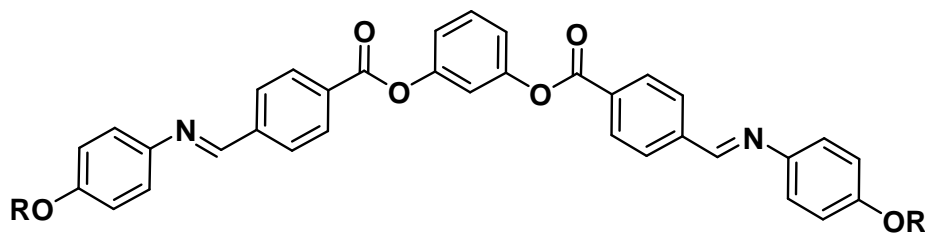


**Fig. 1.16:** Structure of the columnar tetragonal phase.

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

Liquid crystallinity in bent-core or banana-like molecules was first realised by Vorländer in 1929. Vorländer synthesized a number of bent-core mesogens and stated their mesomorphism, accentuating the reduced thermal stability of the mesophase compared to that of calamitic analogues.<sup>[162,163]</sup> However, extensive research activity on bent-core LCs commenced in mid-90's after ferroelectric switching in these achiral molecules was revealed by Niori *et al* in 1996.<sup>[164]</sup> Since then, several hundred bent-core molecules have been synthesized and unique polar order and supramolecular chirality in the mesophase

exhibited by these achiral mesogens has been studied.<sup>[165-167]</sup> In general, molecular structure of bent-core molecules can be regarded as being composed of three components: an angular central core, two linear rigid cores and terminal chains (**Fig. 1.17**). Bent-core molecules exhibit numerous mesophases that are quite unique to this kind and majority of them don't have any resemblance to the mesophases exhibited by calamitic molecules. These phases are referred to as 'B' phases and are numbered according to the sequence of their discovery as B<sub>1</sub>, B<sub>2</sub>, B<sub>3</sub> to the most recent B<sub>8</sub>. A couple of them have several sub-phases i.e., these sub-phases represent a family of related phases. Moreover, some of the B phases possess columnar order while there are others with lamellar order. There are also a few mesophases with poorly resolved phase structures. Besides, conventional nematic and smectic phases has also been observed for bent-core molecules. In addition to the above, biaxial nematic (N<sub>b</sub>), biaxial and polar smectic A phases has also been observed for bent-core mesogens. In fact, bent-core mesogens are the first thermotropic LCs for which a biaxial nematic (N<sub>b</sub>) phase has been explicitly determined.<sup>[168,169]</sup> Potential application of this new kind of truly fascinating materials embrace nonlinear optics (NLO), flexoelectricity, photoconductivity and the design of biaxial nematic phase, etc.<sup>[170]</sup>

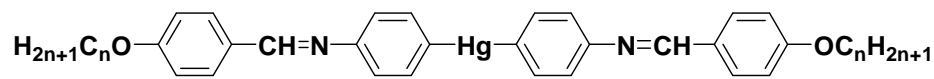


**Fig. 1.17:** General structure of bent-core (banana-shaped) liquid crystals.

### Metallomesogens

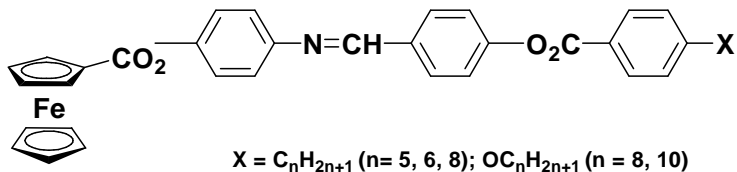
Liquid-crystalline metal complexes are known as metallomesogens.<sup>[171]</sup> Metallomesogens combine the unique physical characteristics displayed by metal coordination complexes (e.g. colour, polarizability, redox behaviour, magnetism, optical and electric properties, etc.) with that of the anisotropic fluids.<sup>[12,172,173]</sup> Besides, incorporation of metal offers unique geometries forming exotic molecular architectures other than the linear, trigonal

and tetrahedral coordination modes exhibited by carbon in organic ligands, which in turn may lead to new types of molecular organization or mesophases.<sup>[12,172,173]</sup> However, the introduction of a metal center in an organic framework often modifies the mesomorphic behaviour of the free ligand (stabilization, modification or suppression of the mesophases of the ligand, or induction of mesophases), thereby posing a challenge in the design of metallomesogens.<sup>[174,175]</sup> The key factors worth considering while designing thermotropic metallomesogens are the role of the metal, the design of the ligands and what effect these would bring on the mesophase behaviour. A major contribution to the phase behaviour and the physical properties of the mesophases is made by the metal center that is incorporated into the core of the mesogen with an anisotropic, rigid organic framework surrounding it.<sup>[176]</sup> Additionally, the radius of the metal ion can influence the transition temperatures and even the type of mesophase.<sup>[147,177]</sup> However, influence of the metal ion on the thermal behaviour of metallomesogens can only be realized in the presence of ligand systems that are able to form complexes with different types of metal ions. Schiff bases feature amongst the earliest and widely preferred ligands for designing metallomesogens. Ease of access, flexibility in design, fine tuning of electronic properties, and coordinating ability towards a wide range of metal ions including main group, transition and inner transition metal ions in different oxidation states are the advantages associated with the Schiff base ligands.<sup>[12,172,173]</sup> The ligand design is fundamental in determining the overall phase behaviour of the resulting complexes. Basic components in the ligand design are: the size and shape of the core, and the length, positioning and number of the tails. Core of the mesogens should be fabricated considering two factors: (1) the inclusion of the metal without disrupting the anisotropy of the core and (2) the desired shape of the core (calamitic or discotic). A long, rigid, core is essential for the formation of mesophase in calamitic metallomesogens and thus, group 9, 10 and 11 metals which predominantly form linear or trans-substituted square planar complexes are ideal.<sup>[178]</sup> The first thermotropic metal-containing liquid crystals were reported by Vorländer in 1910, when he discovered that the alkali metal carboxylates,  $R(\text{CH}_2)_n\text{COONa}$ , formed classical lamellar phases characteristic of soaps.<sup>[179]</sup> Thereafter, in 1923, he also found that the diarylmercury-Schiff bases formed smectic phase (**Fig. 1.18**), and these were the first known examples of metallomesogens derived from Schiff bases.<sup>[180]</sup>



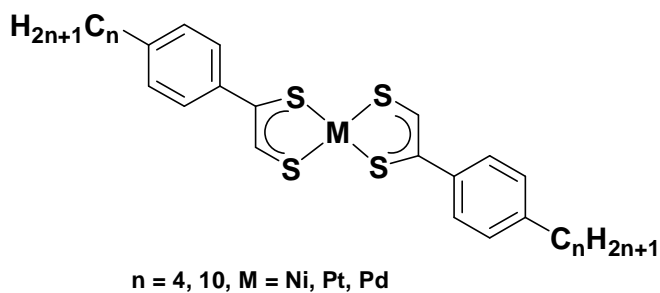
**Fig. 1.18:** Schiff base-mercury mesogens.

Later, smectic ferrocenyl Schiff bases (**Fig. 1.19**) were synthesized by Malthête and Billard in 1976.<sup>[181]</sup>



**Fig. 1.19:** Smectic ferrocenyl Schiff bases.

Giroud and Müller-Westerhoff, in 1977, reported mesogenic nickel and platinum dithiolenes (**Fig. 1.20**) and were the first to pursue advanced materials (novel substances for electronic, optoelectronic, and related applications) among such compounds.<sup>[182]</sup>

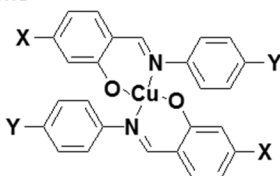


**Fig. 1.20:** Dithiolenes metallomesogen.

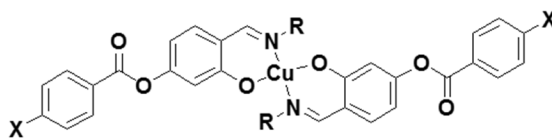
Salicylaldimines have been favourably employed in the synthesis of metallomesogens.<sup>[176,178]</sup> A review by Hoshino have cited a number of examples of salicylaldimine based metallomesogens, the mesophases in which have been well established.<sup>[12]</sup> A large number of metal complexes based on the salicylaldimine ligands have been synthesized using various metal ions such as Cu(II), Ni(II), Pd(II), VO(IV), Mn(III), Fe(III) and lanthanides.



### Two-ring ligand systems

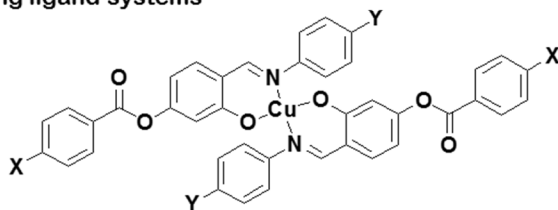


SmA/SmC

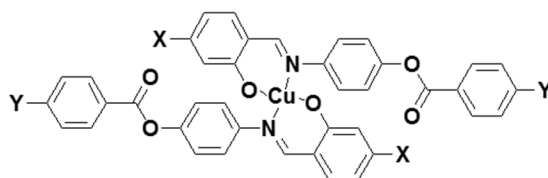


N/SmC

### Three-ring ligand systems



N/SmC



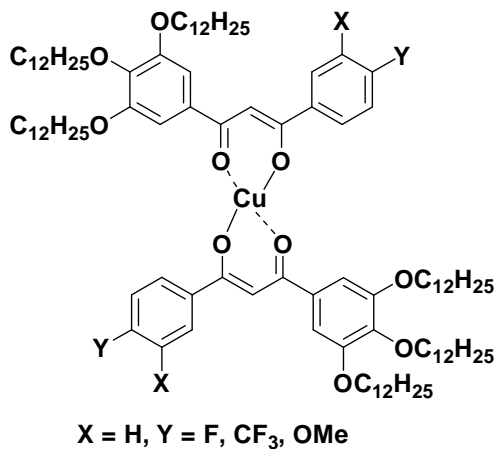
N/SmC

**Fig. 1.21:** The archetypical metal–salicylaldimine systems (Ref.: [12]).

Lamellar smectic mesomorphism in calamitic bis-N-(4-substituted)-salicylaldiminato Cu(II) and Ni(II) complexes with aliphatic spacer were first reported by Ovchinnikov and co-workers.<sup>[183]</sup>

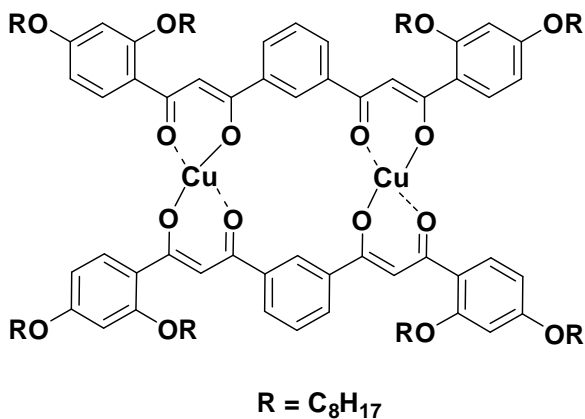
A rigid central core (planar, pyramidal, conical, or a similar geometry) surrounded by several flexible alkyl chains is essential for the formation of mesophase in discotic metallomesogens. Diketonate, salicylaldimine, glyoximate, phthalocyanine, porphyrin, pyridine, and pyrazole groups have been successfully explored in designing the cores for discotic metallomesogens. The first mesogenic complex based on  $\beta$ -diketonates, bis-(1-octyloxyphenyl-1,3-butanedionato) palladium(II) was prepared in 1977.<sup>[184]</sup> Later on, a series of complexes of structurally related  $\beta$ -diketonates were reported by Ohta *et.al* exhibiting columnar mesomorphism.<sup>[185-188]</sup> Swager and co-workers investigated in detail the chemistry of half-disc shaped square-planar copper bis- $\beta$ -diketonate complexes (**Fig. 1.22**).<sup>[189]</sup> Systematic studies on the substituent effects of various unsymmetrical

copper and palladium complexes of  $\beta$ -diketonates were carried out by Lai and co-workers.<sup>[190]</sup>



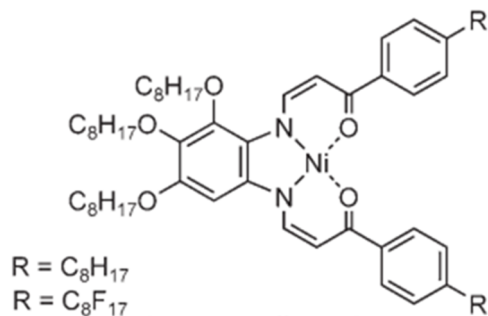
**Fig. 1.22:** Copper bis- $\beta$ -diketonate metallomesogens. (Ref.: [189])

Xie and co-workers reported a binuclear discogen based on the  $\beta$ -diketonate structural motif (**Fig. 1.23**).<sup>[191]</sup>



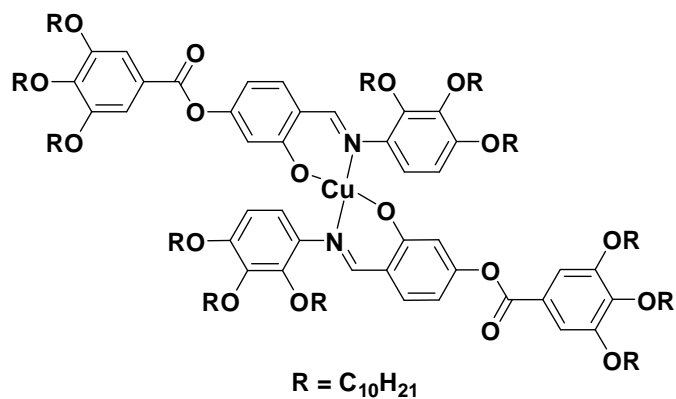
**Fig. 1.23:** Binuclear discogen based on the  $\beta$ -diketonates.

Nickel, copper and oxovanadium complexes with diaminoaryl-bridged enamino-ketone ligands (**Fig. 1.24**) were studied by Szydłowska and co-workers.<sup>[192]</sup>



**Fig. 1.24:** Metallomesogens based on diaminoaryl-bridged enaminoketones.

Salicylaldiminato ligands are electronically related to the enaminoketones (a logical extension of  $\beta$ -diketonates) and thus, should also be suitable for columnar LCs. Though a rich literature on metal salicylaldiminato complexes, displaying smectic and nematic mesophases exists, examples of columnar mesophases are relatively scarce. Serrano and co-workers prepared bis(salicylaldiminato) copper(II) complexes (**Fig. 1.25**) which displayed rectangular columnar mesophases.<sup>[193,194]</sup> Date and Bruce later found that an extended mesogenic core leads to hexagonal columnar mesophases.<sup>[195]</sup> Our group have recently reported zinc(II) bimetallomesogen of tridentate [ONO]-donor salicylaldimine ligand displaying rectangular or oblique columnar phase.<sup>[196]</sup>

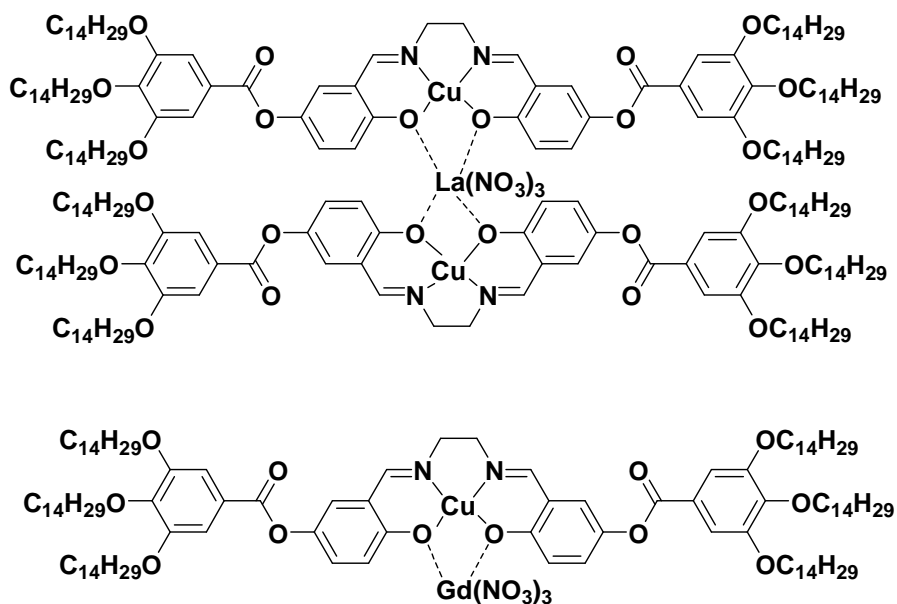


**Fig. 1.25:** Bis(salicylaldiminato) copper(II) complexes. (Ref.: [193,194])

Metal complexes based on tetradentate ‘salen’ or ‘salphen’ (salen = N,N'-ethylene-bis(salicylideneiminato)) Schiff bases with long alkyl or alkoxy chains have also been

efficiently used in designing exotic liquid crystalline materials. The rigidity of the ligand framework offers the required anisotropy for the construction of supramolecular structures favouring mesomorphism. Abe and co-workers reported a series of metal-salen complexes  $\{M = VO(IV), Ni(II), Cu(II) \text{ and } Pt(II)\}$  containing 4-substituted alkoxy chains, displaying either a novel bilayer  $M(Pa2I)$  phase or a 1D lamello-columnar ( $Col_L$ ) phase.<sup>[197-200]</sup> On the contrary,  $Co(II), Ni(II), Cu(II), VO(IV)$ -salen complexes with 5-substituted alkoxy or alkyl chains predominantly displayed SmA mesophases.<sup>[201-205]</sup> Hemi-discotic and polycatenar-like metallomesogens based on  $Mn(III)$ -salen complexes were reported by Espinet and co-workers which display columnar mesophases formed by self-assembling of dimer aggregates.<sup>[206]</sup> A series of 4-substituted  $VO(IV), Zn(II), Ni(II)$  as well as  $Cu(II)$  complexes using cyclohexane/phenylene diamine spacer exhibiting different type of columnar phases were reported by our group lately.<sup>[207-213]</sup>

Apart from these, mixed copper–lanthanide f–d metallomesogens, bearing a di-(salen) core (**Fig. 1.26**), was reported by Binnemans and co-workers to display hexagonal columnar phase.<sup>[214]</sup> Further work along this line was carried out by replacing  $Cu(II)$  with  $Ni(II)$ , all displaying hexagonal columnar phase ( $Col_h$ ) over an extended temperature range.<sup>[215,216]</sup>



**Fig. 1.26:** Mixed copper–lanthanide d–f metallomesogens. (Ref.: [214])

#### 1.4.4. Photophysical properties of metal Schiff base complexes

Photophysics and photochemistry of coordination complexes of transition metals has received cumulative interest since the last few decades for the better understanding of the excited state properties and photochemical reactions.<sup>[217-219]</sup> OLEDs for flat “cold light” sources have caught the fancy of scientists in the past decade<sup>[220-222]</sup> and the technological innovation thereof is considered crucial to cope with the impending energy crisis.<sup>[223]</sup> The interest in luminescent molecules and materials is not only limited to lighting technologies but there are several other fields of research such as imaging, lasers, sensors, switches, etc.<sup>[224]</sup> The emission from transition metal complexes is usually produced from triplet excited states. Strong spin–orbit coupling (SOC) facilitates fast conversion of singlet to triplet excited states via intersystem crossing (ISC).<sup>[225]</sup> Thus, emission from singlet excited states is not favoured in case of transition metal complexes. Yet, there are a number of examples of transition metal complexes that fluoresce with high intensity and some of them have been comprehensively studied.<sup>[212,213]</sup> Singlet emission is predominantly ligand-based fluorescence, which occurs when metal–ligand interactions are weak leading to a small metal contribution in the excited states, and a competitive fluorescence rate constant when compared to the ISC rate constant.<sup>[225]</sup> The research centered on the exploration of photophysical properties of Schiff base complexes in the field of functional materials is still at its infancy.<sup>[226]</sup> One of the first few examples in this area was a novel blue light-emitting diode (LED) based on Zn(II)salen complex, reported by Liu and co-workers.<sup>[227]</sup> Subsequent studies were conducted on conjugated polymers containing Zn(II) and Ni(II) Schiff base complexes which were also reported to have organic LED applications.<sup>[228,229]</sup> In addition to the above, application of Pt(II)-salen and Pt(II)-salphen complexes in high-performance organic LED’s have also been reported by Che and co-workers.<sup>[230]</sup> Other examples of emissive Schiff base complexes include an axially rotating bis-Pt(II)-salphen complex which displays colorimetric and luminescent responses to metal ions.<sup>[231]</sup> In particular, the ability of such bis-Pt(II)-salphen complex to sense Pb(II) ion by phosphorescence techniques is quite interesting. There are also reports on multinuclear salphen systems incorporating Zn(II) which give a colorimetric response in the presence of N-donor systems based on substituted (iso)quinolones.<sup>[232]</sup> Apart from the examples concerning transition metals, U(VI)-salphen complexes are also known to have unusual

photophysical properties.<sup>[233]</sup> An advantage of luminescence by trivalent lanthanide ions is that, the luminescence spectra consist of narrow emission lines of a high coloric purity.<sup>[234,235]</sup> The relative intensity of the emission lines and their fine structure is only marginally influenced by the nature of the ligand in the first coordination sphere. The excited states have a long lifetime at room temperature, on the order of microseconds or even milliseconds.<sup>[234,235]</sup>

Design of materials that are photo-responsive and possess ordered fluid-phases at the same time are of abiding interest because of their interesting applications related to OLEDs, information storage, sensors, lasers and enhanced contrast displays, etc.<sup>[236-238]</sup> The first example of blue emissive one-ring salicylaldimine type Schiff base ligands exhibiting smectic mesomorphism was reported by our group.<sup>[239]</sup> The first examples of d-block metallomesogens exhibiting luminescence in the liquid crystalline state were that of the smectogenic rodlike gold(I) isocyanide complexes described by Espinet and co-workers.<sup>[240]</sup> A series of luminescent square planar Pt(II)-salen complexes containing 4-substituted alkoxy chains of aromatic rings has been reported by Abe and co-workers.<sup>[197]</sup> Other examples include luminescent Zn(II) complexes based on salen-like frameworks which display luminescence in the intercalated smectic C mesophase.<sup>[241]</sup> In addition to the d-block metals, lanthanide-containing metallomesogens are also known to exhibit luminescence in the mesophase. Yang and co-workers have reported on low-melting lanthanidomesogens consisting of Lewis base adducts of a non-mesomorphic salicylaldimine Schiff base ligand forming a smectic A phase at room temperature.<sup>[242]</sup>

## 1.5 Objectives:

In view of the potential applications of the Schiff bases and their metal complexes in diverse fields such as liquid crystallinity, photophysical properties, catalytic and biological activities etc. as highlighted in the aforesaid text, the primary objectives of the present Ph. D. research programme are set as:-

1. To devise synthetic strategy for the synthesis of newer functionalized Schiff base ligands with multiple donor site(s).
2. Complexation with d-block transition metals and isolation in the solid state.
3. Identification, characterization 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 determine the optimized electronic structure of the compounds with the aid of DFT/TDDFT studies.

## REFERENCES

- [1] L. Zhu, N. Chen, H. Li, F. Song, X. Zhu, *Chem. Abstr.*, 2004, **141**, 374026.
- [2] S. Huneck, K. Schreiber, H. D. Grimmecke. *J. Plant Growth Regul.*, 1984, **3**, 75.
- [3] H. Xu, R. Chen, Q. Sun, W. Lai, Q. Su, W. Huang, X. Liu, *Chem. Soc. Rev.*, 2014, **43**, 259.
- [4] A.K. Neeraj, V. Kumar, R. Prajapati, S.K. Asthana, K.K. Upadhyaya, J. Zhao, *Dalton Trans.*, 2014, **43**, 5831.
- [5] A. Kajal, S. Bala, S. Kamboj, N. Sharma, V. Saini, *J. Catal.*, 2013, <http://dx.doi.org/10.1155/2013/893512>. Article ID 893512.
- [6] S. Dave, N. Bansal, *Int. J. Curr. Pharm. Res.*, 2013, **5**, 6.
- [7] Y. Xin, J. Yuan, *Polym. Chem.*, 2012, **3**, 3045.
- [8] K. M. Abuamer, A. A. Maihub, M. M. El-Ajaily, A. M. Etorki, M. M. Abou-Krishna, M. A. Almagani, *Int. J. Org. Chem.*, 2014, **4**, 7.
- [9] I. Kostova, L. Saso, *Curr. Med. Chem.*, 2013, **20**, 4609.
- [10] K. C. Gupta, A. K. Sutar, *Coord. Chem. Rev.*, 2008, **252**, 1420.
- [11] P.G. Cozzi, *Chem. Soc. Rev.*, 2004, **33**, 410.
- [12] N. Hoshino, *Coord. Chem. Rev.*, 1998, **174**, 77.
- [13] H. Schiff, *Ann. Suppl.*, 1864, **3**, 343.
- [14] P. M. V. Kumar, P. K. Radhakrishnan, *Inorg. Chim. Acta*, 2011, **375**, 84.
- [15] Y. Sui, D-Pi. Li, C-H. Li, X-H. Zhou, T. Wu, X-Z. You, *Inorg. Chem.*, 2010, **49**, 1286.
- [16] P. K. Dutta, A. K. Asatkar, S. S. Zade, S. Panda, *Dalton Trans.*, 2014, **43**, 1736.
- [17] P. A. Vigato, S. Tamburini. *Coord. Chem. Rev.*, 2004, **248**, 1717.
- [18] N. E. Borisova, M. D. Reshetova, Y. A. Ustynyuk, *Chem. Rev.*, 2007, **107**, 4679.
- [19] K. Choi, A.D. Hamilton, *Coord. Chem. Rev.*, 2003, **240**, 101.
- [20] R.M. Izatt, K. Pawlak, J.S. Bradshaw, *Chem. Rev.*, 1995, **95**, 2529.
- [21] K. Uzarevic, I. Dilovic, D. M.- Calogovic, D. Sisak, M. Cindric, *Angew. Chem. Int. Ed.*, 2008, **47**, 7022.
- [22] E. M. McGarrigle, D. G. Gilheany, *Chem. Rev.*, 2005, **105**, 1563.
- [23] M. Farahbakhsh, H. Nekola, H. Schmidt, D. Rehder, *Chem. Ber.*, 1997 **130**, 1129.
- [24] D. A. Atwood, M. J. Harvey, *Chem. Rev.*, 2001, **101**, 37.



- [25] M. Dey, C. P. Rao, P. K. Saarenketo, K. Rissanen, E. Kolehmainen, P. Guionneau, *Polyhedron*, 2003, **22**, 3515.
- [26] M. L. Tong, X.-M. Chen, B.-H. Ye, L.-N. Ji, *Angew. Chem. Int. Ed.*, 1999, **38**, 2237.
- [27] W. X. Zhang, C.-Q. Ma, S.-F. Si, *Transition Met. Chem.*, **26**, 2001, 380–383.
- [28] M. Dey, C. P. Rao, P. K. Saarenketo, K. Rissanen, *Inorg. Chem. Commun.*, 2002, **5**, 924.
- [29] J. J. Zhang, H.-J. Zhou, A. Lachgar, *Angew. Chem. Int. Ed.*, 2007, **46**, 4995.
- [30] C. J. Whiteoak, G. Salassaa, A. W. Kleij, *Chem. Soc. Rev.*, 2012, **41**, 622.
- [31] J. Costamagna, J. Vargas, R. Latorre, A. Alvarado, G. Mena, *Coord. Chem. Rev.*, 1992, **119**, 67.
- [32] M. Kojima, H. Taguchi, M. Tsuchimoto, K. Nakajima, *Coord. Chem. Rev.*, 2003, **237**, 183.
- [33] H. Schiff, *Ann. Chem. Pharm.*, 1869, **150**, 193.
- [34] C. K. Jorgensen, *Acta Chem. Scand.*, 1957, **11**, 73.
- [35] C. Ettl, *Ann. Suppl.*, 1840, **35**, 241.
- [36] H. Schiff, *Ann. Chem. Pharm.*, 1869, 151, 186.
- [37] P. Pfeiffer, E. Buchholz, O. Baver, *J. Prakt. Chem.*, 1931, **129**, 163.
- [38] P. Pfeiffer, E. Breith, E. Lubbe, T. Tsumaki, *Ann. Chem. Pharm.*, 1933, **503**, 84.
- [39] P. Pfeiffer, H. Pfitzinger, *J. Prakt. Chem.*, 1936, **145**, 243.
- [40] P. Pfeiffer, T. Hesse, H. Pfitzinger, W. Scholl and H. Thielert, *J. Prakt. Chem.*, 1937, **149**, 217.
- [41] E. M. Page, S. A. Wass, *Encyclopedia of Inorganic Chemistry, 1st edn.*, Wiley, 1994.
- [42] D. C. Crans, J. J. Smee, E. Gaidamuskas, L. Yang, *Chem. Rev.*, 2004, **104**, 849.
- [43] J. Selbin, *Chem. Rev.*, 1965, **65**, 153.
- [44] C. Slebodnick, B. J. Hamstra, V. L. Pecoraro, *Struct. Bonding*, 1997, **89**, 51.
- [45] N. Choudhary, N. G. Connelly, P. B. Hitchcock, G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 1999, 4437.
- [46] Y. Abe, A. Iyoda, K. Seto, A. Moriguchi, H. Yokoyama, *Eur. J. Inorg. Chem.*, 2008, 2148.
- [47] A. Ohta, Y. Yamamoto, H. Kamihata, Y. H. Lee, F. Ichikawa, K. Ohta, Y. Abe, N. Hoshino, M. Kojima, S. Hayami, *Inorg. Chem. Commun.*, 2012, **16**, 89.
- [48] R. L. Richards, *Encyclopedia of Inorganic and Bioinorganic Chemistry*, Wiley, 2011.

- [49] N. Choudhary, N. G. Connelly, P. B. Hitchcock, G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 1999, 4437.
- [50] M. Tsuchimoto, G. Hoshina, N. Yoshioka, H. Inoue, K. Nakajima, M. M. Kojima, S. Ohba, *J. Solid State Chem.*, 2000, **153**, 9.
- [51] A. D. Kermidas, A. B. Papaioannu, A. Vlahos, T. A. Kabanos, G. Bonas, A. Makriannis, C. P. Raptopoulou, A. Terzis, *Inorg. Chem.*, 1996, **35**, 357.
- [52] H. Mimoun, M. Mignard, P. Brechot, L. Saussine, *J. Am. Chem. Soc.*, 1986, **108**, 3711.
- [53] Q. Zeng, H. Wang, W. Weng, W. Lin, Y. Gao, X. Huang, Y. Zhao, *New J. Chem.*, 2005, **29**, 1125.
- [54] J. Hartung, *Pure Appl. Chem.*, 2005, **77**, 1559.
- [55] S.-H. Hsieh, Y.-P. Kuo, H.-M. Gau, *Dalton Trans.*, 2007, 97.
- [56] C. Cordelle, D. Agustin, J.-C. Daran, R. Poli, *Inorg. Chim. Acta*, 2010, **364**, 144.
- [57] G. Romanowski, M. Wera, *Polyhedron*, 2013, **50**, 179–186.
- [58] J. D. Lee, *Concise Inorganic Chemistry, fifth ed.*, Wiley, India, 2007, pp: 806.
- [59] E. S. Aazam, W. A. El-Said, *Bioorganic Chemistry*, 2014, 57.
- [60] D. Chatterjee, S. Mukherjee, A. Mitra, *J. Mol. Catal. A: Chem.*, 2000, **154**, 5.
- [61] D. Ramakrishna, B. R. Bhat, R. Karvembu, *Catal. Commun.*, 2010, **11**, 498.
- [62] S. Di Bella, I. Fragalá, I. Ledoux, J. Zyss, *Chem. Eur. J.*, 2001, **7**, 3738.
- [63] J.D. Lee, *Concise Inorganic Chemistry, fifth ed.*, Wiley, India, 2007, pp: 827-829.
- [64] P. Roy, K. Dhara, M. Manassero, P. Banerjee, *Inorg. Chem. Commun.*, 2008, **11**, 265.
- [65] A. M. Kirillov, M. N. Kopylovich, M. V. Kirillova, M. Haukka, M. F. C. Guedes da Silva, A. J. L. Pombeiro, *Angew. Chem., Int. Ed.*, 2005, **44**, 4345.
- [66] P. Roy, K. Dhara, M. Manassero, P. Banerjee, *Eur. J. Inorg. Chem.*, 2008, 4404.
- [67] M. Thirumavalavan, P. Akilan, M. Kandaswamy, K. Chinnakali, G. S. Kumar, H.K. Fun, *Inorg. Chem.*, 2003, **42**, 3308.
- [68] A. Panja, S. Goswami, N. Shaikh, P. Roy, M. Manassero, R. J. Butcher, P. Banerjee, *Polyhedron*, 2005, **24**, 2921.
- [69] M. Scarpa, F. Vianello, L. Signor, L. Zennaro, A. Rigo, *Inorg. Chem.*, 1996, **35**, 5201.
- [70] A. E. Shilov, G. B. Shul'pin, *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*, Kluwer Academic Publishers, Dordrecht, The Netherlands, 2000.

- [71] T. Akitsu, Y. Einaga, *Polyhedron*, 2006, **25**, 1089.
- [72] T. Akitsu, Y. Einaga, *Polyhedron*, 2005, **24**, 2933.
- [73] H. Okawa, S. Nakamura, S. Kida, *Inorg. Chim. Acta*, 1986, **120**, 185.
- [74] J.M. Fernandez, O.L. Ruiz-Tamirez, R.A. Toscano, *Trans. Met. Chem.*, 2000, **25**, 511.
- [75] S. Yamada, *Coord. Chem. Rev.*, 1999, **190–192**, 537.
- [76] S. J. Wezenberg, A. W. Kleij, *Angew. Chem. Int. Ed.*, 2008, **47**, 2354.
- [77] S. Frassinetti, G. Bronzetti, L. Caltavuturo, M. Cini, C. D. Croce, *J. Environ. Pathol. Toxicol. Oncol.*, 2006, **25**, 597.
- [78] H. N. Kim, W. X. Ren, J. S. Kim, J. Yoon, *Chem. Soc. Rev.*, 2012, **41**, 3210.
- [79] D.W. Domaille, E. L. Que, C. J. Chang, *Nature Chemical Biology*, 2008, **4**, 168.
- [80] Y. Dong, R. Fan, P. Wang, L. Wei, X. Wang, H. Zhang, S. Gao, Y. Yang, Y. Wang, *Dalton Trans.*, 2015, **44**, 5306.
- [81] X. Wang, S. Chen, R. Fan, F. Zhang, Y. Yang, *Dalton Trans.*, 2015, **44**, 8107.
- [82] Z. Zhang, J. F. Ma, Y. Y. Liu, W. Q. Kan, J. Yang, *Cryst. Eng. Comm.*, 2013, **15**, 2009.
- [83] S. L. Zheng, X. M. Chen, *Aust. J. Chem.*, 2004, **57**, 703.
- [84] A. Erxleben, *Coord. Chem. Rev.*, 2003, **246**, 203.
- [85] P. Jiang, Z. Guo, *Coord. Chem. Rev.*, 2004, **248**, 205.
- [86] R. C. Evans, P. Douglas, C. J. Winscom, *Coord. Chem. Rev.*, 2006, **250**, 2093.
- [87] S. N. Wang, *Coord. Chem. Rev.*, 2001, **215**, 79.
- [88] E. C. Escudero-Adán, J. Benet-Buchholz and A. W. Kleij, *Inorg. Chem.*, 2008, **47**, 4256.
- [89] A. J. Gallant, J. H. Chong, M. J. MacLachlan, *Inorg. Chem.*, 2006, **45**, 5248.
- [90] S. J. Wezenberg, E. C. Escudero-Adán, J. Benet-Buchholz, A. J. Kleij, *Chem.–Eur. J.*, 2009, **15**, 5695.
- [91] A. C. W. Leung, M. J. MacLachlan, *J. Mater. Chem.*, 2007, **17**, 1923.
- [92] J. K. -H. Hui, M. J. MacLachlan, *Dalton Trans.*, 2010, **39**, 7310.
- [93] E. N. Jacobsen, *Acc. Chem. Res.*, 2000, **33**, 421.
- [94] J. M. Ready, E. N. Jacobsen, *J. Am. Chem. Soc.*, 2001, **123**, 2687.
- [95] W. Hirahata, R. M. Thomas, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.*, 2008, **130**, 17658.
- [96] E.N. Jacobsen, F. Kakiuchi, R.G. Konsler, J.F. Larrow, M. Tokunaga, *Tetrahedron Lett.*, 1997, **38**, 773.

- [97] M.H. Wu, E.N. Jacobson, *Tetrahedron Lett.*, 1997, **38**, 693.
- [98] Z. Xi, H. Wang, Y. Sun, N. Zhou, G. Cao, M. Li, *J. Mol. Catal. A Chem.*, 2001, **168**, 299.
- [99] T. Mykaiyama, T. Yamada, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 17.
- [100] P. Mastrorilli, C. F. Nobile, G.P. Surana, L. Lopez, *Tetrahedron*, 1995, **51**, 7943.
- [101] I. Ferhadeze, J. R. Petro, R. de la Salud, *Tetrahedron*, 1996, **52**, 12031.
- [102] K. S. Ravikumar, F. Barber, J. P. Bugui, D. Bonnet-Dolpon, *Tetrahedron*, 1998, **54**, 7457.
- [103] W.S. Kima, Y. K. Choi, *Appl. Catal. A Gen.*, 2003, **252**, 163.
- [104] T. Hayashi, *J. Organomet. Chem.*, 1999, **576**, 195.
- [105] P. G. Helm Chen, *J. Organomet. Chem.*, 1999, **576**, 204.
- [106] H. Brunner, I. Demi, W. Dirnberger, B. Number, W. Reiber, *Eur. J. Inorg. Chem.*, 1998, 43.
- [107] H. Brunner, C. Krumei, *J. Mol. Catal. A Chem.*, 1999, **142**, 7.
- [108] H. Y. Zhou, J. Cheng, S. J. Lu, H. X. Fu, H. Q. Wang, *J. Organomet. Chem.*, 1998, **556**, 239.
- [109] B. H. Xie, C.G. Xia, S. J. Lu, K. J. Chen, Y. Kou, Y. Q. Yin, *Tetrahedron Lett.*, 1998, **39**, 7365.
- [110] E. J. Jang, K. H. Lee, J. S. Lee, Y.G. Kin, *J. Mol. Catal. A Chem.*, 1999, **138**, 25.
- [111] E. J. Jang, K. H. Lee, J. S. Lee, Y. G. Kin, *J. Mol. Catal. A Chem.*, 1999, **144**, 431.
- [112] B. D. Clercq, F. Verpoort, *J. Mol. Catal. A Chem.*, 2002, **180**, 67.
- [113] D. E. De Vos, P. P. Knops-Gerrits, D. L. Vanoppen, P. A. Jacobs, *Supramol. Chem.*, 1995, **6 (1/2)**, 49.
- [114] S. R. Thomas, K. D. Janla, *J. Am. Chem. Soc.*, 2000, **122**, 6929.
- [115] D. Chatterjee, A. Mitra, *J. Mol. Catal. A Chem.*, 1999, **144**, 363.
- [116] S. Iyer, G. M. Kulkarni, C. Ramesh, *Tetrahedron*, 2004, **60**, 2163.
- [117] A. S. Gruber, D. Zim, G. Ebeling, A. L. Monteiro, *J. Dupont, Org. Lett.*, 2000, **2**, 287.
- [118] T. Fukuda, T. Kutsuki, *Synlett.*, 1995, 825.
- [119] K. N. Venugopala, B. S. Jayashree, *Indian Journal of Heterocyclic Chemistry*, 2003, **2**, 307.

- [120] S. Malladi, A. M. Isloor, S. Isloor, D. S. Akhila, *Arabian Journal of Chemistry*, 2013, **6**, 335.
- [121] H. H. Essa, F. Kandil, A. Falah, *Iraqi Journal of Science*, 2012, **53**, 230.
- [122] E. Ispir, S. Toroglu, A. Kayraldiz, *Transition Met. Chem.*, 2008, **33**, 953.
- [123] K. V. Sashidhara, J. N. Rosaiah, G. Bhatia, J. K. Saxena, *Eur. J. Med. Chem.*, 2008, **43**, 2592.
- [124] Nithinchandra, B. Kalluraya, S. Aamir, A. R. Shabaraya, *Eur. J. Med. Chem.*, 2012, **54**, 597.
- [125] B. S. Creaven, B. Duff, D. A. Egan, *Inorg. Chim. Acta*, 2010, **363**, 4048.
- [126] S. Dhanya, A. M. Isloor, P. Shetty, P. G. Nayak, K. S. R. Pai, *Arabian Journal of Chemistry*, 2010.
- [127] L. J. K. Boerner, J. M. Zaleski, *Curr. Opin. Chem. Biol.*, 2005, **9**, 135.
- [128] P. Mendu, C. G. Kumari, R. Ragi, *J. of Fluoresc.*, 2015, **25**, 369.
- [129] M. A. Phaniband, S. D. Dhumwad, S. R. Pattan, *Med. Chem. Res.*, 2011, **20**, 493.
- [130] S. A. Patila, V. H. Naika, A. D. Kulkarnia, P. S. Badamib, *Spectrochim. Acta Part A: Mol. Biomol. Spectrosc.*, 2010, **75**, 347.
- [131] V. C. da Silveiraa, J. S. Luzb, C. C. Oliveirab, I. Grazianic, M. R. Cirioloc, A. M. da Costa Ferreiraa, *J. Inorg. Biochem.*, 2008, **102**, 1090.
- [132] M. A. Neelakantana, F. Rusalraja, J. Dharmarajaa, S. Johnsonrajaa, T. Jeyakumarb, M. S. Pillai, *Spectrochim. Acta Part A: Mol. Biomol. Spectrosc.*, 2008, **71**, 1599.
- [133] F. Reinitzer, *Monatsch. Chem.*, 1888, **9**, 421; for English translation see *Liq. Cryst.*, 1989, **5**, 7.
- [134] O. Lehmann, *Z. Phys. Chem.*, 1889, **4**, 462.
- [135] D. Vorländer, *Kristallinisch-Flussige Substanzen*, Enke, Stuttgart, Germany, 1908.
- [136] D. Vorländer, *Ber. Dtsch. Chem. Ges.*, 1907, **40**, 1970.
- [137] G. Friedel, *Ann. Phys.*, 1922, **18**, 273.
- [138] G. W. Gray, *Molecular Structure and the Properties of Liquid Crystals*, Academic Press, London, U.K., 1962.
- [139] C. Tschierske, *Curr. Opin. Colloid Interface Sci.*, 2002, **7**, 355.
- [140] S. Kumar, *Chemistry of Discotic Liquid Crystals: From Monomers to Polymers*, CRC Press, Taylor & Francis Group, 2011.

- [141] D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess, V. Vill, *Handbook of Liquid Crystals, Vol. 2 A: Low Molecular Weight Liquid Crystals I*; Wiley-VCH: Weinheim, 1998, pp.4.
- [142] P. G. de Gennes, *The Physics of Liquid Crystals*, Oxford University Press, Oxford, 1974.
- [143] H. S. Kitzerow, C. Bahr, *Chirality in Liquid Crystal*; Springer: New York, 2001.
- [144] I. Dierking, *Textures of Liquid Crystals*; Wiley-VCH: Weinheim, 2003.
- [145] R. W. Date, E. F. Iglesias, K. E. Rowe, J. M. Elliott, D. W. Bruce, *Dalton Trans.*, 2003, 1914.
- [146] S. Chandrasekhar, B. K. Sadashiva, K. A. Suresh, *Pramana*, 1977, **9**, 471.
- [147] B. Donnio, D. Guillon, R. Deschenaux, D. W. Bruce, In *Comprehensive Coordination Chemistry II*, Vol. 7, J. A. McCleverty, T. J. Meyer, (eds.), Elsevier, Oxford, U.K., 2003, pp. 357–627.
- [148] A. N. Cammidge, R. J. Bushby, In *Handbook of Liquid Crystals*, Vol. 2B, D. Demus, J. Goodby, G. W. Gray, H. W. Spiess, V. Vill, (eds.), Wiley-VCH, Weinheim, Germany, Chap. VII, 1998, pp. 693–748.
- [149] H. K. Bisoyi, S. Kumar, *Chem. Soc. Rev.*, 2010, **39**, 264–285.
- [150] K. Praefcke, In *Physical Properties of Liquid Crystals: Nematics*, D. A. Dunmur, A. Fukuda, G. R. Luckhurst, (eds.), INSPEC, London, U.K., 2001, pp. 17–35.
- [151] M. Langner, K. Praefcke, D. Kruerke, G. J. Heppke, *Mater. Chem.*, 1995, **5**, 693.
- [152] A. Grafe, D. Janietz, T. Frese, J. H. Wendorff, *Chem. Mater.*, 2005, **17**, 4979.
- [153] P. H. J. Kouwer, W. F. Jager, W. J. Mijs, S. J. Picken, *Macromolecules*, 2002, **35**, 4322.
- [154] B. Alameddine, O. F. Aebischer, W. Amrein, B. Donnio, R. Deschenaux, D. Guillon, C. Savary, D. Scanu, O. Scheidegger, T. A. Jenny, *Chem. Mater.*, 2005, **17**, 4798.
- [155] S. Laschat, A. Baro, N. Steinke, F. Giesselmann, C. Hägele, G. Scalia, R. Judele, E. Kapatsina, S. Sauer, A. Schreivogel, M. Tosoni, *Angew. Chem. Int. Ed.*, 2007, **46**, 4832.
- [156] F. Morale, R. W. Date, D. Guillon, D. W. Bruce, R. L. Finn, C. Wilson, A. J. Blake, M. Schroder, B. Donnio, *Chem. Eur. J.*, 2003, **9**, 2484.
- [157] S. K. Prasad, D. S. S. Rao, S. Chandrasekhar, S. Kumar, *Mol. Cryst. Liq. Cryst.*, 2003, **396**, 121.
- [158] E. Fontes, P. A. Heiney, W. H. de Jeu, *Phys. Rev. Lett.*, 1988, **61**, 1202.
- [159] I. G. Voigt-Martin, R. W. Garbella, M. Schumacher, *Liq. Cryst.*, 1994, **17**, 775.

- [160] R. Ziessel, L. Douce, A. El-Ghayoury, A. Harriman, A. Skoulios, *Angew. Chem. Int. Ed.*, 2000, **39**, 1489.
- [161] T. Yasuda, H. Ooi, J. Morita, Y. Akama, K. Minoura, M. Funahashi, T. Shimomura, T. Kato, *Adv. Funct. Mater.*, 2009, **19**, 411–419.
- [162] K. Fuchs, E. E. Katscher, *Ber. Dtsch. Chem. Ges.*, 1929, **62**, 2381.
- [163] D. Vorländer, A. Apel, *Ber. Dtsch. Chem. Ges.*, 1932, **65**, 1101.
- [164] T. Niori, T. Sekine, J. Watanabe, T. Furukawa, H. Takezoe, *J. Mater. Chem.*, 1996, **6**, 1231.
- [165] H. Takezoe, Y. Takanishi, *Jpn. J. Appl. Phys.*, 2006, **45**, 597.
- [166] N. Gimeno, I. Pintre, M. Martínez-Abadía, J. L. Serrano, M. B. Ros, *RSC Adv.*, 2014, **4**, 19694.
- [167] S. Kumar, A. N. Gowda, *Liquid Crystals Reviews*, 2015, **3**, 99.
- [168] B. R. Acharya, A. Primak, S. Kumar, *Phys. Rev. Lett.*, 2004, **92**, 145506.
- [169] G. R. Luckhurst, *Angew. Chem. Int. Ed.* 2005, **44**, 2834.
- [170] Q. Li Y. Zhang, *Electric- and Light-Responsive Bent-Core Liquid Crystals: From Molecular Architecture and Supramolecular Nanostructures to Applications, In Intelligent Stimuli-Responsive Materials: From Well-Defined Nanostructures to Applications*, Chapter 6 (ed Q. Li), John Wiley & Sons, Inc., Hoboken, NJ, USA, 2013. doi: 10.1002/9781118680469.
- [171] R. W. Date, E.F. Iglesias, K. F. Rowe, J. M. Elliott, D. W. Bruce, *Dalton Trans.*, 2003, 1914.
- [172] A. M. Giroud-Godquin, P. M. Maitlis, *Angew. Chem. Int. Ed.*, 1991, **30**, 375.
- [173] J.-H. Lee, S.-M. Choi, B. D. Pate, M. H. Chisholm, Y.-S. Han, *J. Mater. Chem.*, 2006, **16**, 2785.
- [174] E. Cavero, S. Uriel, P. Romero, J.L. Serrano, R. Giménez, *J. Am. Chem. Soc.*, 2007, **129**, 11608.
- [175] E. Terazzi, S. Suarez, S. Torelli, H. Nozary, D. Imbert, O. Mamula, J. P. Rivera, E. Guillet, J. M. Benech, G. Bernardinelli, R. Scopelliti, B. Donnio, D. Guillon, J. C. G. Bünzli, C. Piguet, *Adv. Funct. Mater.*, 2006, **16**, 157.
- [176] J. L. Serrano, *Metallomesogens: Synthesis, Properties, and Applications*, (VCH, Weinheim), 1996.

- [177] E. Terazzi, S. Torelli, G. Bernardinelli, J. P. Rivera, J. M. Benech, C. Bourgoigne, B. Donnio, D. Guillon, D. Imbert, J. C. G. Bünzli, A. Pinto, D. Jeannerat, C. Piguet, *J. Am. Chem. Soc.*, 2005, **127**, 888.
- [178] S. A. Hudson, P. M. Maitlis, *Chem. Rev.*, 1993, **93**, 861.
- [179] D. Vorländer, *Ber. Dtsch. Chem. Ges.*, 1910, **43**, 3120.
- [180] D. Vorländer, *Z. Phys. Chem. Stoechiom. Verwandtschaftsl.*, 1923, **105**, 211.
- [181] J. Malthête, J. Billard, *Mol. Cryst. Liq. Cryst.*, 1976, **34**, 117.
- [182] A.-M. Giroud, U. T. Müller-Westerhoff, *Mol. Cryst. Liq. Cryst.*, 1977, **41**, 11.
- [183] I. V. Ovchinnikov, Y. G. Galyametdinov, G. I. Ivanova, L. M. Yagfarova, *Dokl. Akad. Nauk. SSSR*, 1984, **276**, 126.
- [184] B. J. Bulkin, R. K. Rose, A. Santoro, *Mol. Cryst. Liq. Cryst.*, 1977, **43**, 53.
- [185] K. Ohta, G. J. Jiang, M. Yokoyama, S. Kusabayashi, H. Mikawa, *Mol. Cryst. Liq. Cryst.*, 1981, **66**, 283.
- [186] K. Ohta, G. J. Jiang, M. Yokoyama, S. Kusabayashi, H. Mikawa, *Mol. Cryst. Liq. Cryst.*, 1981, **69**, 131.
- [187] K. Ohta, M. Yokoyama, H. Mikawa, *Mol. Cryst. Liq. Cryst.*, 1981, **73**, 205.
- [188] K. Ohta, M. Yokoyama, S. Kusabayashi, H. Mikawa, *J. Chem. Soc. Chem. Commun.*, 1980, 392.
- [189] H. Zheng, B. Xu, T. M. Swager, *Chem. Mater.*, 1996, **8**, 907.
- [190] C.-W. Chien, K.-T. Liu, C. K. Lai, *J. Mater. Chem.*, 2003, **13**, 1588.
- [191] J.-Q. Jiang, Z.-R. Shen, J. Lu, P.-F. Fu, Y. Lin, H.-D. Tang, H.-W. Gu, J. Sun, P. Xie, R.-B. Zhang, *Adv. Mater.*, 2004, **16**, 1534.
- [192] J. Szydłowska, A. Krówczynski, U. Pietrasik, A. Rogowska, *Liq. Cryst.*, 2005, **32**, 651.
- [193] J. Barberá, R. Giménez, N. Gimeno, M. Marcos, M. D. C. Pina, J. L. Serrano, *Liq. Cryst.*, 2003, **30**, 651.
- [194] M. Marcos, A. Omenat, J. Barberá, F. Durán, J. L. Serrano, *J. Mater. Chem.*, 2004, **14**, 3321.
- [195] R. W. Date, D. W. Bruce, *Liq. Cryst.*, 2004, **31**, 1435.
- [196] C. R. Bhattacharjee, C. Datta, G. Das, D. Das, P. Mondal, S. K. Prasad, D. S. S. Rao, *Liq. Cryst.*, 2013, **40**, 942.



- [197] Y. Abe, Y. Takagi, M. Nakamura, T. Takeuchi, T. Tanase, M. Yokokawa, H. Mukai, T. Megumi, A. Hachisuga, K. Ohta, *Inorg. Chim. Acta*, 2012, **392**, 254.
- [198] Y. Abe, N. Nakazima, T. Tanase, S. Katano, H. Mukai, K. Ohta, *Mol. Cryst. Liq. Cryst.*, 2007, **466**, 129.
- [199] Y. Abe, K. Nakabayashi, N. Matsukawa, H. Takashima, M. Iida, T. Tanase, M. Sugibayashi, H. Mukai, K. Ohta, *Inorg. Chim. Acta*, 2006, **359**, 3934.
- [200] Y. Abe, H. Akao, Y. Yoshida, H. Takashima, T. Tanase, H. Mukai, K. Ohta, *Inorg. Chim. Acta*, 2006, **359**, 3147.
- [201] A. Ohta, Y. Yamamoto, H. Kamihata, Y. H. Lee, F. Ichikawa, K. Ohta, Y. Abe, N. Hoshino, M. Kojima, S. Hayami, *Inorg. Chem. Commun.*, 2012, **16**, 89.
- [202] R. Paschke, D. Balkow, E. Sinn, *Inorg. Chem.*, 2002, **41**, 1949.
- [203] L. Aiello, M. Ghedini, M. La Deda, D. Pucci, O. Francesconi, *Eur. J. Inorg. Chem.*, 1999, 1367.
- [204] A. Serrette, T. M. Swager, *J. Am. Chem. Soc.*, 1993, **115**, 8879.
- [205] K. Ohta, Y. Morizumi, T. Fujimoto, I. Yamamoto, K. Miyamura, Y. Gohshi, *Mol. Cryst. Liq. Cryst.*, 1992, **214**, 161.
- [206] R. Chico, C. Dominguez, B. Donnio, S. Coco, P. Espinet, *Dalton Trans.*, 2011, **40**, 5977.
- [207] C. Datta, R. Chakrabarty, G. Das, C. R. Bhattacharjee, P. Mondal, *Liq. Cryst.*, 2014, **41**, 541.
- [208] C. R. Bhattacharjee, C. Datta, G. Das, P. Mondal, *Liq. Cryst.*, 2012, **39**, 819.
- [209] C. R. Bhattacharjee, C. Datta, G. Das, R. Chakrabarty, P. Mondal, *Polyhedron*, 2012, **33**, 417.
- [210] C. R. Bhattacharjee, G. Das, P. Mondal, S. K. Prasad, D. S. S. Rao, *Inorg. Chem. Commun.*, 2011, **14**, 606.
- [211] C. R. Bhattacharjee, G. Das, P. Mondal, *Eur. J. Inorg. Chem.*, 2011, 5390.
- [212] C. R. Bhattacharjee, G. Das, P. Mondal, S. K. Prasad, D. S. S. Rao, *Eur. J. Inorg. Chem.*, 2011, 1418.
- [213] C. R. Bhattacharjee, G. Das, P. Mondal, N. V. S. Rao, *Polyhedron*, 2010, **29**, 3089.
- [214] K. Binnemans, K. Lodewyckx, B. Donnio, D. Guillon, *Chem. Eur. J.*, 2002, **8**, 1101.
- [215] K. Binnemans, K. Lodewyckx, *Supramol. Chem.*, 2003, **15**, 485.

- [216] K. Binnemans, K. Lodewyckx, B. Donnio, D. Guillon, *Eur. J. Inorg. Chem.*, 2005, 1506.
- [217] V. Balzani, F. Scandola, *Supramolecular Photochemistry*, Ellis Horwood, Chichester, U.K., 1991.
- [218] V. W.-W. Yam, K. M.-C. Wong, *Chem. Commun.*, 2011, **47**, 11579.
- [219] D. Kumaresan, K. Shankar, S. Vaidya, R. H. Schmehl, *Top. Curr. Chem.*, 2007, **281**, 101.
- [220] B. W. D'Andrade, R. J. Holmes, S. R. Forrest, *Adv. Mater.*, 2004, **16**, 624.
- [221] Y. R. Sun, N. C. Giebink, H. Kanno, B. W. Ma, M. E. Thompson, S. R. Forrest, *Nature*, 2006, **440**, 908.
- [222] R. C. Evans, P. Douglas and C. J. Winscom, *Coord. Chem. Rev.*, 2006, **250**, 2093.
- [223] N. Armaroli, V. Balzani, *Angew. Chem., Int. Ed.*, 2007, **46**, 52.
- [224] J. F. Callan, A. P. de Silva, D. C. Magri, *Tetrahedron*, 2005, **61**, 8551.
- [225] Y. Y. Chia, M. G. Tay, *Dalton Trans.*, 2014, **43**, 13159.
- [226] C. J. Whiteoak, G. Salassa, A. W. Kleij, *Chem. Soc. Rev.*, 2012, **41**, 622.
- [227] G. Yu, Y. Liu, Y. Song, X. Wu, D. Zhu, *Synth. Met.*, 2001, **117**, 211.
- [228] O. Lavastre, I. Illitchev, G. Jegou, P. H. Dixneuf, *J. Am. Chem. Soc.*, 2002, **124**, 5278.
- [229] A. C. W. Leung, J. H. Chong, B. O. Patrick, M. J. MacLachlan, *Macromolecules*, 2003, **36**, 5051.
- [230] C.-M. Che, C.-C. Kwok, S.-W. Lai, A. F. Rausch, W. J. Finkenzeller, N. Zhu, H. Yersin, *Chem.–Eur. J.*, 2010, **16**, 233.
- [231] Z. Guo, W.-L. Tong, M. C. W. Chan, *Chem. Commun.*, 2009, 6189.
- [232] S. J. Wezenberg, E. C. Escudero-Adán, J. Benet-Buchholz, A. W. Kleij, *Org. Lett.*, 2008, **10**, 3311.
- [233] A. E. Vaughn, D. B. Bassil, C. L. Barnes, S. A. Tucker, P. B. Duval, *J. Am. Chem. Soc.*, 2006, **128**, 10656.
- [234] K. Binnemans, *J. Mater. Chem.*, 2009, **19**, 448.
- [235] S. Faulkner, S. J. Pope, B. P. Burton-Pye, *Appl. Spectrosc. Rev.*, 2005, **40**, 1.
- [236] J. Hanna, *Opto-Electron. Rev.*, 2005, **13**, 259.
- [237] M. O'Neill, S.M. Kelly, *Adv. Mater.*, 2003, **15**, 1135.
- [238] F. Vera, J. L. Serrano, T. Sierra, *Chem. Soc. Rev.*, 2009, **38**, 781.

- [239] C. R. Bhattacharjee, G. Das, P. Goswami, P. Mondal, S. K. Prasad, D. S. S. Rao, *Polyhedron*, 2011, **30**, 1040.
- [240] P. Espinet, M. A. Esteruela, L. A. Ore, J. L. Serrano, E. Sola, *Coord. Chem. Rev.*, 1992, **17**, 215.
- [241] D. Pucci, I. Aiello, A. Bellusci, A. Crispini, M. Ghedini, M. L. Deda, *Eur. J. Inorg. Chem.*, 2009, 4274.
- [242] Y. T. Yang, K. Driesen, P. Nockemann, K. Van Hecke, L. Van Meervelt, K. Binnemans, *Chem. Mater.*, 2006, **18**, 3698.