

CHAPTER I

I n t r o d u c t i o n

Liquid crystals represent states of matter intermediate between the crystalline solid and the isotropic liquid. Liquid crystalline phases are referred to as mesophases and a compound which exhibits a mesophase is known as a mesogen. A transition to the mesophase can be brought about by the action of heat on certain compounds or their mixtures (thermotropic mesophases) or by the action of a suitable solvent on some solutes (lyotropic mesophases).

The work carried out and described in this thesis concern thermotropic liquid crystals.

1.1 Thermotropic liquid crystals

In 1988 Reinitzer¹ observed the first thermotropic liquid crystal in cholesteryl benzoate. Since then a wide variety of thermotropic liquid crystals have been synthesised. Thermotropic liquid crystals are generally exhibited by compounds composed of either rod-shaped or disc-shaped molecules; the mesophases obtained by the former are called calamitic liquid crystals and those by the latter as discotic liquid crystals. Mesophases of rod-like molecules are classified broadly into three types: nematic, cholesteric and smectic phases.

1.1.1 Nematic liquid crystal

In this type of liquid crystal the elongated molecules tend to orient approximately parallel to one another. The preferred axis of orientation of the molecules is called the director. Figure 1.1 represents the arrangement of molecules in two dimensions in a nematic phase.

1.1.2 Cholesteric liquid crystal

Cholesteric liquid crystal is almost a nematic type of liquid crystal except that it is composed of optically active molecules which give rise to a helical structure with its

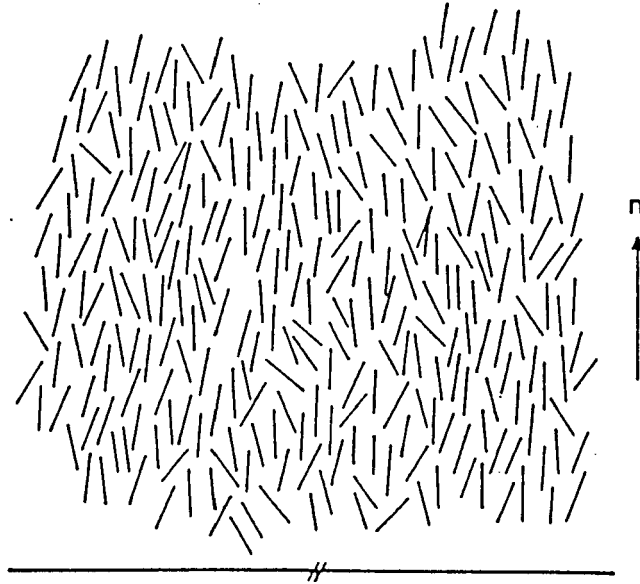


Fig.1.1. Schematic representation of the molecular arrangement in the nematic phase (after Leadbetter³).

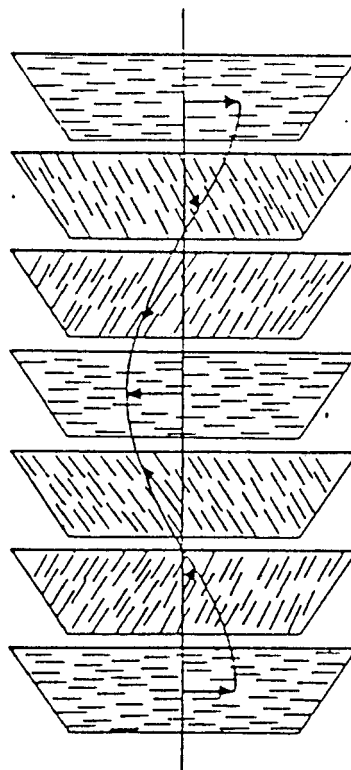


Fig.1.2. Schematic representation of the molecular arrangement in the cholesteric phase (after Chandrasekhar⁴).

twist axis perpendicular to the director. Certain compounds showing the cholesteric phase also exhibit other mesophases called *Blue phases*² between the cholesteric and isotropic phases, over a very small range of temperature. Figure 1.2 represents the arrangement of molecules in the cholesteric phase.

1.1.3 Smectic liquid crystals

Smectic liquid crystals have stratified structures and different kinds of molecular arrangements are possible within these layers. Depending on the molecular arrangement and the extent of interlayer correlation, smectics can be classified into different groups.

Smectic A: In smectic A (S_A) phase the molecules are parallel to the layer normal. The lateral distribution of the molecules within each layer is random. The molecules are able to rotate freely about their long axes within each layer. A schematic drawing of the molecular arrangement in S_A phase is shown in figure 1.3.

Smectic C: In smectic C phase the molecular long axes are tilted with respect to the normal of the layer planes (figure 1.4). The tilt direction is maintained throughout the layers.

If the molecules are chiral then the S_C phase has a helical twist of the director. The tilt precesses around the layer normal. This phase is called chiral smectic C phase or smectic C* phase.

In addition to the smectic A and smectic C phases, there are a few other modifications of the smectic phase. These have been designated as smectic B, D, E, F, G, H and I phases based on the different molecular arrangements as determined by X-ray diffraction studies. The highly ordered orthogonal smectic E phase is exhibited by a few β -diketones described in this thesis. In this phase the molecules have an orthorhombic array within each layer and adopt a herringbone packing which explains the biaxiality of the phase. The molecular arrangement in this phase is schematically shown in figure 1.5. The various phase types of liquid crystalline

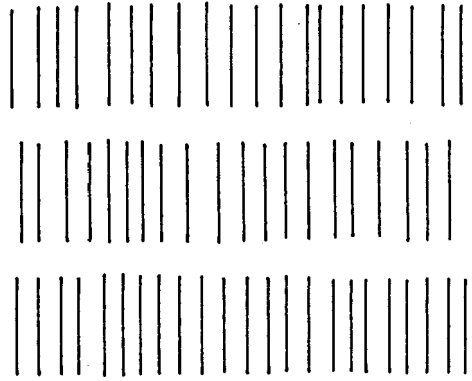


Fig.1.3. Molecular arrangement in the smectic A phase.

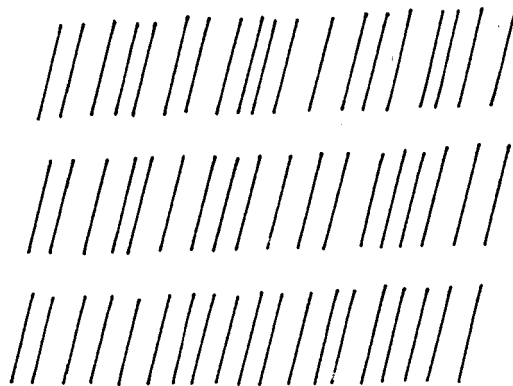


Fig.1.4. Tilted molecular arrangement in the smectic C phase.

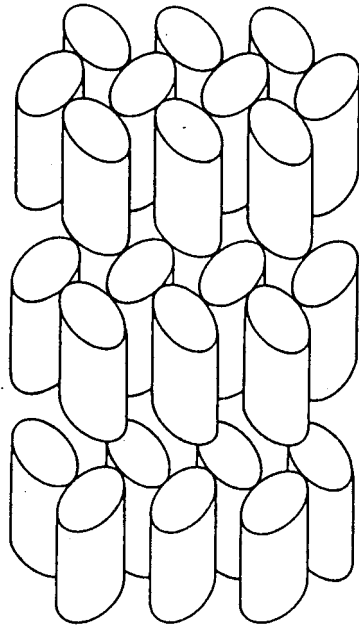


Fig.1.5. Herringbone structure of the smectic E phase (after Gray and Goodby⁵).

phases are summarised in table 1.1.

According to Leadbetter,³ when a structure has long range positional order in three dimensions, it is called a crystal, despite the presence of various other kinds of disorder. These crystal phases possess considerable disorder of molecular orientation and are certainly mesophases, but the nomenclature of these crystal phases can be changed from S_E , S_G , S_H , S_F to just E, G, H, or F phases.

The variants of polymorphism are summarised in table 1.2.

1.2 Discotic liquid crystals

The mesophases exhibited by compounds composed of disc-like molecules are known as discotic liquid crystals. The first discotic liquid crystal was synthesised and identified in this laboratory in 1977 by Chandrasekhar *et al.*⁶ Discotic phases may be classified into two fundamental types: columnar and nematic.

In columnar phases, the molecules are stacked one upon another two form columns which may be arranged in hexagonal, tetragonal, rectangular or tilted arrays. Along the axes of the columns a long range order (designated as D_O) or disorder (designated as D_d) of molecules can exist. No sequence rule has been possible to be derived with respect to the occurrence of the ordered and disordered columnar phases.

The nematic phases are anisotropic fluids with a single order parameter with a tendency to align the disc-shaped molecules parallel to each other. Reentrant behaviour has been observed in many discotic compounds.⁷ Many metal complexes (such as those based on phthalocyanines, porphyrins or even metal β -diketonates) also form discotic mesophases. The different molecular arrangements of discotic liquid crystals have been shown in figure 1.6.

Table 1.1

principal calamitic mesophases (after Leadbetter³)

| | | | | |
|-----------------|--|----------------------------|---|---|
| | Disordered crystal | Liquid crystal | | |
| | Layer structures | Smectic | | Nematic |
| Ordered crystal | Orthogonal: molecules parallel to c, perpendicular to ab plane | E B | Based on weakly coupled ordered layers - 'two- dimensional' systems | Based on one- dimensional density wave (liquid layers) |
| | | | S_B^h | S_A $(S_{A1}, S_{A2}, S_{Ad}, S_{A\sim})$ |
| | | | | N |
| | Tilted: molecules parallel to c, at angle < $\pi/2$ to ab plane | $a > b$ H G $a < b$ K J | S_F | S_C |
| | Cubic structures | | S_I | $(S_{C1}, S_{C2}, S_{Cd}, S_{C\sim})$ |
| | D other | | | |
| | | | | Isotropic liquid |

Table 1.2

Polymorphic variants (after Sackmann³⁷)

| Monomorphic | Dimorphic | Trimorphic |
|---|--|--|
| N | S _A N | S _B S _A N |
| S _A | S _B N | S _C S _A N |
| S _B | S _C N | S _G S _A N |
| S _C | S _G N | S _E S _A N |
| S _E | S _B S _A | S _G S _B N |
| S _I | S _C S _A | S _I S _C N |
| | S _E S _A | S _E S _B S _A |
| | S _G S _C | S _B S _C S _A |
| | S _I S _C | S _E S _C S _A |
| | S _E S _B | S _I S _C S _A |
| | S _G S _I | S _G S _C S _A |
| | S _G S _F | S _G S _B S _A |
| | | S _G S _F S _A |
| | | S _F S _I S _C |
| | | S _G S _I S _C |
| Tetrarnorphic | Pentamorphic | Hexamorphic |
| S _G S _B S _A N | S _G S _B S _C S _A N | S _G S _F S _B S _C S _A N |
| S _E S _B S _A N | S _H S _G S _C S _A N | S _G S _F S _I S _C S _A N |
| S _B S _C S _A N | S _G S _I S _C S _A N | S _K J _I S _C S _A N |
| S _G S _C S _A N | S _G S _F S _C S _A N | S _H S _G S _F S _C S _A N |
| S _I S _C S _A N | S _K J _I S _C N | |
| S _H S _G S _C N | S _G S _F S _I S _C S _A | |
| S _E S _B S _C S _A | S _H S _G S _F S _C S _A | |
| S _G S _B S _C S _A | | |
| S _G S _F S _C S _A | | |
| S _H S _G S _C S _A | | |
| S _G S _I S _C S _A | | |
| S _K S _I S _C N | | |

Temperature

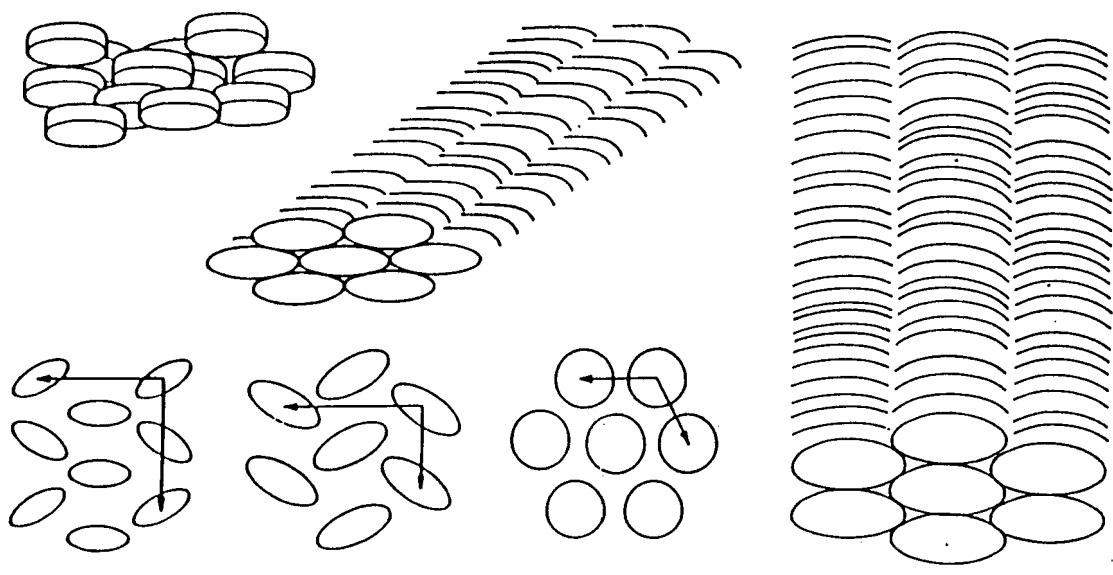


Figure 1.6. Schematic representation of the molecular arrangements in discotic mesophases. (after Chandrasekhar⁴).

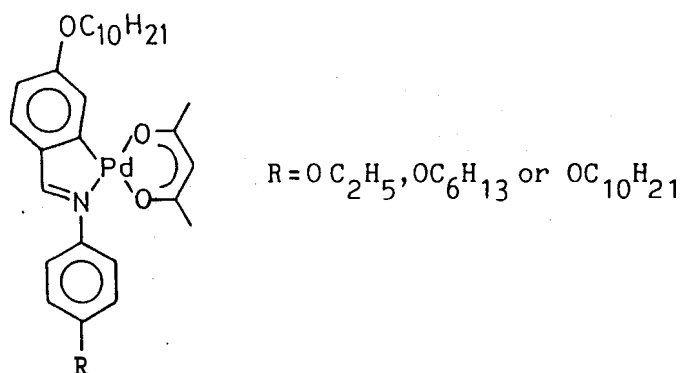
1.3 Metallomesogens

Metal complexes of organic ligands which exhibit liquid crystalline behaviour are known as metallomesogens. Many examples of liquid crystalline metal complexes have been reported over the years and many of these are discussed in the review articles by Giroud-Godquin and Maitlis⁸ and Espinet et al.⁹ The first thermotropic metal containing liquid crystals were reported by Vorlander¹⁰ in 1910. He found that the alkali-metal carboxylates, $R-(CH_2)_nCOONa$ forms classical lamellar phases on heating. Since then many new types of mesogenic metal complexes have been synthesised. It is only in the last decade or so that metal containing liquid crystalline substances are being investigated in greater detail. Giroud and Muller-Westerhoff¹¹ were the first to use *d* block elements to obtain metallomesogens. Many types of ligands can be used to obtain complexes. Metal complexes of β -diketones have been investigated with virtually every metal in the periodic table. Similarly N-salicylideneamine derivatives can also coordinate with various metal ions to yield metal chelates. Monodentate ligands usually tend to give nematic and smectic phases. Varieties of monodentate ligands, such as cyanobiphenyls,¹² n-alkoxystilbazols,¹³ monostilbazoles,¹⁴ distilbazoles,¹⁵ 4-substituted pyridenes,¹⁶ ferrocenes,¹⁷ etc. have been used to obtain metal chelates.

Bidentate ligands such as β -diketones and N-salicylideneamine derivatives exhibit calamitic or discotic mesophases depending upon the number and nature of the substituents. Polydentate ligands such as derivatives^{of} phthalocyanines, porphyrins or annulenes predominantly exhibit discotic phases. However, not all the metal chelates show liquid crystalline behaviour. A majority of complexes with linear, square planar and square pyramidal geometries have so far been found to be mesogenic though a few metalloenesogens with octahedral and tetrahedral geometries have also been reported in the literature.^{18,19} Depending upon the number and/or nature of the substituents these complexes exhibit discotic or calamitic mesophases. In this thesis bidentate ligands such as substituted β -diketones and N-salicylideneamine deriva-

tives have been used to form metal complexes.

In addition to the above, a large number of other metallomesogens are known. Baena et al.²⁰ synthesised a P shaped two-dimensional symmetry perturbed mononuclear palladium complexes of the type shown below and observed that the melting



temperature of the complexes are lower and also exhibit less ordered phases than the free ligands. Octasubstituted phthalocyanines containing copper,²¹ tin,²² zinc,²³ cobalt,²⁴ manganese,²³ nickel,²⁵ lutetium,²⁶ silicon²⁵ and lead^{22,24} are known to show discotic phases. Discotic phases have been reported in a patent²⁷ for a series of substituted dibenzotetra [14] annulenes containing nickel(II), palladium(II), platinum(II), cobalt(II) or copper(II) metal atoms. These complexes have been used in electro- or thermo-optical displays.

1.4 Effect of metal atom on mesomorphic properties of metallomesogens

The geometry of a metal complex depends upon the type of bonding associated with the metal atom. A survey of the literature indicates that metallomesogens can be formed by incorporating alkali metals, alkaline earth metals²⁸ or *d* block elements. Alkali and alkaline earth metals can form bonds with oxygen, nitrogen and carbon atoms to yield metal complexes which are linear. Wide varieties of metallomesogens incorporating *d* block elements are known. For example, mesogenic oxovanadium(IV) and iron(III) complexes have *d*¹ and *d*⁵ electronic configuration respectively in their outermost orbital and show square pyramidal geometry in the

resulting complexes. Electronic configuration of d^8 type generally leads to square planar geometry around the metal atoms. Complexes of Au(II), Pt(II), Pd(II), Ni(II), Ir(I), Rh(I) and Fe(O), etc., have d^8 electronic configuration and square planar geometry. Similarly mesogenic copper(II) complexes with d^9 configuration also exhibit square planar geometry. Very few mesogenic complexes such as those of zinc(II), cadmium(II) and mercury(II) show tetrahedral geometry.

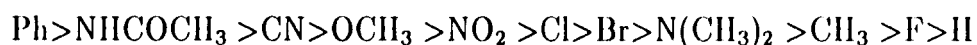
The square planar geometry renders efficient molecular packing and results in metallomesogens with high thermal stability while complexes with square pyramidal and tetrahedral geometries do not pack well and afford either mesophases with low thermal stability or non-mesogenic complexes.

1.5 Effect of substituents on the mesophases

Any terminal group which increases the molecular polarisability without increasing the molecular breadth too much, increases the thermal stability of the resulting mesophase. The terminal group efficiency order which has been compiled²⁹ for smectic phase in rod-like aromatic systems is



and the nematic group efficiency order is



These orders give a broad idea about the probability of obtaining a particular type of mesophase. These orders hold good for metallomesogens also but for some exceptions. For example terminal bromo and fluoro substituents in the ligands afford metal chelates which enhance smectic mesophases and those with methoxy, ethoxy, ethyl and methyl groups exhibit nematic mesophase. However, in complexes bis[1-(4-cyanophenyl)-3-(4''-n-alkylbiphenyl)propane-1,3-dionato]copper(II) and their palladium(II) complexes,³⁰ the terminal cyano substituent which lies high in the nematic

group efficiency order and low in smectic order, promotes a smectic A phase. Substitution of terminal hydrogen atoms by any other group which increases the polarisability without increasing the breadth of the molecule, enhances the thermal stability of the mesophases.

1.6 Trends in homologous series

Generally, a homologous series of compounds is synthesised to examine the trend in the mesomorphic properties. Gray and coworkers³¹ have synthesised a large number of homologous series of calamitic mesogens and found several smooth curve relationships for mesophase-mesophase and mesophase-isotropic transition temperatures. Broadly speaking the following trends are usually observed.

1. The mesophase to isotropic transition temperature usually falls with increasing chain length.
2. When a compound exhibits nematic and smectic phases, usually the thermal stability of smectic phase increases as the chain is lengthened, the lower homologues are purely nematic, the higher ones are purely smectic while the intermediate homologues exhibit both these mesophases.
3. The nematic to isotropic transition temperatures alternate and lie on two smooth curves one for the odd homologues and the other for the even homologues.
4. The trend in the melting points in a homologous series is unpredictable and no generalisation can be made.

These features are also found in some homologous series of compounds incorporated with metal atoms. So far, very few homologous series of compounds containing metal atoms have been synthesised. An examination of these homologous series show a general decrease in nematic to isotropic and smectic A to isotropic transition temperatures as the chain is lengthened.

1.7 Molecular structure and mesomorphic behaviour

While the purely organic mesomorphic compounds contain a rigid core and one or two aliphatic chains, metallomesogens generally consist of an aromatic core and two or more flexible alkyl chains. Metallomesogens may be obtained from either mesogenic or non-mesogenic ligands. In certain cases the complexes obtained show similar phase behaviour as the ligands. This is perhaps due to a very small change in the molecular shape as a result of introduction of a metal atom, as in the case of phthalocyanines.³² Sometimes the complexes obtained from mesogenic or non-mesogenic ligands, exhibit very different mesophases and this is due to considerable difference in the resultant structure of the chelates. In this thesis, all these different types of possibilities have been discussed, viz., formation of mesogenic complexes from mesogenic and non-mesogenic ligands, formation of non-mesogenic complexes from mesogenic ligands, etc.

Mesophase formation in metallomesogens also depends on intermolecular forces. If the intermolecular forces are too strong or too weak, then no mesophases are obtained even if the molecular geometry is right. The mesogenic properties of metal complexes are dominated by ligands and their arrangement, i.e., overall shape of the molecule. Thus, long monodentate ligands tend to give calamitic mesophases, while flat, disc-like polydentate ligands give discotic phases.

1.8 Applications

Liquid crystalline materials have been used for display applications for over two decades. The technology using these materials became successful because of its passive nature which provided the combined characteristics of low power and viewability in bright light. Table 1.3 lists the current applications for liquid crystal displays.³³ Cholesteric liquid crystals exhibit a colour-temperature response mechanism on the molecular scale. This effect has been made use of widely in thermography, i.e., for mapping the surface temperature distribution in operating devices which reveals

Table 1.3

Current applications for liquid crystal displays

*

| | |
|----------------------------------|--------------------------------|
| Analytical Instruments | Jewelry, Assorted |
| Auto Dashboards | Marine Engine Indicators |
| Auto Radios & Clocks | Marine Speedometers |
| Battlefield Computers | Marine Depth Finders |
| Blood Pressure Indicators | Overhead Projector Plates |
| Calculators | Pens |
| Cameras | pH Meters |
| Cash Registers | Photocopy Machines |
| Clock Radios | Point-of-Purchase Displays |
| Digital Pyrometers | Point-of-Sale Terminals |
| Digital Multimeters | Portable Radios |
| Digital Thermometers | Portable Computers |
| Electric Shavers | Portable Word Processors |
| Electronic Billboards | Portable Oscilloscopes |
| Exercise Equipment | Telephones |
| Gasoline Pump Indicators | Toys & Games |
| Hand-Held TV | TV Channel Indicators |
| Hand-Held Terminals | Typewriters, Editing |
| Hand-Held Data Collection | Vacuum Cleaners |
| Heart Monitoring Devices | VCR Channel Indicators |
| Highway Signs | Windometers |
| Household Appliances | Wrist Watches |

* (after Castellano³³)

any hidden structural characteristics by localisation of heat or conduction paths. Cholesteric liquid crystals have also been used in aerodynamics testing, in disposable thermometers as temperature sensors to detect tumors, etc. Ferroelectric liquid crystals have been widely explored for display applications due to its unique properties of bistability, speed, linear response with field, etc.

In addition to these applications, liquid crystals have been used as stationary phases in gas-liquid chromatography and as solvents in nuclear magnetic resonance spectroscopy. They have also been used as solvents in many chemical reactions.

Metal complexes of organic ligands with mesomorphic properties offer new possibilities due to the large, polarisable electron density, which is a feature of almost every metal atom. The reason for introducing a metal atom into a liquid crystal is to generate novel substances for use in molecular electronics, as new electrical or magnetic switches, as electrical conductors and as new optical devices. Mesogenic phthalocyanines are of interest as potential one-dimensional conductors.³² Memming et al.³⁴ used the micelle formation in metallomesogens as a converter of light energy into electrical current with SnO₂ electrodes on which complexes were spread as a monolayer, i.e., a photovoltaic cell. Mesomorphism and thermochromism in metal complexes suggest a possibility of finding applications in imaging devices. Metallomesogens have also been proposed to be used as passive NIR blockers³⁵ in laser addressable or thermal recording materials. The incorporation of alkali metal cations into cholesteric crown ethers causes a change in the helical pitch which can be made the basis of an alkali-metal sensor.³⁶

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