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Liquid Crystals in Advanced Sensing Applications: A Review

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ABSTRACT

This review article covers recent approaches to utilize liquid crystalline (LC) properties in sensory applications. With description of interesting recent researches in the field of LC-sensing, the article shows how the novel synthetic technology, modern fabrication techniques and molecular engineering in liquid crystalline materials leads to the formation of new self-organized soft materials with improved physical properties for modern analytical applications.

KEYWORDS: *liquid crystals, analytical chemistry, chip-based sensors, fabrication technology*

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1. INTRODUCTION

Liquid crystals (LCS) are condensed phase matter whose symmetries lie between those of 3-dimensional periodic crystals and isotropic liquids. The LCS are widely present as organic molecules, micellar solution of surfactants, main and side chain polymers. Many biological systems in nature such as proteins, cell membranes and viruses also show LC phases. The LCS have strong covalent forces that preserve molecular identity and much weaker Van der Waals, short-range exponential interactions that define intermolecular correlations [1,2]. The typical intermolecular energy responsible for the stability of LC phases is comparable to the thermal energy, and thus LCS fall in the category of soft materials. The soft nature of LCS, coupled with anisotropic optical and dielectric properties gives rise to many electro-optic effects at low voltage, which makes LCS useful in cellular phones, notebook computers, navigators, flat-panel TVs etc [3,4]. In recent years the properties LCS are also exploited to design three dimensional displays, flexible organic electronics, organic lighting, the solar cells of the future based on organic photovoltaic semiconductors and sensors for the detection of chemicals and biomolecules [5,6]. The knowledge of structural properties of LC phases is a crucial factor for their application. The commonly used experimental techniques to study the structural properties of LC phases are Polarizing optical microscopy (POM), Differential scanning calorimetry (DSC), Thermo gravimetric analysis (TGA), Differential thermal analysis (DTA), X-ray diffraction (XRD), Raman spectroscopy, Infrared (IR) spectroscopy etc. [7-9].

The unique properties of LCS are polarizability anisotropy and its anisometric shape. The anisometric shape induces the anisotropic intermolecular interactions responsible for the origin of various LC phases. During crystal to mesophase transition, the molecules gain translational as well as rotational freedom and as a result, changes in molecular arrangement, intra/inter molecular interaction and molecular symmetry take place. Raman spectroscopy gives plenty of information about molecular changes during phase transitions [10-12]. The study of density functional theory (DFT) on the other hand gives information about the chemical properties such as; shape, size and conformational changes of the molecule that may be induced in mesophases. In recent years, there have been significant advances in unconventional applications of LCS in chemical and biological sensors [13-15]

1.1. Liquid Crystals

Liquid crystals are the most fascinating state of matters that exhibit intermediate properties between the "fluidity" of conventional liquid and the "order" of solid crystals. The order in a crystal is usually both positional and orientational. Due to positional order the molecules are constrained to occupy specific sites in a lattice and due to orientational order the molecular axes lie in a specific direction. The molecules in liquid, on the other hand, diffuse randomly throughout the sample container with the molecular axes tumbling randomly. The phases with more order than liquid but less order than crystals are called liquid crystalline phases or mesophases. These thermodynamically stable states with symmetry intermediate between that of a crystalline solid and an isotropic liquid, posses many of the mechanical properties of liquids e.g., high fluidity, zero shear modulus and anisotropic optical and magnetic properties of crystals [16-19].

1.1.1. History of Liquid Crystals

In 1850, W. Heintz reported that stearin melted from a solid to a cloudy liquid at 520C, changed to an opaque liquid at 580C, and then to a clear liquid at 620C [20]. Reinitzer, in year 1888, an Austrian botanist, during investigation of synthesized derivative of a cholesteryl benzoate, found that it passes through a viscous and cloudy state between crystalline and liquid phases [21]. German physicist Otto Lehmann observed this material by polarizing optical microscope and found an optical anisotropy as well as fluidity. He named this state as liquid crystal [22]

1.1.2. Classification of Liquid Crystals

Liquid crystals originate due to intra and inter molecular interactions, shape and size of molecules. These molecular interactions can be controlled in two ways: firstly, applying external heat energy which affects the thermal motion of the molecules; secondly, introducing new molecules to change neighbouring interaction environment (or interacting molecules) in a solvent. According to this, LCS are divided into two categories; Thermotropic liquid crystals and Lyotropic liquid crystals (Figure 1.1). Lyotropic LCS phases are formed by amphiphilic molecules of a material in a suitable solvent and thus concentration controls the LC phases in addition to temperature. Thermotropic LCS shows LC phases in certain temperature range. The transition temperature from the crystal to the mesophase is called the melting point, while the transition temperature from the mesophase to the isotropic liquid is called the clearing point. When thermodynamically stable mesophases are obtained both on heating and cooling, the phases are called enantiotropic. If the mesophase is obtained only in cooling cycle, the phases are called monotropic. The different shape and size of molecules pose different internal physical property which is also very important factor for LCS. Depending on shape and size of the molecules, thermotropic LCS are mainly of three types: Calamitic (rodlike), Discotic (disclike) and Bentcore (V -shaped) liquid crystals. In this review, the focus is mostly on calamitic liquid crystals. Other molecular shapes have also been reported to exhibit a variety of LC phases, such as wedge-shaped, T-shaped [23].

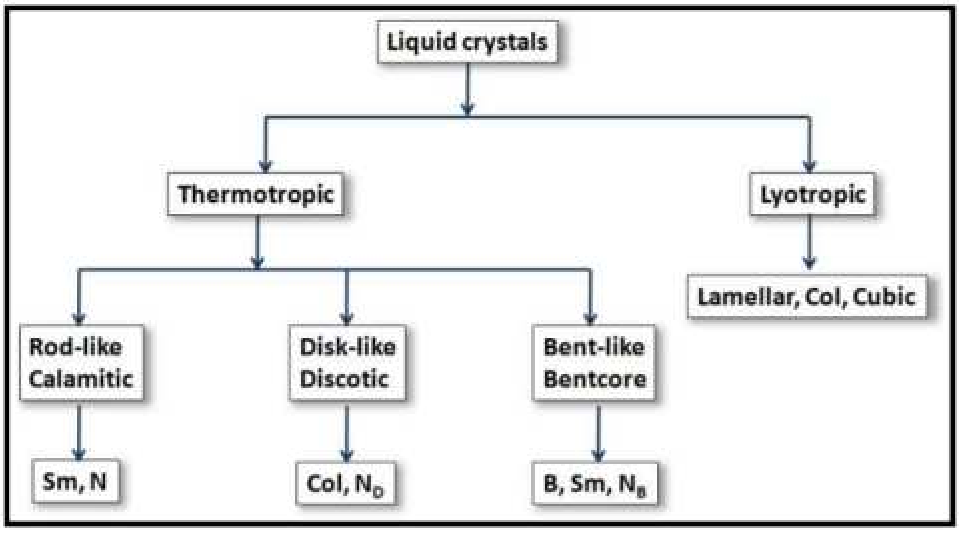

Figure 1.1. Classification of Liquid crystals

1.1.3. Calamitic Liquid Crystals

The different type of LC phases of a mesomorphic system depends fundamentally on the molecular properties of the substance. One of the important factors in the formation of LC phases is an overall strong anisotropy of the molecular shape of the compound. Another factor is the difference in chemical properties of the two distinct moieties that usually form the mesomorphic compound. Calamitic LCS are made up of rod-like molecules. These molecules possess an elongated shape, that is, the molecular length is significantly greater than the molecular breadth. It contains a rigid core and a flexible chain attached to the core. The rigid core produces the anisotropy in the LC system. The core is more often aromatic, but it can also be alicyclic. The linking group between the rings maintains the linearity and polarizability anisotropy of the core. LC molecules require a certain amount of flexibility to stabilize the molecular alignment within the mesophase structure. It is provided by the terminal substituents which are usually straight alkyl or alkoxy chains. The typical chemical structure of these molecules can be represented by the general template, as shown in Figure 1.2. where A and B are core units (benzene, naphthalene, biphenyl, etc.), R and R' are flexible moieties such as normal and/or branched alkyl groups, M and N are generally small lateral substituents (—Cl, —Br, —NO_2, —CH_3, —OCH_3, —CN, etc). Y is a linking group to the core units, and X and Z are linking groups of terminal chains and core units [24]. These moieties give a dual personality to the overall molecule and different parts of the molecular structure interact locally with similar regions of neighbouring molecules causing a type of internal phase separation. The stability of LC phases can be amplified by increasing the lengths or polarizability of the molecules. The length of the hydrocarbon chain at terminal positions of the mesogen plays an important role in determining the phase structure. As a general rule, the compounds having short alkyl chains tend to be nematogens, while those having longer alkyl chains are smectogens [24,25].

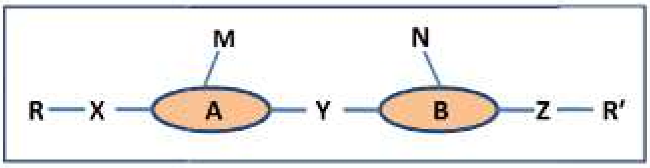

Figure 1.2. General structural template for calamatic liquid crystals.

The nature of the central core, linking groups, and lateral substituents impart significant effect on the mesophase morphology and physical properties of Calamitic LCS. Based on POM observation, Friedel [26] classified the liquid crystal phases into three types; (a) nematic (N), (b) smectic (Sm) and (c) cholesteric (Ch).

A. Nematic Phase

In the nematic phase, the molecules are oriented into a particular direction, but there is no order in the molecular position shown in Figure 1.3(a). This is a one- dimensional ordered phase and the simplest LC phase. To exist in nematic phase, the molecules are required to be free to translate and rotate about their long axis. The preferred direction of orientation of molecules is called director, defined by n. In general, nematic molecules are centro-symmetric; their physical properties are the same in the +n and the -n directions. In other words, if the individual molecules carry a permanent electric dipole, they will assemble in such a way that the bulk dipole moment vanishes. In most nematic phases the molecules are rotationally and orientationally disordered with respect to their short axes, and consequently, the phase is optically uniaxial. However, in some cases particularly for molecules with broad molecular shapes, the degree of rotational freedom of the molecules about their long axes is restricted. This could lead to a preferred macroscopic ordering of the board shaped molecules to give a biaxial nematic phase. Nematics have fluidity similar to that of ordinary (isotropic) liquids but they can be easily aligned by an external magnetic or electric field. An aligned nematic has the optical properties of a uniaxial crystal and this makes them extremely useful in LCD [27].

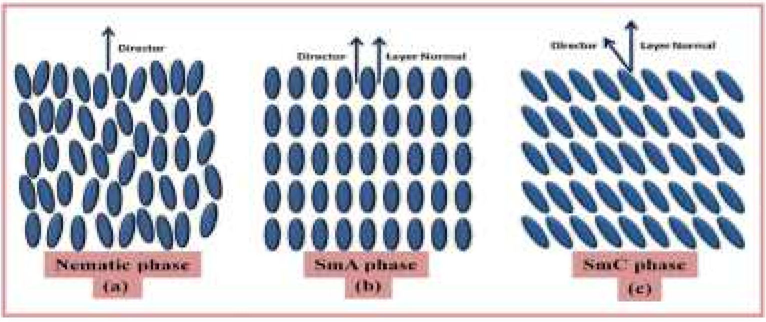

Figure 1.3. Schematic representation of calamitic LC phase; (a) Nematic phase, (b) SmA phase and (c) SmC phases

B. Smectic Phase

In Smectic (Sm) LC phase, ("smectos" comes from the Greek word meaning "clay" or "grease"), the molecules are arranged in a layered structure. The molecules pose short range positional order along with orientational order. The positional order is short ranged within the layer but long ranged between layers. Thus, in the family of smectic phases, the long-range orientational order is preserved and some degree of translational order is present in one dimension where the molecules are arranged on average in equidistant layers. The interlayer interactions are weak compared to the lateral forces between the molecules and the layers are able to slide over one another relatively easily. This property gives rise to fluid property with higher viscosity than nematic phase. Smectic LCS are classified depending on the inclination of the director axis with respect to the layer normal and also on packing of the molecules in the layer. Total number of smectic phase cannot be specified but the following types have been defined: SmA, SmB_{hex}, Smc, SmF, and Sml.

In the SmA phase, the molecules are arranged in layers with their long molecular axis parallel to the layer normal and the phase has uniaxial symmetry as shown in Figure 1.3(b). The axes of orientational and positional order coincide, thus the director is parallel to the smectic layer normal. Typically, the average distance between the layers (usually called smectic layer spacing or layer thickness) is comparable with the molecular length of the compound. Inside the layers, the molecules move like a liquid and there is little correlation among the molecules belonging to adjacent layers.

The SmC phase has the same layer structure of the SmA, but the molecules are tilted with respect to the layer normal shown in Figure 1.3(c). The molecules forming the SmC phase are tilted in a preferred direction inside the layers and the tilt direction of the molecules in various layers is correlated. In this phase too, there is no positional correlation either within the layers or between the layers. Both SmA and SmC phases possess unstructured layers, that is, the layers correspond to that of a two-dimensional (2D) liquid. Smectic B (SmB), smectic F (SmF), and smectic I (Sml) phases are more ordered smectic phases in which the molecules possess hexagonal order within the layers. However, the layers do not possess positional order between them. The molecules in the SmB phase are orthogonal to the layer planes and located at the corners and centers of a network of hexagons. The SmF and Sml phases are tilted analogues of the SmB phase, in which the molecules are tilted toward the side of the hexagonal net and toward the apex of the hexagonal net, respectively. These five phases are true smectic phases and in normal phase sequences would be expected to be found in the increasing order as; I → N → 9 → SA → SC → SF → SB → K[9,17].

C. Cholesteric Phase

When a small quantity of chiral material is added in a nematic LCS, the molecules are oriented in a plane and planes are twisted along a helical axis and this phase is referred as cholesteric or chiral nematic. The twist direction is determined by the chirality of the molecules. It is believed that this is achieved by the chiral dopant creating a chiral environment for all of the other achiral molecules, and hence a helical macrostructure is generated [28]. The pitch of a chiral nematic phase is the distance along the helix over which the director rotates by 3600. The helical structure has the ability to selectively reflect light of a wavelength equal to that of the helical pitch length. The pitch length is dependent on temperature and also colour of the reflected light. This is the basis behind the commercially successful use of chiral nematic materials in thermochromic thermometer devices and other devices that change colour with temperature [28,29].

When the constituent molecules of the SmC phase are chiral, the phase is called SmC* phase. The phase structure is basically the same as SmC phase except that the molecular chirality causes a slight and gradual change in the direction of the molecular tilt. There is no change in the tilt angle with respect to the layer normal. This change in tilt direction from layer to layer gradually describes a helix [28,29].

1.1.4. Discotic Liquid Crystals

Discotic liquid crystal contains usually disc shaped molecules composed of a core based on benzene or triphenylene to which several peripheral groups are attached. Discotic LCS have two basic types of mesophase: columnar and discotic nematic phases. When the crystalline order is lost in one direction (i.e. the system is melted in one dimension), one obtains a periodic stack of discs in columns; such systems are called columnar phases. The different columns constitute a regular 2D array and hence the structure has translational periodicity in two dimensions, but not in three. The Discotic nematic phase, like its Calamitic analogue, is the least ordered mesophase and the least viscous. A smectic like phase is also reported but the precise arrangement of the molecules in each layer is not yet fully understood. In the columnar structures the molecules are stacked upon each other, building columns which may be arranged in hexagonal, rectangular, tetragonal and tilted variants as shown in Figure 1.5 [29,30].

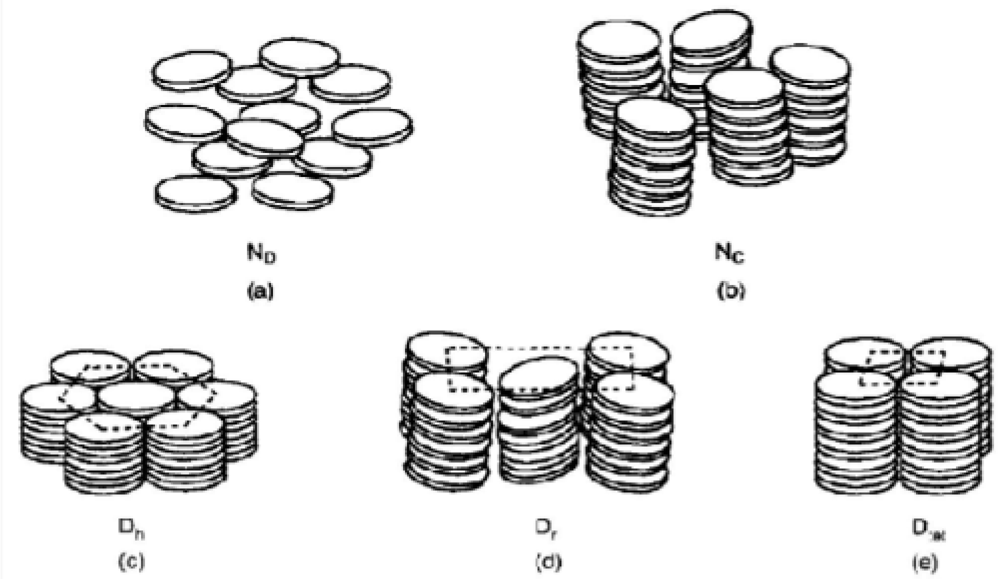

Figure 1.5. Schematic representation of five discotic phases: (a) ND, nematic discotic; (b) Nc, columnar nematic; (c)D_h, discotic hexagonal; (d) D_r, discotic rectangular; (e) D_{tet}, discotic tetragonal.

1.2. Liquid Crystal based Sensor for Chemicals and Biomolecules

The development brought pollution of air, food and water and our environment. The industrial waste product when disposed in open environment and in rivers causes pollution of environment. The water is becoming contaminated with hazardous heavy metal ions and other impurities. Highly sensitive methods of detection of specific chemical compound do exist, but these methods require laboratory-based instrumentation and thus are not suited for measurement of personal exposure. It is necessary to develop an alternative approach to highly sensitive, real-time, affordable chemical and biological monitoring systems that will be broadly useful. Also to understand accumulation and toxicity from environmental exposure, it is necessary to be able to selectively detect a variety of synthetic organic chemicals.

LCS have traditionally been used in displays and other electro-optical devices where the orientation of LCS is manipulated by applying an external electric field to display the information and have become ubiquitous in our daily life. In recent years, there have been significant advances. LCS have been investigated as exquisitely sensitive agents for developing new molecular sensing and detection tools for chemical and biological molecules [31, 32]. The unique and primary advantage of this class of intriguing materials is the perturbation in local ordering LCS by bio/chemical species which can be observed by microscope or even the naked eye [33, 34]. Therefore, it provides a new platform for developing bio/chemical detection and potentially label-free sensing systems. These sensor systems provide a sensor platform with a small footprint (<5mm diameter) for portability, reversible response for real-time monitoring and constant surveillance, direct visual indication or easy integration into optical or electronic reporting systems and easy operation. Fabrication of such detection system is sufficiently simple which may also useful to design wearable personal sensors for exposure to environmental pollutants. This combination of attributes makes LC sensors attractive for a range of applications whose adoption is currently inhibited by the cost or complexity of other technologies.

1.2.1. Interactions of Liquid Crystals with Light

Light is a combination of electric and magnetic fields that are perpendicular to each other. Both fields vibrate in perpendicular planes with respect to the direction of wave propagation. When an unpolarized light enters the polarizer on the left, the light is linearly polarized in the direction indicated by the arrow labelled on the polarizer as shown in Figure 1.7. Next, the polarized light travels through the analyzer, which allows only light waves that are parallel to the analyzer polarization position (labelled on the analyzer) to pass. Since there is no light polarized along the analyzer polarization position, the wave passing through the polarizer is subsequently blocked by the analyzer and no light is observed. The concept of using two polarizers which are oriented at right angles with respect to each other is known as crossed polarization and is the fundamental principle of polarized light microscopy.

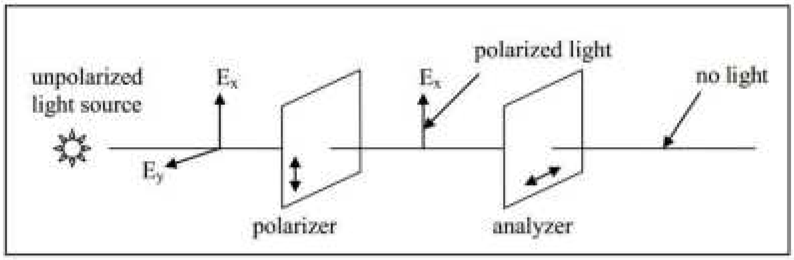

Figure 1.7. The effect of crossed polarizer and analyzer on the incoming light source.

LCS are anisotropic materials and thus the velocity of light polarized parallel and perpendicular to the director of LCS are different. This phenomenon is known as double refraction or birefringence. When LCS are in homeotropic orientations or uniformly planar orientations, all the light emerging from the first polarizer is polarized along one direction. When the emerging light is extinguished by the second polarizer, LCS appear dark under the crossed polarizers. On the other hand, when LCS are in their tilted or randomly planar orientations, the polarized light emerging from the first polarizer can be decomposed into component parallel to the director and component perpendicular to the director which have zero phase differences. When passing through the LCS having a tilted orientation, the two decomposed components propagate at different velocities and get out of phase. Thus, some light will emerge from the second polarizer and shows bright texture.

1.2.2. Orientations of Liquid Crystals at Interfaces

There are many factors which can affect the orientational order of LC molecules at interfaces i.e. solid-LC interface or aqueous-LC interface. When the interface properties are changed, the orientations of interfacial LCS molecules are changed. This minute change of LC orientations can be amplified and causes an orientational transition in the bulk of LCS because LC molecules can communicate their orientations to regions up to one hundred micrometers away [34]. The transition and reorganisation of the LC molecules are accompanied by a change in its optical appearance, which is visible to the naked eye, due to the birefringence of LCS. Generally, there are three main types of LC orientations at interface; homeotropic, homogeneous (planar) and tilted orientations (Figure 1.8). When LCS are oriented homeotropically, the director of LCS is pointing perpendicular to the surface (Figure 1.8a). When LCS are in uniformly planar orientations, the director lies parallel in the plane of the surface and pointing to one direction (Figure 1.8b). There is another condition in which LCS are in randomly planar orientations and the director is pointing to arbitrary directions. In the case of tilted orientations, the director is pointing to one direction to the surface (Figure 1.8c). These orientations of LCS can be disrupted in the presence of foreign molecules at the interface.

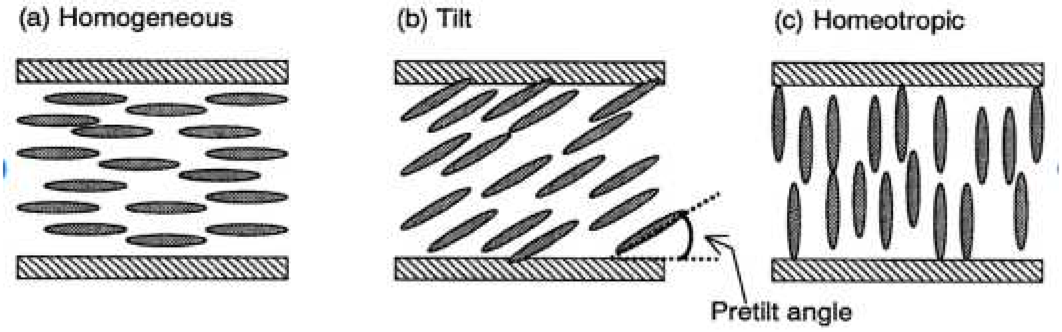

Figure 1.8. Types of orientations of LCS at interface; (a) homogenous, (b) tilted; (c) homeotropic,

N,N-dimethyl-Noctadecyl-3-aminopropyltrimethoxysilyl chloride (DMOAP) and octadecyltrichlorosilane (OTS) were generally used for homeotropic anchoring for LC molecules at solid surface. DMOAP/OTS coated on the solid surface has its long hydrocarbon chain aligned perpendicularly to the surface and thus the LCS anchored on it will be oriented perpendicular to the surface due to hydrophobic interactions between the chain of LC and DMOAP/OTS. For LC sensor system the most frequently used LC is 4-cyano-4'- pentylbiphenyl (5CB), which exhibits liquid crystallinity in the nematic phase at room temperature, a simple and handy choice for constructing optical detectors performed at ambient condition.

1.2.3. Liquid Crystal Sensor at Solid -LC interface

A schematic representation of a solid - LC interface based sensor is shown in Figure 1.9. An LC film is stabilized by the capillary force generated by a spacer of mylar film (6 Vim) or transmission electron microscopy (T EM) Cu/Au grid (20 Yim) between two glass substrate. One slide is chemically or physically modified and the other slide is coated with organosilanes (for homeotropic orientation). The LC molecules orient perpendicular to the substrate (Figure 1.9) by the interaction of LC molecules and the molecule supported on glass substrate. In this orientation, the LC does not change the polarization of incident light transmitted through the film and the LC appears dark when viewed between two crossed polarizers placed on either side of the LC film (Figure 1.9c). Upon exposure of target on the sensor system, target molecule diffuses through the LC film and binds with the molecule supported on the substrate. In doing so, the LCS are displaced from its interaction with the molecule supported on glass and the LC loses its homeotropic orientation (Figures 1.9 (b) and (d)). This orientation of LCS changes the polarization of transmitted light, causing a dark to bright texture in the intensity of light passing through the crossed polarizing system (Figure 1.9 d). The changes in the orientation of LCS due to minor changes in surface energy or in the chemical environment can be easily detected by the simple POM. With this principle, several molecular receptors and their corresponding target analytes have been successfully used to detect organic vapours with high sensitivity [34-47]. For example, metal ions coated on substrate were used to detect organophosphonates [86,87] and carboxylic acids on substrate were used to detect organoamines [35,36]. LCS are also able to interact with surface anchored proteins such as [48-58]. When the concentration of proteins exceeds a certain threshold, the orientations of LCS are disrupted to give a bright optical texture. Else, the LC optical image will remain dark. Kim and co-workers [48] studied the interactions of LCS with single-stranded DNA (ssDNA) immobilized on a solid surface in a direction normal to the surface and found that LCS are orientated homeotropically on ssDNA region. When DNA targets were added, the optical appearance of LCS is changed from dark to bright as the DNA target binds with ssDNA and form double-stranded(dsDNA) which disrupted the homeotropic orientations of LCS. LC based sensor for detection of biomolecules using growth nanoparticle solution also has been reported [59,60].

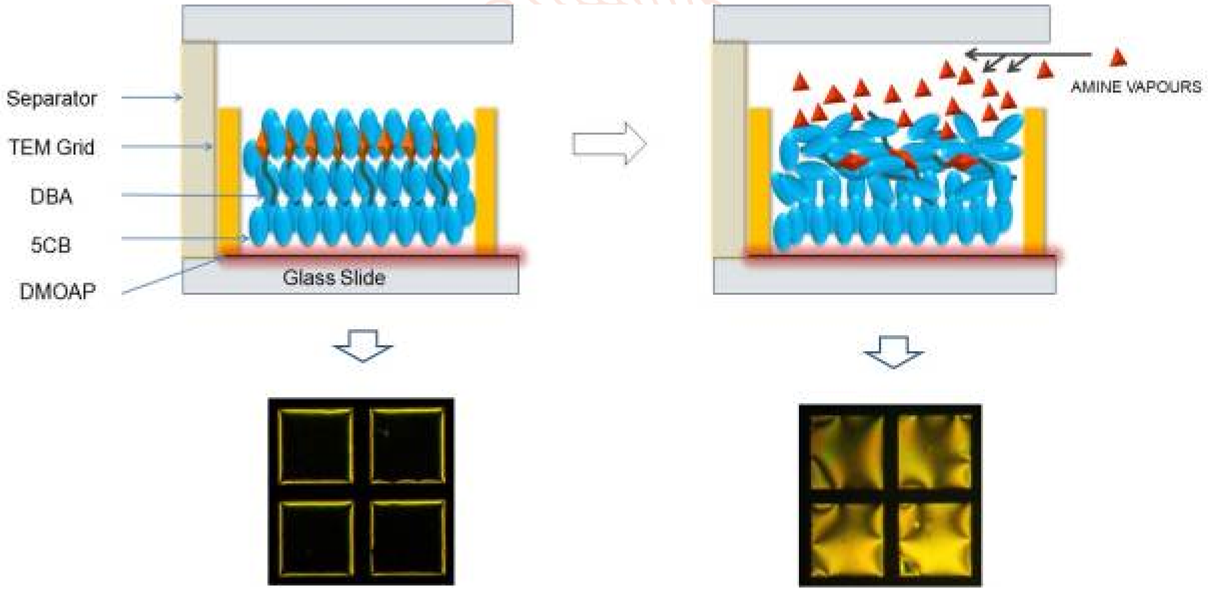

Figure 1.9. Schematic illustration of orientational transitions of the 5CB molecules doped with DBA after exposure of hydrazine vapour into the optical cell from homeotropic orientation to planar/tilted orientation

1.2.4. Biomolecular Sensing at Liquid Crystal—Aqueous Interfaces

Water plays a key role in preserving the structure and functionality of many biomolecules. The interface formed between thermotropic LCS and immiscible water provides new opportunities to create biological sensors based on LCS. The geometry of a typical experiment performed to report biomolecular interactions at the LC—aqueous interface is shown in Figure 1.10 [33]. The LC is hosted in the pores of a TEM grid that is supported on a glass slide coated with a self-assembled monolayer of OTS. Immersion of the LCS filled grid into an aqueous phase lead to the formation of a stable interface between the aqueous phase and LCS (Figure 1.10 A). In the absence of adsorbates at the aqueous—LC interface, many liquid crystals (including nematic 5CB) will assume an orientation that is locally parallel to the interface, giving bright texture (Figure 1.10 B). When the LC is anchored parallel to the interface (planar anchoring), the LC must undergo splay and bend distortions in order to accommodate the competing orientations at the aqueous and supporting solid interfaces (Figure 1.10 E). In addition, interactions between the LC and the vertical surfaces of the confining metallic grid give rise to a radial, inward-directed director profile. When adsorbates (e.g., surfactant) present in aqueous solution, the adsorbates (surfactants) are placed at the LC-aqueous interface due to their amphiphilic nature. Due to the interaction between LCS and adsorbates(surfactants), LCS are oriented normal to the interface (homeotropic anchoring) (Figure 1.10 C). In this configuration the LCS aligned homeotropically at both the LC-aqueous and LC-solid interfaces will experience no variation in orientation across the thickness of the liquid crystal film (Figure I. 10 F). As only one index of refraction of the liquid crystal (the so-called ordinary refractive index) will interact with light transmitted through the liquid crystal, the polarization of the light will be preserved and the liquid crystal will appear dark between crossed polarizers [32,33,61].

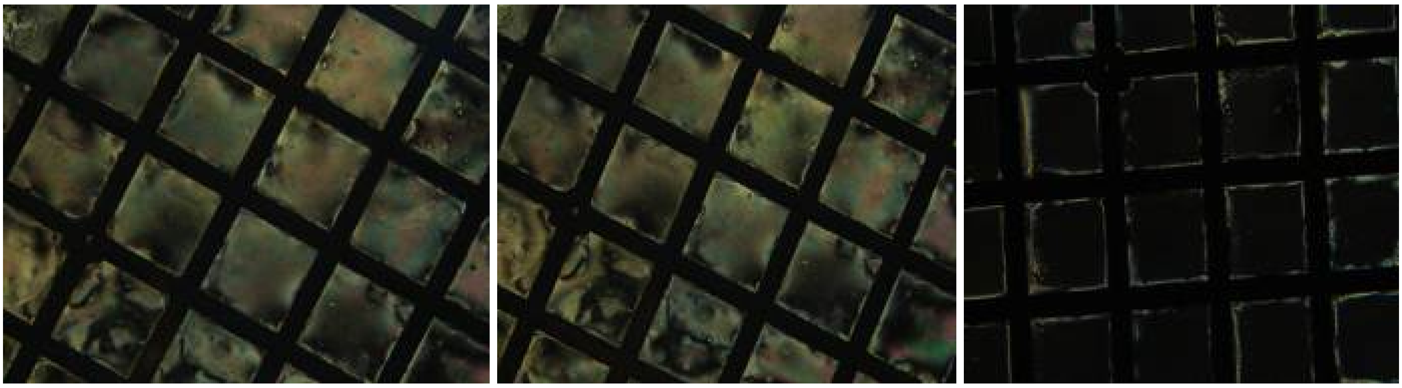

Figure 1.10. Illustration of a LC film hosted in a TEM grid supported on an OTS-treated

Abbott's group studied effects of different surfactants (adsorb at the LC-aqueous interface) on the orientations of LCS [104]. They found that when bolaform structure surfactants are used such as 11 -(hydroxyundecyl)trimethylammonium bromide (H TAB), LCS are oriented in planar orientations due to the loop configuration of surfactants at the interface. However, when other linear surfactants (such as SDS, CT AB) are used, the tilted orientations of these surfactants at the interface cause homeotropic orientations of LCS. These homeotropic orientations induced by linear surfactants depend on the concentration used. When a low concentration of surfactants is used, LCS assume planar orientations because low density of surfactants adsorbed at the interface do not trigger the orientational change of LCS. They also report that the change in the orientations of LCS occurs mainly due to the hydrophobic interactions between LCS and the hydrocarbon tail. Surfactants with short linear hydrocarbon tail groups do not induce an anchoring change, even at concentrations up to their critical micelle concentration. Surfactants with chain lengths of at least about 8-12 carbon atoms are required to induce the anchoring change. The induced transition by the surfactants is insensitive to the nature of the surfactant hydrophilic head group [62-64].

Brake and co-workers reported that contact of an aqueous dispersion of phospholipids solution (in the form of vesicles) with the interface of LCS resulted in the spontaneous formation of a monolayer of lipid at the LC-aqueous interface and an associated homeotropic transition in the LCS [65]. Lin et al. also decorate the aqueous-LC interface with glycolipids [66]. The self-assembly of glyocolipids at the interface with the aliphatic chains anchored in the LCS phase orientate the LCS homeotropically. It has been also shown that amphiphilic polymers at LC-aqueous interface are strongly coupled to the ordering of the LCS, and the presence and organization of these molecules can be reported through changes in the optical appearance of the LCS [67-68]. A series of more complex interfacial phenomena, such as specific binding events involving proteins [69-71], enzymatic reactions [72-75], host guest interaction [76] at LC- aqueous interfaces have shown to trigger dynamic orientational transitions in LCS. LCS based sensor are also able to detect glucose [77-79], urea [80] and hazardous heavy metal ions [81-85].

1.2.5. Liquid crystal based sensors using host guest inclusion complexes:

Cyclodextrins (CD) are cyclic oligosaccharides built up from a-1-4-linked six, seven, or eight D-(+)-glucopyranose subunits referred to as a-, b-, and g- CD respectively [86]. CD comprises of a hydrophobic internal cavity and hydrophilic external surface [87]. Corresponding to their molecular structure and shape, they acquire a unique ability of entrapping guest molecules in their internal cavity. As a result, a host-guest complex is formed between cyclodextrins and guest molecules [88, 89]. Among the mentioned cyclodextrins, b-CD is the most widely used as they are easily accessible due to its appropriate internal cavity diameter and high water-solubility [86]. Industrial discharge are responsible for one of the major environmental pollution problems in the world, because they release undesirable dye effluents (environmentally hazardous contaminants). Industrial wastewater contains dyes mixed with various contaminants at a variety of ranges.

A new air-supported LC system for reporting host–guest inclusion complexation using cyclodextrins as the host molecules was reported [76]. Inclusion of SDS into b-CD disrupted the interaction between LCs and SDS, which allowed the LC to re-orient to its bright planar alignment. On the other hand, when MB was added into the b-CD–SDS solution, the SDS released from the cavity of b-CD interacted with 5CB, which induced an orientational transition of the LCs from a planar to homeotropic state. Thus the host–guest inclusion of MB into b-CD was reported indirectly by using SDS as a probe. This method could be used to judge inclusion events directly for guest molecules that can induce a change in the orientation of LCs. This work demonstrates the development of a simple and cost effective liquid crystal-based imaging tool for real-time reporting of host–guest inclusion complexation events.

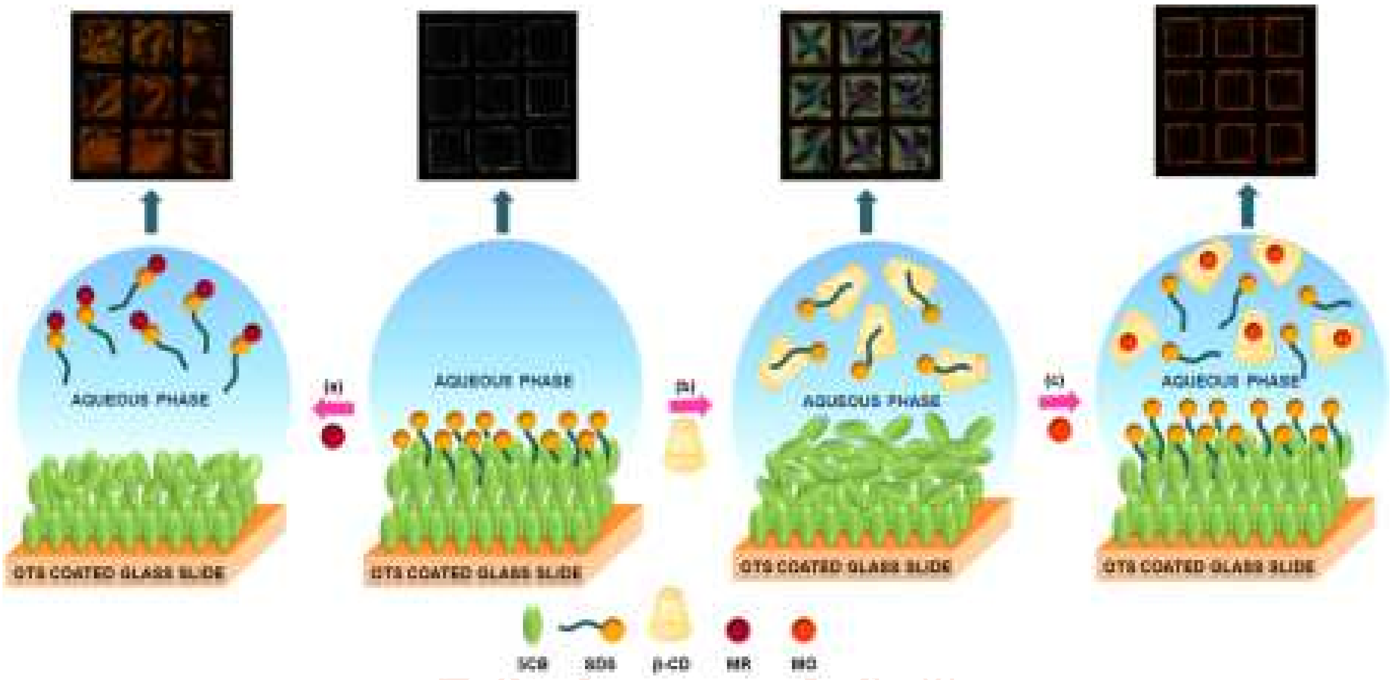

Figure 1.11: Reporting host–guest inclusion complexation using a liquid crystal sensor. Route a: interaction between b-CD and SDS. Route b: interaction between b-CD and MB, using SDS as a probe.

The literature survey presented on mesogenic ligands and their metal complexes reveals that mesogenic ligands and their metal complexes reveals that Synthesis of fairly good number of mesogenic ligands and their metal complexes, their structural characterization based on IR, UV-VIS, NMR, Mass and mesogenic properties studied by polarizing optical microscopy and X-ray diffraction have been reported. Most of the thermotropic mesogens are rod like with rigid cores containing the metal and the ligating atoms and flexible n-alkyl or n-alkoxy tail extending out along the molecular axes. Few attempts have been made towards development of develop LC-based optical sensors for fast, effective and selective detection of HM ions at ultra-trace level in real (natural) water samples via observing changes in phase behaviour of LCs (5CB, E7) at LC/aqueous interface. Thus liquid crystal (LC)-based optical sensors have emerged as alternative frameworks of the conventional sensors due to their simple experimental mechanisms and minimal experimental cost.

The literature also indicates on introduction of b-CD at 5CB/aqueous interface with SDS in aqueous solution, homeotropic to planar transition of LCs was observed as a result of inclusion of hydrophobic tail of SDS into the hydrophobic cavity of b-CD. No attempts has been made towards sensing of HM ions through host-guest inclusion complexes.

Thus in view of above observations, it is thought worthwhile to prepare and characterize amphiphilic surfactant having selectivity and specificity towards particular analyte (HM ions) at LC/aqueous interface via modulation of their structural features. This opens a new field of the LC sensor for fast, precise, and selective detection of metal ions (analytes) of interest with a very low detection limit.

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