ABSTRACT

Liquid Crystals (LC), the captivating materials have gained utmost importance in recent years due to their wide commercial viabilities in various display applications. LC mesogenic phase is an intermediate state of accretion between crystalline solid and amorphous liquid. They are classified as thermotropic LC (temperature dependent) and lyotropic LC (solvent concentration). Friedrich Reinitzer, in the year 1888 first examined the physico-chemical properties of cholesteric liquid crystals. Complementary inter molecular hydrogen bonds are formed between a proton donor and an electron acceptor atoms of carboxylic acids. Moreover, the mesogenic properties of HBLC can be tuned easily by varying the types of bonding, constitution of donor/acceptor moieties and their molar composition. HBLC harvests a greater interest in forming novel liquid crystalline materials due to their ease of expanding the rigid rod segment of individual components. Thus it leads to the inducement of new mesogenic phases, which are not observed in the precursors.

Hence, hydrogen bond is observed to profoundly influence the clearing points, enthalpy values and phase polymorphism exhibited by the mesogens. Considering these arguments, a successful attempt is made in designing, synthesizing and characterizing seventeen intermolecular hydrogen bonded series comprising of 95 complexes, which consists of a variety of chemical constitution including chiral substitution configured on the molecular frame.
Design, synthesis and characterization of HBLC and HBFLC entail novel homologous series with 16 HBLC and 1 HBFLC series. In this work the precursor is either p-n alkyloxy benzoic acids (BAO) or p-n alkyl benzoic acids (BA) mixed with other precursor which may be mesogenic or non mesogenic in nature.

All the complexes synthesized exhibit rich phase polymorphism due to the self-assembled structures produced by intermolecular hydrogen bonding. The interesting orthogonal phases observed during the doctoral studies are N, N\textsubscript{h} and Ch while the other LC phases are observed to exhibit tilted structures.

In order to establish the formation of intermolecular hydrogen bond and to verify the formation of the proposed organic molecule of the synthesized mesogenic complexes, chemical characterization viz., FTIR and NMR techniques have been used out respectively.

Various conventional phases viz., cholesteric (Ch), nematic (N), smectic C (Sm C), smectic F (Sm F) and smectic G (Sm G) exhibited by different homologous series are identified with the standard textures. These textures are recorded, retrieved and analyzed.

Novel smectic orderings viz., smectic X (Sm X) and smectic R (Sm R) have been identified by Polarizing Optical Microscopic (POM) studies. These structures are confirmed by various experimental techniques including Differential Scanning Calorimetry (DSC), optical tilt angle and dielectric measurements. From the data of POM and DSC, the phase diagrams for each of the seventeen HB series are constructed.

Phase transition temperatures and the corresponding enthalpy (\Delta H) values both in heating and cooling cycle are evaluated. From the DSC data,
the phase diagram of the series is constructed. Transitions in DSC thermograms may be classified as monotropic and enantiotropic depending upon their occurrence in heating and cooling cycles. Order of transition exhibited by the individual phases basing the Navard -Cox (N-C) ratio, thermal analysis is elucidated.

Temperature variation of tilt angle $\theta$ (T) reflecting the growth of order parameter in smectic phases is measured by optical extinction method. It is found that the tilt angle increases with decreasing temperature and attains the saturated value. The large magnitudes of the tilt angle observed are attributed to the enhanced orientational disorder introduced by the lengthy flexible part of the molecule. The experimental values are fitted to a power law. It is inferred that Mean Field value of the critical exponent $\beta$ ($\beta = 0.5$) is in good agreement with the value obtained from the experimental results.

When a mesogenic phase such as nematic or cholesteric is subjected to an applied field, there is a change in the textural observation when it exceeds certain threshold value. At a lower threshold value, light modulation is observed and on further increase of the field, optical shuttering is observed.

Light modulation can be used for optical filtering action. In the present work, the initial blue wavelength with no external field has been transformed to red with the application of field. In case of the optical extinction, the observed texture prefer homeotropic like alignment with light being optically extinct. This phenomenon is often referred to as optical extinction of light otherwise known as shuttering action. Thus, these mesogens can be used as ON and OFF states to the application of external field.
Dielectric permittivity ($\varepsilon'$) and dielectric loss ($\varepsilon''$) are studied in various liquid crystalline phases with varying frequency range (5 Hz – 13 MHz). Hence Dielectric dispersion curves and Arrhenius plots are analyzed. For all the complexes the dispersion curves, appear to be asymmetric about $\varepsilon''_{\text{max}}$. Such a non-Debye’s type of off-centered dispersion is analyzed in the wake of Cole-Davidson theory. The yield regarding the distribution parameter ($\alpha$) and the activation energy are interpreted in terms of structure of LC.

Helical pitch is measured with an optical setup comprising of a He-Ne red laser with the help of 10µm liquid crystal cell. The first and second order diffraction patterns are related to the helicoidal structure in smectic phases, viz., smectic C, smectic X and smectic X*. The canal like textures of smectic X* and other LC phase renders the grating element to form the diffraction pattern. The unwinding of helix is measured from the varying radius of the diffraction rings with respect to the temperature.

An optical filter is a device that filters out one or more attributes at its input, from whatever that passes through it. The results obtained from the measurement makes the phase to be utilized as desirable filters depending upon the specific wavelength region.

Spontaneous polarization measurements ($P_s$) are carried out in the chiral phases exhibited by the ferroelectric mesogens. The derived parameters like the response time ($\tau$) and tortional viscosity ($\eta$) are estimated. Field induced phase transition i.e., ($E_1$) is observed in ferroelectric complexes, from which E-T phase diagram is constructed.