ABSTRACT

Liquid crystals are fascinating self–assembled soft materials in which the molecules are orientationally ordered and partially positionally ordered. Liquid crystals easily response to small perturbations like the electric field, magnetic field, surface effect, etc. for which they find applications in diversified fields along with display technology.

At present high definition displays (AMLCDs) with a viewing angle of ~178 degrees are available in the market. Twisted nematic liquid crystals are generally used in such displays. The high value of response time (~ms) governing the frame rate, ghost effect and contrast ratio is still a matter for further improvement. As a result, ferroelectric liquid crystal (FLC) and antiferroelectric liquid crystal (AFLC) draw a special interest from the last decades of the 20th century due to their low response time (μs). But manifold problems were faced in the development of displays based on FLCs. Some of them are small cell spacing (1–2 μm) to unwind the helix, the problem of mechanical shock due to unstable molecular anchoring at the surface, contrast ratio, etc. The AFLCs are promising materials to solve the issues because of their fascinating properties – tristable switching behavior, micro-second order response time, intrinsic analog gray-scale capability, hemispherical viewing angle (in-plane switching geometry) high contrast ratio and no-ghost effect, etc. AFLCs are also interesting for the basic studies in soft condensed matter field as these materials show various sub-phases with distinct macroscopic properties. So enough scope is here for the improvement of the display industry in the coming years with fascinating properties of antiferroelectric liquid crystals.

Physical properties of six antiferroelectric liquid crystals and their three mixtures have been studied in this dissertation using different experimental techniques viz. polarizing optical microscopy, differential scanning calorimetry, synchrotron X-ray diffraction, dielectric spectroscopy, electro-optic study. The first four compounds (**DM0, DM1, DM2, and DM3**) are biphenyl benzoate core-based, in which the number and position of lateral fluorination in the core differ. The first compound DM0 is a core protonated compound but in DM1 one fluorine atom is introduced at ortho position of the benzoate core, while it is introduced at position meta in DM2, but in DM3 fluorine atoms are introduced both at ortho and meta positions of the benzoate core structure. In chapter 3, the effect of lateral fluorination on the mesogenic behaviour of these four compounds is discussed. All the four compounds exhibit Cr–SmC$_A$*–SmC*–SmA*–Iso phase sequence but in different temperature ranges. Due to lateral fluorination, the clearing point decreases in all the fluorinated compounds but the melting point and the stability of SmC$_A$* phase decrease or increase depending upon the position of lateral fluorination. Layer spacings increase in DM1 and DM2 whereas it is found to decrease in DM3. All the compounds show a tricritical nature of SmC*-SmA* transition and orthoconic nature of tilt. They also exhibit very large dielectric increments in SmC* phase but in singly fluorinated DM1 and DM2 its value is less and in doubly fluorinated DM3 it is more than the core protonated compound. Four relaxation modes (P$_L$, P$_H$, GM, and SM) are observed and their critical frequencies are found to decrease in all fluorinated compounds. Domain mode is also observed. Fluorination results in the slower response under a square pulse, of the order of a few hundred microseconds.

Properties of a binary eutectic antiferroelectric mixture, formed mixing 50 wt.% of two pure compounds DM0 and DM3 are discussed in chapter 4. The behaviour of the mixture is not always found to be proportional to the concentration of the protonated and the fluorinated components although it shows the same phase sequence as in the pure compounds but with an increased range of SmC$_A$* phase. In this eutectic mixture also four collective relaxation modes (P$_L$, P$_H$, GM, and SM) are observed and their critical frequencies are found to lie in between the pure compounds. However, P$_L$ and SM critical frequencies are not proportional to the concentration of the pure compounds but for P$_H$ and GM they are almost proportional. The critical field for the suppression of the P$_L$ and Goldstone modes is found to increase significantly. The GM mode dielectric increment decreased substantially. SmC*–SmA* transition temperature (T_c) is found to increase linearly with a bias field and the phenomenon has been explained using the Landau model. Spontaneous polarization is found to be in between those of the pure compounds. Switching time also exhibits similar behaviour and observed to be about a few hundred microseconds.

Motivated by the formulation of the binary eutectic mixture, a room temperature multi-component high tilt antiferroelectric mixture is prepared by mixing DM0, DM1, DM2, and DM3 in equal wt.% and is discussed in chapter 5. The range of SmC$_A$* phase is increased significantly and extended far below room temperature

(~ -8°C to 65 °C), keeping the phase sequence the same as the pure compounds. Some properties of the mixture are found to be equal to the average of the pure compounds. The mixture is of orthoconic nature and SmC*-SmA* transition shows tricritical nature like the pure compounds. Correlation lengths across and within the layers are found to increase from paraelectric to ferroelectric to antiferroelectric phases. Four collective modes *viz.*P_L, P_H, GM and SM and the domain mode are observed. f_{SM} and $\Delta\varepsilon_{SM}$ were found to follow the Curie–Weiss law. T_c is found to increase with bias which was explained using the Landau model. The mixture also exhibits sub-millisecond switching, near the onset of SmC_A* phase.

The key feature behind the compatibility of LCs and CNTs is the highly anisotropic nature of both. In the recent past, few groups studied the CNT composite of ferroelectric liquid crystals (FLCs). But studies on nanocomposites of antiferroelectric liquid crystals are very less. In chapter 6 we have made a comparative study of the dynamic behaviour and electro-optic response of the pure AFLC (DM1) and its MWCNT composite (0.12 wt.%). The phase boundaries are lowered and the stability of the SmA* and the SmC* phases are found to increase but that of SmC_A* phase is decreased. Distinct textural changes are observed in different phases in the nanocomposite. Pitch of the helicoidal structure is found to increase with decreasing temperature in the pure compound in both the tilted phases, the opposite trend is observed in the composite in the SmC* phase. The absolute values and the ranges of the anti-phase antiferroelectric mode critical frequency (f_{PH}) and the absorption strength (ε''_{PH}) are found to decrease in the doped system. In the composite, the dielectric increment ($\Delta\varepsilon_{GM}$) of GM decreases and the critical frequency (f_{GM}) increases and has been explained using generalized Landau theory. The critical field for suppression of the Goldstone mode is increased by 2 times in the composite, signifying the helical structure in the nanocomposite is more stable than in the pure compound. A significant reduction of spontaneous polarization and switching time is observed in the composite. A lower value of conductivity in the composite signifies trapping of impurity ions by the CNTs.

To probe the structure-property relationship further, we have investigated the effect of fluorination in the achiral chain in chapter 7. For this, we have selected two partially fluorinated terphenyl based pure antiferroelectric liquid crystals 4F6T and 6F6T. While the first compound has 4 fluorinated carbon atoms and 6 oligomethelene

spacers, the second one has 6 fluorinated carbon atoms and the same 6 oligomethelene spacers in the achiral chain. Another compound 5F6T, having 5 fluorinated carbon atoms and 6 oligomethelene spacers in the achiral chain, belonging to the above homologous series, was studied and published by our group before, its results are compared with the present compounds for the sake of better understanding of structure-property relations. The molecules of this series structurally differ from the DM series, discussed in Chapter 3, by the number of fluorinated carbon atoms at achiral chain, instead of alkoxy group in the chain carbonyl group is attached here, the core is doubly fluorinated terphenyl based instead of biphenyl benzoate in DM series. Here we discuss the change of properties of these three compounds due to the major change with respect to the biphenyl benzoate core-based series as well as the change of properties of compounds within the series due to the change of the number of fluorinated carbon atom at ahiral chain.

Although all of them exhibited Cr-SmC$_A$*- SmC*-SmA*-Iso phase sequence, the melting point is observed to decrease with increasing achiral chain length but the clearing point shows the opposite trend, range of SmC$_A$* and SmC* phases showed odd-even effect like the molecular dipole moments and spontaneous polarization. Layer spacings, average intermolecular distances and correlation lengths across the smectic planes are also observed to increase with achiral chain length. Like DM series, SmC*-SmA* transition shows tricritical nature. Dielectric increments are found to decrease with increased achiral chain. Both soft mode and Goldstone mode critical frequencies are found to decrease with decreasing temperature in the lower derivative but opposite behaviour is observed in the higher derivative. Both the compounds, however, show Curie–Weiss behaviour in soft mode near T_c. Goldstone mode critical frequency is much higher in 6F6T. Both P$_L$ and P$_H$ modes are observed in SmC$_A$* phase in 6F6T but in 4F6T only P$_H$ is observed and in 5F6T both modes are absent. Optical tilts exhibited orthoconic nature of the SmC$_A$* phase in both the compounds. However, X-ray tilt is much less and the discrepancy has been explained. Both the compounds show sub-millisecond order switching time which is also found to increase with achiral chain length. Antiferroelectric-ferroelectric transition temperature (T_{AF}) is observed to decrease with increasing ac field, effect is more in the higher derivative compared to the lower one. There is an indication of the presence of a *sub-phase* (SmC$_\alpha$*) between SmA* and SmC* phases in 6F6T. These two compounds are expected to be suitable for the preparation of mixtures suitable for display and non-display applications because of their orthoconic nature, sub-millisecond switching time and moderate spontaneous polarization. Thus the number of fluorinated carbon in the achiral part is found to influence the mesogenic properties of various liquid crystalline systems.

Conclusions of all the experimental results have been summarized in Chapter 8.