Thesis Title: Studies on the nematic phases of flexible and rigid bent-core liquid crystals - extension to polymers for energy harvesting applications

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Abstract:

Liquid crystals (LCs) are an indispensable part of our day-to-day life – they are widely regarded as the material for modern-day electro-optic devices and displays. Lower control voltages, high birefringence, and anisotropic properties of LCs make them an excellent candidate for optical and electro-optic devices. Among the vast pool of exotic mesophases offered by LCs (e.g., nematic (N), smectic-A (SmA), smectic-C (SmC), smectic-C* (SmC*), blue phases (BP)), the nematic phase has been proven to be ideal from the application point of view because of its reduced viscosity and more dynamic control over the others. The LC materials used in present-day devices have a rod-like molecular shape, and they are called the calamitic LCs. Over the last few years, a new kind of LCs, called the banana-shaped or bent-core LCs, have gained significant attention owing to their unique and interesting properties, such as polarity, chirality and biaxiality, that are envisaged as the paving stones for the next-generation faster-switching displays. Among these unique features, polarity is regarded as the most important one because it causes a ferroelectric-like behaviour in the nematic phase with sub-millisecond switching. A key method for experimentally realizing this ferroelectric-like polar order is to selectively orient the locally polar, highly ordered microstructures, called the cybotactic clusters, in the nematic phase of bent-core LCs. Also, the nematic phases of bent-core LCs manifest several unusual physical properties, such as, giant flexoelectric response, low-frequency dielectric relaxation, and unusual electro-convection scenarios, which may be related to the presence of cybotactic clusters. Another interesting variant of the nematic phases of bent-core LCs have recently been discovered, called the twist-bend nematic (N_{tb}) phase, which may find applications in tunable diffraction gratings and reflective displays. Moreover, from a structure-property relationship point of view, minute variations in the molecular structure and terminal or lateral substituents may largely affect the resulting LC mesophases of bent-core LCs and their associated properties.

Therefore, the broad aim of the thesis is to investigate the different physical properties of bent-core liquid crystals (LCs), especially in their nematic (N) phases, to develop a better understanding of the underlying ferroelectric nature, the formation of cybotactic clusters, and the influence of various internal and external factors on the formation of these clusters. The field-induced polarization behaviour in the twist-bend nematic phase is also investigated in its pure and nanoparticles doped variants. Towards the end of the thesis, piezoelectric energy harvesting application has been explored by using a lipidated pseudopeptide compound as efficient fillers in the polyvinylidene fluoride (PVDF) polymer matrix, and the potential application of LCs in such energy harvesting devices are also discussed.

The first two chapters of the thesis discuss the basic concepts, classifications, and properties of LCs, piezoelectricity, piezoelectric polymers, and the various experimental methods and techniques used. In the third chapter, we present a comparative study of three achiral, unsymmetrical, four-ring bent-core LC compounds bearing a long alkyloxy chain at one end and differing only in the terminal substituent moiety (-CH_3, -Cl, and NO_2) at the other end. The methyl and chloro substituted compounds manifest a cybotactic nematic phase while the nitro substituted compound shows only a layered smectic phase. Through a detailed experimental investigation, we establish that cybotactic clusters and polar end moieties, although a prerequisite for a ferroelectric-like response, do not necessarily result in a ferroelectric nematic phase. In chapter 4, we focus on the cybotactic clusters of bent-core nematic LCs and investigate the effects of coupling and confinement on the formation of these clusters from a theoretical analogue. We develop a phenomenological model for bent-core nematic LCs in the Landau-de Gennes (LdG) framework and demonstrate that an enhanced coupling invokes augmented formation of clusters in the LC bulk. We also observe that an enhanced coupling promotes a weak nematic-like order above the isotropic supercooling temperature, and that a systematic variation of the boundary conditions do not affect the cluster formation in the bulk. In chapter 5, we investigate the effects of CdSe/ZnS core-shell type spherical quantum-dots (QDs) dispersion on cybotactic clusters of the bent-core nematic LCs. Experimentally, we observe that the incorporation of QDs result in reduced orientational order parameter, reduced cluster size, and increased activation energies. The reduction in cluster size is qualitatively estimated by the collective mode relaxation frequency ratio for the pure and doped LCs. We also complement our experimental observations with a modified, novel LdG-type free-energy for doped systems, built on the premises of our work in chapter 4. It provides validation to our models developed in these two chapters from an experimental viewpoint.

In chapter 6, we turn our attention to the twist-bend nematic phase of bent-core LCs. A flexible core bent-core LC (CB7CB) is studied in its nematic and twist-bend nematic phase in both pure and TiO_2 nanoparticles (NPs) dispersed variant. We observed a threshold-dependent polarization current response in both the phases of pure CB7CB due to field-induced reorientation of cybotactic clusters and the deformation of twist-bend helical structures. The studies in the NPs dispersed variant reveal that the net polarization has competing contributions from both ferroelectric-like and ionic origin (only at lower frequencies), but it becomes dominantly ferroelectric-like at higher frequencies. In chapter 7, we make an attempt to explore energy harvesting applications and discuss the possibilities of LC-assisted dynamic energy harvesting. As a first step, to demonstrate the proof of concept or viability, we use a lipidated pseudopeptide compound as efficient fillers in polyvinylidene fluoride (PVDF) polymer matrix to enhance the net ferroelectric and piezoelectric properties. We also demonstrate its application in mechanical energy harvesting by fabricating superior performing devices in a low-cost and facile fabrication route. Towards the end of this chapter, we briefly discuss the possibility of extension of this work to LCs, especially bent-core LCs with cybotactic clusters, as fillers in the light of their anisotropic nature, ferroelectric, flexoelectric, and piezoelectric properties. This direction will be explored as a promising future scope of the present thesis. The studies reported in this thesis open new avenues to explore bent-core LCs, especially in their nematic phase, from both fundamental and applied research point of view.