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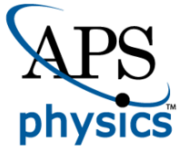


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Flexoelectric Polarization studies in Bent-Core nematic liquid crystals

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The flexoelectric polarization (P_f) of four bent-core nematic LCs has been measured using the pyroelectric effect. Hybrid aligned nematic cells are fabricated for measuring the pyroelectric response over the entire range of the nematic phase. It is found that the magnitude of flexoelectric polarization P_f and the sum of the flexoelectric coefficients $|e_1+e_3|$ for the bent-core LCs studied here are 4-6 times higher than for the calamities. P_f is found to depend on the transverse dipole moment of LC molecules. However $|e_1+e_3|$ values are by no means giant as $|e_3|$ alone had been reported for a bent-core nematic system previously. The dependence of the sum of ‘splay and bend flexoelectric coefficients’ is discussed in terms of the shape of the molecule and of the dipole moment directed normal to the molecular axis.

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I. INTRODUCTION

The bent-core (BC) liquid crystals (LCs) exhibit rich science since these show a wide variety of nematic and smectic phases. The nematic phase of a BC system shows up unusual characteristics and a myriad of interesting properties in addition to those exhibited by the calamitic nematics. Due to a complexity of the phenomena exhibited by BC systems even in their nematic phase, the nature of this phase being debated at present needs to be fully understood for designing a new generation of devices [1]. One of such possibilities is to have devices for energy harvesting, in which case the mechanical energy is converted into electrical one. Flexoelectricity is one of the important properties of these BC nematics. The flexoelectric effect in fluids is somewhat similar to the piezoelectric effect in solids. Piezoelectricity is induced by a positional strain whereas flexoelectricity is due to a curvature strain. The flexoelectric effect has the potential of forming the basis of technologies that rely on the electromechanical coupling. In LCs, bend or splay distortions can create a polarization. The flexoelectric effect was predicted for the first time by Meyer [2] who also gave the expression

for flexoelectric polarization (\mathbf{P}_f) as $\mathbf{P}_f = e_1(\nabla \cdot \mathbf{n})\mathbf{n} + e_3(\nabla \times \mathbf{n}) \times \mathbf{n}$, where, e_1 and e_3 are flexoelectric coefficients corresponding to splay and bend distortions of the director field, respectively. In the direct flexoelectric effect, a gradient of the strain leads to \mathbf{P}_f and in the converse flexoelectric effect, the external electric field E leads to a gradient in the stress curvature and consequently leads to \mathbf{P}_f . Normally in the absence of external perturbations, net \mathbf{P}_f is zero. LC molecules that exhibit a large magnitude of P_f are usually anisotropic in shape and these have usually a large permanent dipole moment directed normal to the long molecular axis. Such molecules are either banana or pear shaped ones.

Several models exist in the literature that describe the contribution of various deformations to \mathbf{P}_f but according to one of the most accepted ones given by Helfrich, the flexoelectric coefficient e_3 due to bend distortions is proportional to the bend angle, the bend elastic constant and the transverse dipole moment (μ_\perp) [3,4]. According to this model $e_3 = \mu_\perp \Theta K_{33} (b/a)^{2/3} N^{1/3} / (2k_B T)$, here K_{33} is the bend elastic constant, Θ is the kink angle between the two arms of the molecule, T is the absolute temperature, k_B is the Boltzmann constant, a and b denote the length and the breadth of the molecule of the mesogen and N is the number density of molecules, *i.e.* $N = \rho N_A / M$, where, M is molecular weight, N_A is Avogadro number and ρ is the density. Even though the phenomenological and the statistical approaches of Helfrich give rise to a magnitude of flexoelectric coefficient ≤ 10 pC/m [5, 6], there are reports that these values could be much higher for specially designed molecules [7,8]. For a typical BC molecule the bent angle is $\sim 60^\circ$ whereas for most calamitic LC molecule it is $\leq 3^\circ$. One might therefore expect larger values of e_3 due to a larger bent angle as well as this may be enhanced by a large transverse dipole moment μ_\perp present in many bent-core systems. The contributions of quadrupolar moments to the flexoelectric polarization was initially discussed by Prost and Marcerou [9] and these have been described as significant for calamitics. Based on the Helfrich model however, the flexoelectric coefficient e_3 for the BC nematics, in principle at least, should be much greater than for calamitic LCs [7].

A mixture of the rod like and BC molecules in the nematic phase has exhibited anomalous trends in the splay (K_{11}) and bend (K_{33}) elastic constants [10-14] and in some cases leads to large flexoelastic ratio $((e_1 - e_3)/K)$ [13]. Recently, bimesogenic materials with large flexoelectric coefficients have been designed. This has allowed the driving voltage for certain types of electro-optic devices to be reduced [4-5, 14], thereby extending their useful operation in many applications. However it is required that measured values of the polarization as well as

the flexoelectric coefficients for a range of BC systems be investigated. Kumar *et al* [15] and Van Le *et al* [16] find magnitude of $|e_3| \sim 4$ pC/m (5K below T_{NI}) and ~ 16 pC/m (5K below T_{NI}) for two differently substituted resorcinol derivatives by electro-optic approaches. Harden *et al* developed a mechanical technique, in which they engineered bent distortions and obtained $|e_3|$ of a BC nematic as ($|e_3|=62000$ pC/m) [7]. This observation though highly desirable in applications has not been independently verified. Measurements have been made on the same as well as on the similar BC systems using different experimental methods [6,16]. The major difference in the approach has been that the other researchers use reverse definition of flexoelectric effect, *i.e.* they study the electro-optical effect of mechanical distortions brought about by the electric field. Nevertheless it had been suggested by de Gennes and Prost [17] that in general for the observations pertaining to the direct effect to remain valid, the compound for investigation must be ‘ultrapure and free of ions’. It is not clear from the work of Harden *et al* [7] whether they took this precaution in their investigations.

Here we present results of the temperature dependencies of P_f and $|e_1+e_3|$ observed in symmetric BC LCs over the entire temperature range of the nematic phase. The method used involves techniques based on the pyroelectric effect [18, 19]. This technique is direct in the sense that distortions created by the alignment (rather those created by the mechanical device is the case of Harden et al [7]) give rise to the flexoelectric polarization and its temperature dependencies. The nematic alignment is distorted by surfaces in this case. The system is calibrated with a known value of the spontaneous polarization (P) of a material at a given temperature. We find relatively large values of P_f and $|e_1+e_3|$ in BC nematics when compared to the classical calamatic ones. Also we discuss their dependencies on the transverse dipole moment of the molecule.

II. EXPERIMENT

The compounds under study are based on 4-cyanoresorcinol bisbenzoate BC LCs synthesized by the Halle group whereas an oxadiazole based BC LC is synthesized by the Moscow group. The basic chemical structures are given in Fig 1. Table 1 lists terminal alkyl chains (R_1, R_2), phase sequence and the phase transition temperatures. Based on the results of x-ray scattering studies, one of the four materials (BC4) has few, if any, clusters present in its nematic phase and behaves quite normally, whereas the others three (BC7, BC7_(OOC) and ODAZ 9) exhibit nematic phase with cybotactic clusters of the smectic C type [1, 20,21].

Figure 1

Table 1

We use a simple pyroelectric technique for the direct measurement of P_f [22]. The key advantage of this experimental technique is that it determines the absolute value of macroscopic flexoelectric polarization in the absence of external field. Also it selects the principal component of the polarization due to the polar ordering without influence of the ions in a LC material contributing to it. The specific ionic conductivity of C4 and C9 LCs, 10°C below the I-N transition are of the order of $2.5 \times 10^{-7} \text{ S.m}^{-1}$, whereas that of the oxadiazole is $5.6 \times 10^{-6} \text{ S.m}^{-1}$ higher by a factor of 20. Experiments were carried out using a stabilised light source of 15 Watts. The source is a halogen lamp, the power supply to which is electronically regulated. Only a fraction of the intensity is incident on the LC cell and the balance is diffused. The intensity of the source is modulated at a frequency of 170 Hz. This frequency is selected so as to avoid a possible interference of the output signal from the harmonics of the mains frequency of 50 Hz. A higher frequency of 170 Hz as opposed to say 120 Hz reduces the response of ions to the alternating signal. Since the pyroelectric signal level is rather weak, the output locked to the frequency of light modulation is measured using a lock-in amplifier.

By definition, the pyroelectric constant in crystallography can be expressed as $\gamma_0 = dP/dT$, where P is the spontaneous polarization of the crystal and T is the temperature. Here we are considering macroscopic polarization P^* instead of P and the corresponding macroscopic pyroelectric coefficient $\gamma = dP^*/dT$. Due to the surface interactions between the ITO substrates and the LC molecule, the magnitude of pyroelectric signal is found not to be completely zero even in the isotropic state. The surface polarization is found to be independent of temperature and is subtracted from the measured value which is calculated by integrating the pyroelectric coefficient over a change in temperature in the limits as below:

$$P^*(T) = \int_{T_i}^T \gamma(T) dT \quad (1)$$

The absolute calibration of the amplitude of the pyroelectric voltage P_v is carried out using a commercial ferroelectric LC mixture, KCFLC10R (Kingston Chemicals Ltd.) with a known value of P^* . The temperature dependent γ was determined from the measured pyroelectric voltage P_v for all materials under study. The pyroelectric responses in planar and homeotropic cell configurations were studied at first. As pyroelectric response from both surfaces of planar and homeotropic cells are equal in magnitude and opposite in direction we cannot therefore find any response from planar or homeotropic cells. Hence we use a Hybrid Aligned Nematic

(HAN) cell in which the director profile through the cell tilts by an angle of approximately 90° from one surface to the next with a large degree of bend and splay distortions occurring in the cell. The indium tin oxide (ITO) coated glass substrates with two opposite surfaces subjected to different surface treatments (homogeneous and homeotropic) have been used to construct a HAN cell. The bottom glass plate is spin coated with RN1175 polymer (Nissan chemicals, Japan) for creating planar alignment of the nematic director. The top ITO substrate is treated with a polymer AL 60702 (JSR Korea) in order to achieve a homeotropic alignment.

III. RESULTS AND DISCUSSIONS

HAN cells (Fig. 2a) are extensively used for measurements of the flexoelectric coefficients in the nematic LCs as the bend and splay distortions produce a flexoelectric field [13, 18,19]. LCs filled in a HAN cell are considered as one dimensional with, $\partial/\partial x = \partial/\partial y = 0$ and the director can be denoted by, $n_x = \hat{X} \cos \theta$, $n_y = 0$ and $n_z = \hat{Z} \sin \theta$. In configuration of a HAN cell, the director is oriented along the normal z to the homeotropic surface with $\theta_d = \pi/2$ at $z=d$ and on the planar surface with $\theta_o = 0$ at $z=0$, the director is oriented along the x axis *i.e.* where d is the layer thickness and θ is the angle between the director and the normal, z to the substrates. In this case,

$$P_x = (-e_1 \sin^2 \theta + e_3 \cos^2 \theta) \frac{d\theta}{dz} \quad (2)$$

$$P_z = \frac{1}{2} (e_1 + e_3) \sin 2\theta \frac{d\theta}{dz} \quad (3)$$

For a constant θ_o and θ_d the z -component of the P_f can be calculated as:

$$P_f = \langle P_f^z \rangle = \frac{1}{d} \int_0^d P_f^z dz = \frac{e_1 + e_3}{4d} (\cos 2\theta_o - \cos 2\theta_d) = \frac{e_1 + e_3}{2d} \quad (4)$$

The total polarization is the sum of flexoelectric polarization P_f , polarization from the planar, P_{sp} and the homeotropic P_{sh} surfaces. The two surface polarizations have not been independently measured. However the measured signal for a given sample is subtracted from that in its isotropic state, this difference signal determines P_f . Figures 2b and 2c show the texture of a HAN cell filled with the LC. The texture a typical texture of a HAN cell is neither too bright nor too dark and it shows a domain boundary as the defect line. These observations were carried out on a 3.4 μm cell filled with BC4 using polarizing optical microscope (Olympus BX 52) equipped with a hot stage and a temperature controller (Eurotherm 2604).

Figure 2

For confirming the validity and the accuracy of the system, we first make measurements on a prototype calamitic liquid crystal 5CB. The contribution of surface polarization from both surfaces of the HAN cell is different. The pyroelectric signal is independent of the direction of irradiation [19]. The pyroelectric coefficient is measured by altering temperature by ΔT a small step in temperature from the light source. The temperature of a cell is varied over the entire temperature range of the nematic phase. We find the magnitude of P_f as ~ 0.04 nC/cm² at 26°C which agrees exactly with the reported in the literature [19]. The dc conductivity of 5CB at this temperature is $\sim 8.85 \times 10^{-8}$ S.m⁻¹. Then we measure P_f of a homologous series of cyanoresorcinol BC compound having transverse dipole moment, $\mu_{\perp} \sim 3.4$ D. Figure 3 shows the temperature dependence of P_f and the corresponding γ for 5CB, BC4 (n=4), BC7 (n=7) and BC7_(OOC) (n=7).

Figure 3

A sharp peak appears in the pyroelectric response which corresponds to the Iso→N transition. Here, P_f rises from zero in the isotropic state to a finite value in the nematic phase. Since e_1 and e_3 in our experiments are not measured separately, the sum of the flexoelectric coefficients $|e_1+e_3|$ is estimated using Eqn.3. Figure 4 gives temperature dependencies of $|e_1+e_3|$. The flexoelectric coefficient of 5CB at 25°C using HAN cells has been reported in the literature as $|e_1-e_3|=25$ pC/m [23] and $|e_1+e_3|=8.4$ pC/m [19]. Here we obtain $|e_1+e_3|=7.7$ pC/m for 5CB at 26°C which is in reasonable agreement with the literature.

Figure 4

A comparison of the results of cyanoresorcinol LCs with 5CB shows that the sum of the flexoelectric coefficients is ~ 6 times larger than for the calamitic shape of the prototype liquid crystal. Although μ_{\perp} is the same for various cyanoresorcinol compounds under study, the temperature range of the nematic phase in each case is different being dependent on the length of the terminal alkyl chain. In these materials, BC7 exhibits nematic phase over a large temperature range of $\sim 62^{\circ}\text{C}$ ($T_{\text{NI}}-T = 62^{\circ}\text{C}$) and even larger $\sim 78^{\circ}\text{C}$ for BC7_(OOC) ($T_{\text{NI}}-T=78^{\circ}\text{C}$). The results for the sum of flexoelectric coefficients for BC4, BC7, and BC7_(OOC) at a reduced temperature are not very different from each other. The material BC7_(OOC) shows $P_f \sim 0.31$ nC/cm² and $|e_1+e_3| \sim 31.6$ pC/m and BC7 shows $P_f \sim 0.22$ nC/cm² and $|e_1+e_3| \sim 19.3$ pC/m. Salter *et al.* reported only the difference of the flexoelectric coefficients $|e_1-e_3|$ in 4-cyanoresorcinol compound as 17 pC/m at 10K below the phase transition temperature [24].

Later Balachandran *et al* used a uniform lying helix technique and determined $|(e_1-e_3)|$ as a function of the reduced temperature for homologues of 4- cyanoresorcinols. They found these values to be lying in the range $\sim 19 - 24.4$ pC/m depending on the reduced temperature [25]. These values are nevertheless much larger than obtained for calamitic LCs. **A sum of the flexoelectric coefficients for the BC systems has not been widely investigated in the literature;** reported as ~ 35 pC/m for one of the bent core systems [15]. One of the main challenges faced in obtaining precise results is to achieve a better homeotropic alignment of a bent-core liquid crystal in a HAN cell. We measure the sum of these coefficients for an oxadiazole systems which do exhibit nematic phase over a wide range of temperatures. These are known to form clusters of various types and these systems have been extensively investigated over recent years using X-rays and N.M.R [26,27]. Figure 5 shows P_f and a corresponding value of the pyroelectric coefficient γ . Results for $|e_1+e_3|$ of ODAZ-9 are obtained as a function of temperature. P_f at 101°C of ODAZ-9 is ~ 0.08 nC/cm² and $|e_1+e_3|$ is ~ 13 pC/m. The temperature dependence of $|e_1-e_3|$ for the oxadiazole based BC compound reported recently shows that these values range from 10 to 15 pC/m across the nematic region [27]. Results are summarized in Table 2.

Figure 5

Table 2

For discussing the dependence of the flexoelectric coefficient on μ_\perp for the systems studied, we have investigated only three sets of liquid crystals. In 5CB $\mu_\perp = 0$, whereas for BC4, BC7 and BC7(OOC), $\mu_\perp = 3.4$ D and for ODAZ $\mu_\perp = 2.3$ D. Results for the BC systems are higher than for calamitic 5CB but among the BC systems themselves, results are not very different from each other. A trend is seen in the dependence of P_f on μ_\perp (column 4, Table 2) however an unambiguous dependence of the flexoelectric coefficient on μ_\perp cannot be ascertained from a limited set of results. The 5.00 ± 0.01 P_f in column 4, Table 2 is dependent on the temperature range of the nematic phase than on the system itself. For ODAZ-9 ($T_{NI}-T=15^\circ\text{C}$), $P_f \sim 0.08$ nC/cm² which is 3 to 4 times lower than for cyanoresorcinol LCs. To compare the results of BC LC materials with 5CB, we choose the magnitudes of P_f and $|e_1+e_3|$ at a temperature 9°C below the Iso-N phase transition.

IV. CONCLUSIONS

In summary, we report the results of P_f and the sum of flexoelectric coefficient $|e_1+e_3|$ for the four different symmetric BC LCs. P_f is measured using a simple pyroelectric technique. HAN cells are constructed to obtain the pyroelectric response which yields P_f over the entire nematic temperature range. X-ray diffraction studies reveal that SmC type clusters are present in BC7, BC7_(OOC) and ODAZ-9 over the entire range of nematic phase but are measurably absent in BC4 [1,21]. The experimental results reveal that P_f and $|e_1+e_3|$ of these BC nematics are 4-6 times larger when compared to calamitics. When we compare the effective flexoelectric polarization of the four BC compounds, P_f is found to be higher for cyanoresorcinol compounds by ~3-4 times than for the oxadiazole *i.e.* the magnitudes of P_f and $|e_1+e_3|$ of LCs are linearly dependent on $T_{NI}-T$ and possibly on the transverse dipole these systems. This may imply that $|e_1| \ll |e_3|$. The flexoelectric polarization of BC LCs continues to be of significant interest since it is higher for the BC systems than for the calamitics and these can be increased by increasing the transverse dipole moment and the angle between the two arms of the molecule.

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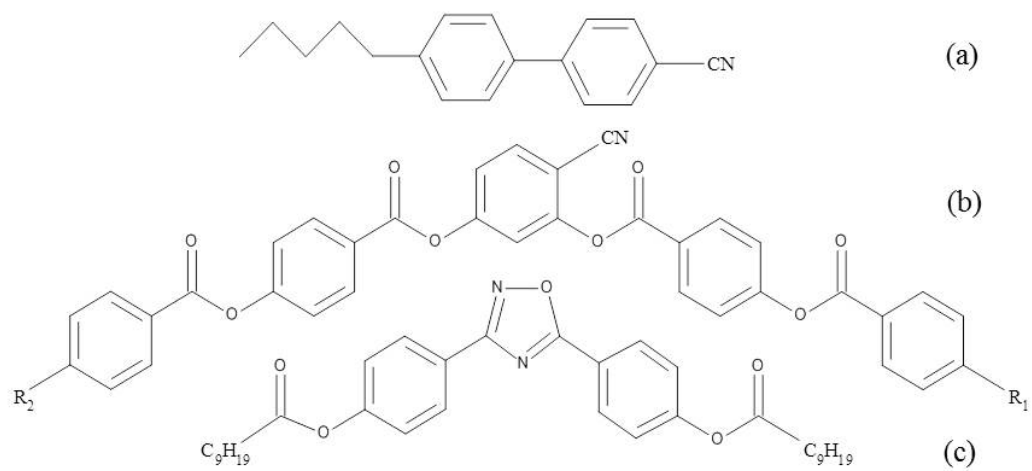


Figure 1

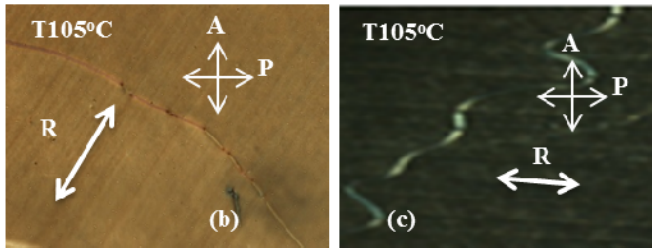
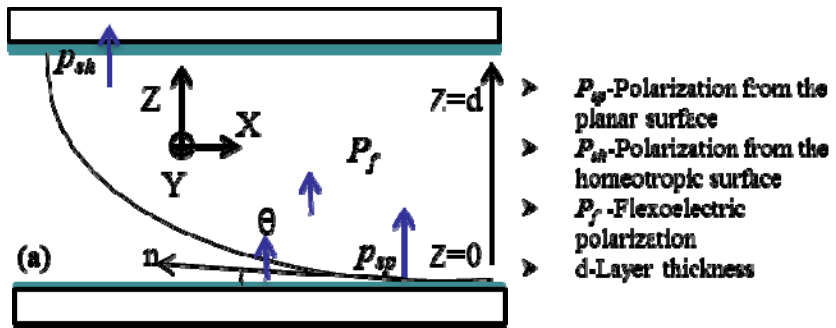


Figure 2

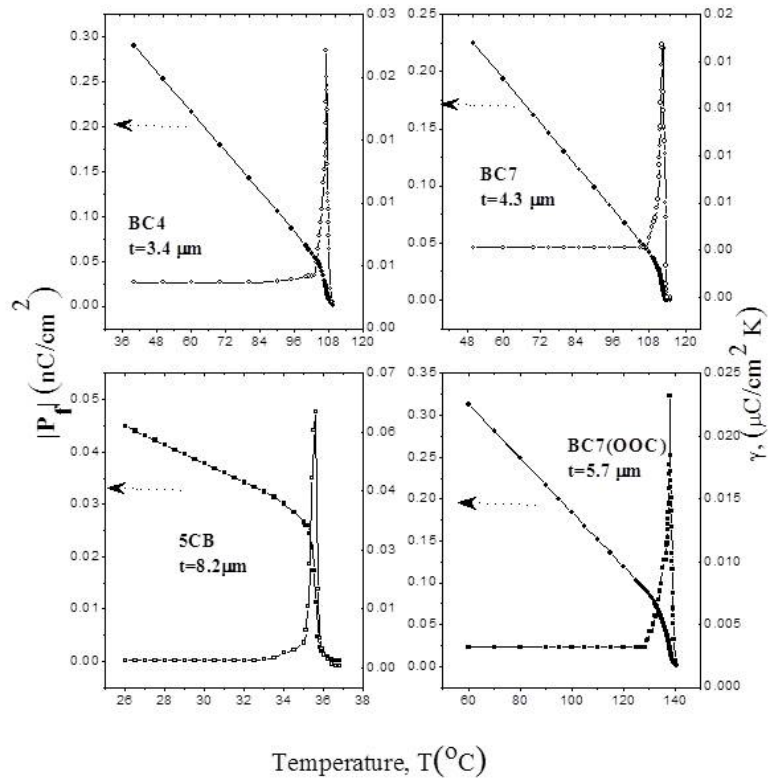


Figure 3

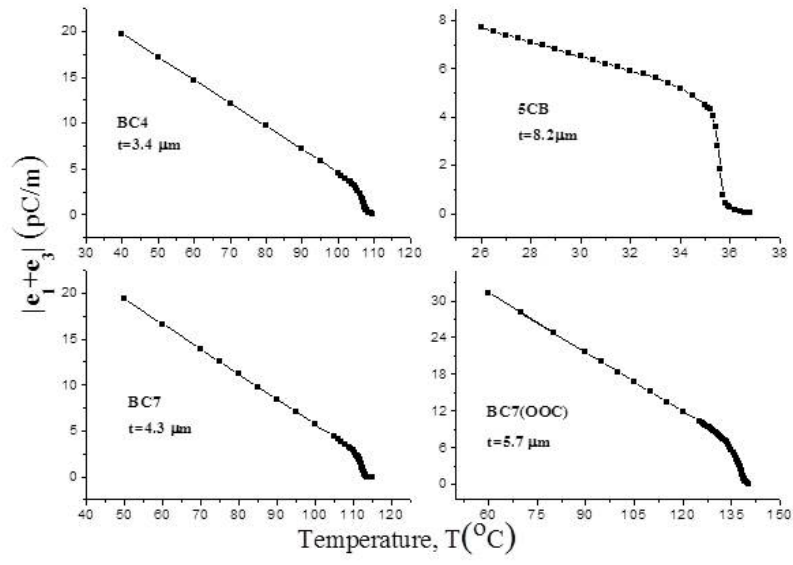


Figure 4

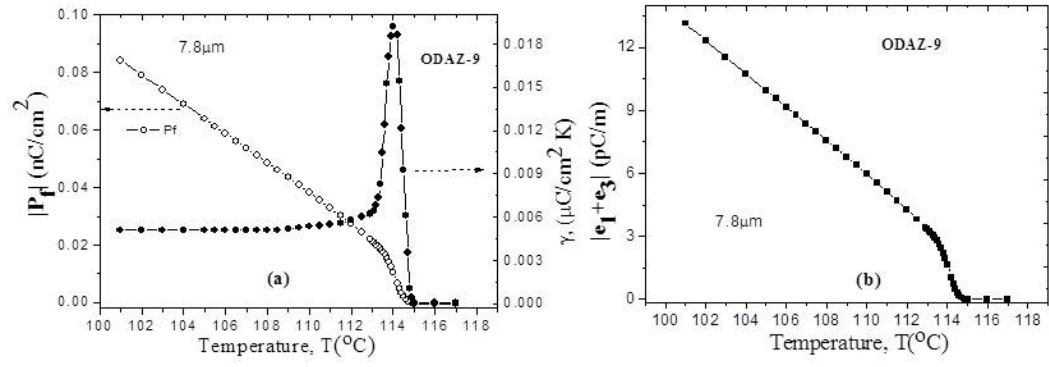


Figure 5

Table 1

Material	R₁and R₂	M.W.	Phase sequence
(1) 5CB	-	253	Cr18°C N 35°C I
(2) BC4	C ₄ H ₉	676	Cr 38°C N 106°C I
(3) BC7	C ₇ H ₁₅	760	Cr 42°C N 111°C I
(4) BC7 _(OOC)	OOCC ₇ H ₁₅	816	Cr 60°C (SmC 83°C)N 138°C I
(5) ODAZ-9	C ₉ H ₁₉	562	Cr 66°C SmA 99°C N114°C I

Table 2

LC Material	μ_{\perp} (D)	$ (e_1+e_3) $ (pC/m)	P_f (nC/cm ²)	$T_{NI}-T$ (°C)	P_f (nC/cm ²) 9°C<T _{NI}
(1) 5CB	0.0	7.7	0.04	9	0.04
(2) BC4	3.4	19.7	0.29	67	0.07
(3) BC7	3.4	19.3	0.22	62	0.06
(4) BC7 _(OOC)	3.4	31.6	0.31	78	0.09
(5) ODAZ-9	2.3	13.0	0.08	15	0.06

Figure Captions:

Figure 1: Molecular structure of (a) 5CB (b) 4-cyanoresorcinol bisbenzoate homologues BC LC and (c) 1, 2, 4-oxadiazole BC LC.

Figure 2: (Color online) (a) The geometry of a HAN cell, (b) and (c) are the polarizing optical textures of the cell at 105°C with the rubbing direction parallel and at an angle of 45° to the polarizer. The domain boundary is shown as a defect line.

Figure 3: Temperature dependence of the flexoelectric polarization, P_f (●) measured by the pyroelectric technique and the corresponding pyroelectric signal, γ (○) of LC materials, 5CB ($t=8.2\mu\text{m}$), BC4 ($n=4$, $t=3.4\mu\text{m}$), BC7 ($n=7$ $t=4.3\mu\text{m}$) and BC7_(OOC) ($R_1=R_2=OOC_7H_{15}$, $t=5.7\mu\text{m}$). Measurements were carried out using HAN cells with the cell thickness given in parenthesis upon cooling process from the isotropic state.

Figure 4: Magnitude of flexoelectric coefficients $|(e_1+e_3)|$ (■) as a function of temperature for various liquid crystals, 5CB ($t=8.2\mu\text{m}$), BC4 ($n=4$, $t=3.4\mu\text{m}$), BC7 ($n=7$ $t=4.3\mu\text{m}$) and BC7_(OOC) ($R=OOC_7H_{15}$, $t=5.7\mu\text{m}$); t is the cell thickness.

Figure 5: Temperature dependence of (a) the P_f (●) measured by the pyroelectric technique and corresponding γ (○) and (b) $|(e_1+e_3)|$ (■) of BCLC material ODAZ-9. Measurements are carried out on a 7.8 μm thick HAN cell while cooling down the sample from the isotropic state.

Table Captions:

Table 1: LC materials and their phase sequences while cooling down from the isotropic state

Table 2: The sum of flexoelectric coefficients, the flexoelectric polarization P_f , transverse dipole moment μ_{\perp} . A range of temperatures from the isotropic–nematic transition to a temperature within the nematic phase of the BC LC materials under study.