

2022

## Spontaneous Symmetry Breaking and Linear Electrooptic Response in the Achiral Ferronematic Compound

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### Recommended Citation

Yadav, N., Panarin, Y. P., Jiang, W., Mehl, G. H., & Vij, J. K. (2022). Spontaneous Symmetry Breaking and Linear Electrooptic Response in the Achiral Ferronematic Compound. Technological University Dublin. DOI: 10.21427/MV4X-YK73

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Funder: Irish Research Council

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# Spontaneous Symmetry Breaking and Linear Electrooptic Response in the Achiral Ferronematic Compound.

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**Abstract:** A compound with the constituent non-chiral molecules, DIO, known to exhibit three nematic subphases namely N, N<sub>X</sub> and N<sub>F</sub>, is studied by polarizing microscopy as function of the alignment layers on one of the substrates, no alignment on any of the substrates, alignment layer on both substrates with parallel and antiparallel rubbing, different cell spacings. The cell with one alignment layer is also studied by electro-optics. N is found to be a conventional nematic phase, but it shows two additional unusual features: chiral domains of opposite chirality and the linear EO response to the applied signal under certain experimental conditions. The emergence of chiral domains is explained by a segregation of the stable helical conformers of the opposite chirality, these preferring to form chiral domains, each with optical rotation power of  $\pm 4^\circ/\mu\text{m}$ . This is the first example of helical segregation observed in non-chiral molecules in the high temperature nematic phase. The conformers are suggested to arise from the rotations of the aromatic rings either left-handed or right-handed. Unlike the ordinary nematic liquid crystalline phase, linear electrooptical response to the applied electric field (i. e. to its fundamental frequency) is observed, this confirms the polar nature of this phase. The N<sub>F</sub> is the ferroelectric nematic as reported previously. The strong polar azimuthal surface interaction energy in N<sub>F</sub> phase stabilizes a homogeneous structure in planar aligned LC cells rubbed parallel and in cell rubbed antiparallel, it gives a twisted structure. The transmission spectra simulated using Berreman's 4 x 4 matrix method for different cell conditions and for different angles between the Polarizer and the Analyzer quantitatively confirm the twisted structures in antiparallel rubbed cells that agree with experimental observations. The twist angle of  $170^\circ$  is found between the directors from the top to the bottom in antiparallel rubbed cells as opposed to  $180^\circ$  observed previously.

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## 37 **1. Introduction**

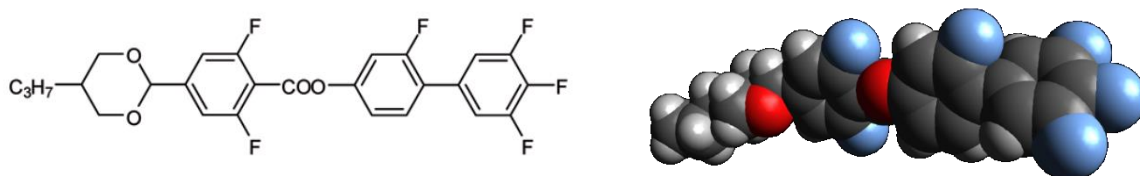
38 Despite predictions for the existence of ferroelectric nematic phase ( $N_F$ ) made over a  
39 century ago by Born [1], this phase has only been recently discovered in a limited number  
40 of chemical systems: two nematic phases in RM 734-series [2], three nematic subphases in  
41 DIO [3] and in a highly fluorinated rigid mesogens with similar molecular structure to DIO  
42 but without the ester group being present [4]. In these systems, the conventional nematic  
43 phase is observed at higher temperatures while the  $N_F$  phase is observed at lower  
44 temperatures. This three-dimensional liquid crystalline compound displays spontaneous  
45 polar ordering with extremely large order parameter ( $\geq 0.9$ ) and it also exhibits an extremely  
46 large spontaneous polarization ( $\sim 5 \mu\text{C}/\text{cm}^2$ ) [2,3,5]. To form the ferroelectric state in the  
47 nematic phase, the dipole moments in these materials,  $\mu$  should be as large as  $\sim 10$  D, such  
48 that the interactions withstand the thermal fluctuations [6], that tentatively satisfy the  
49 equation,  $\frac{\mu^2}{\epsilon_0 \epsilon V} > k_B T$ , where  $V$  is the molecular volume,  $k_B$  is the  $T$  is the thermal energy.  
50 The pre-requisites for the formation of ferroelectric nematic phase are that the constituent  
51 molecules should have large dipole moment and a specific relative arrangement of  
52 neighboring molecular dipoles. This has recently been theoretically confirmed by  
53 Madhusudana [7]. The other recently proposed theoretical models suggest the importance  
54 of including the flexo-dipolar terms in the Landau energy expansion. These are found to  
55 play important role in providing stability to the ferroelectric nematic phase [8,9,10] with  
56 different splay deformations. However, the fluorinated  $N_F$  materials [3,4] do not show splay  
57 deformations and in these cases, ferroelectricity in a ferroelectric nematic phase may be of  
58 different origin than of the splay nematic. Therefore, the  $N_F$  phase needs further  
59 investigations using a range of complementary physical techniques to clarify the structure  
60 – property relationship. Furthermore, the mechanism for the nematic-nematic transitions  
61 and the structural characteristics of the new nematic phases needs investigations in greater  
62 detail.

63 This material exhibits three different nematic phases: nematic (N), intermediate  
64 nematic ( $N_X$ ) and the ferroelectric ( $N_F$ ) phases. Work presented in this paper is focused on  
65 studying the high temperature nematic phase of DIO not attempted, to our knowledge, in  
66 the literature so far. Chiral domains of opposite handedness are observed under sample  
67 confinement conditions arising presumably from chiral symmetry breaking. Furthermore,  
68 we investigate the response of a planar aligned cell, in the high temperature nematic phase,  
69 to the sinusoidal signal applied at a frequency in the range 10 Hz to 10 kHz both for the

70 fundamental and its second harmonic frequency. In this experiment, a finite response is  
71 observed at the fundamental frequency of the applied signal in a conventional paraelectric  
72 nematic phase. In addition, we investigate texture in a planar antiparallel rubbed cell and  
73 based on the comparison of experimental results with those of the simulations, a twisted  
74 structure of the directors is observed from the bottom to the top substrates. These  
75 quantitative results being reported in the  $N_F$  phase reveal differences to those already  
76 reported in the literature. In this experiment, a finite response is observed at the  
77 fundamental frequency of the applied signal in contrast to the observations of the response  
78 at the second harmonic frequency from a conventional paraelectric nematic phase. In  
79 addition, we investigate texture in a planar antiparallel rubbed cell by drawing a  
80 comparison of the experimental results with those of the simulations.

## 81 2. Results and Discussion:

82 Structure of the compound DIO and its phase transition temperatures are given in  
83 Figure 1. The phase sequence is confirmed as Iso - N -  $N_X$  -  $N_F$  by differential scanning  
84 calorimetry (DSC); Iso refers to the isotropic state, N to the ordinary nematic phase,  $N_X$   
85 to an unknown nematic and  $N_F$  is a ferroelectric nematic phase.  $N_X$  is characterized as having  
86 a modulated structure at the nanoscale level and is found to be smectic-like  $SmZ_A$   
87 antiferroelectric [11].



88  
89 FIG. 1. Molecular structure, Van der Waals molecular shape and the phase  
90 sequence of DIO.  
91

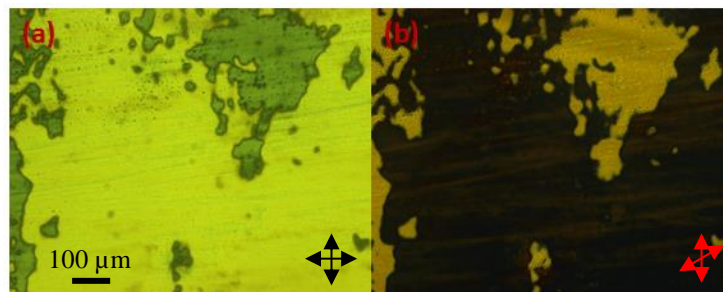
92 This compound was first synthesized by Nishikawa et. al [3]. For the works reported here,  
93 DIO is resynthesized by the group of G. H. Mehl at the University of Hull, Hull, UK.  
94

### 95 2.1. Observation of the Chiral domains in the high temperature N phase

96 The textural studies using POM are extremely useful for determining the  
97 characteristics of the LC phases. The textures of DIO were studied in Ref. [3,11,12,13] in  
98 thin planar and homeotropic aligned cells. In the present study, commercial planar cells of  
99 varying thicknesses viz. 2-25  $\mu\text{m}$  designed by E.H.C. Co. Ltd. were used unless otherwise  
100 specified. Texture of the ferronematic phase (including DIO and compounds of RM734-  
101 series) were found to be strongly dependent on the surface treatments, temperature/phase

102 and the cell thickness due to the strong interaction between the large molecular dipole  
103 moment and the surfaces [5,14]. This raises an interesting question – what textures will  
104 be realized in the bulk? To address this, we perform the optical study of a specially  
105 prepared 5  $\mu\text{m}$  cell with only one rubbed surface. This cell was prepared by sandwiching  
106 two ITO coated glass substrates, out of which only one of them was coated with RN1175  
107 (Nissan Chemicals) and subsequently rubbed after keeping it at a temperature of 250°C for  
108 one hour in the oven while the other substrate was uncoated and unrubbed. In such a case  
109 of one-surface rubbed cell, the molecular director at this surface is anchored along the  
110 rubbing direction, while the director on the opposite second surface is free to rotate. In this  
111 case, the texture should show the natural structure of that of bulk.

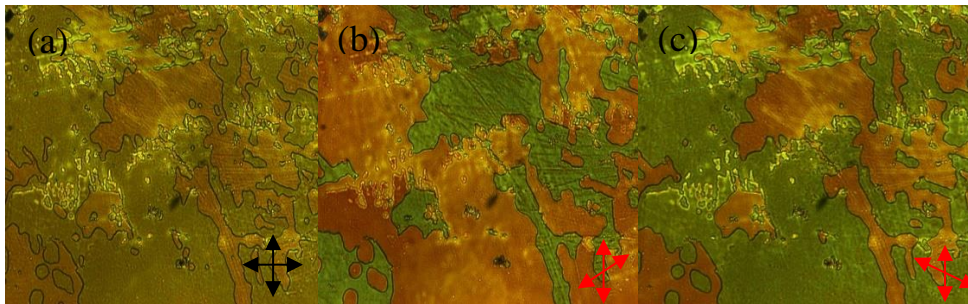
112 The textures were recorded on cooling from the isotropic state down to the  $N_F$  phase  
113 via  $N$  and  $N_X$  subphases. In a conventional  $N$  phase, the textures of one rubbed surface  
114 cells are expected to be homogeneously planar, however these show two opposite optically  
115 active areas/domains in the cell, shown in Figure 2. By rotating the analyzer by an angle  
116 of +20° (clockwise), one domain in Fig. 2b appears dark. The reverse is true for the second  
117 domain (not shown in the Figure), it shows extinction by an anticlockwise rotation  
118 (opposite rotation) of the analyzer by an angle of -20°. This means that domains of the  
119 opposite chirality do exist even in the high temperature ordinary (paraelectric) nematic  
120 phase that emerges just below the Iso- $N$  phase transition temperature when at least one of  
121 the two planar alignment surfaces of the cell is unrubbed. Hence, this natural texture  
122 represents a conglomerate of stochastically distributed chiral areas/domains with the  
123 experimentally determined optical activity, with the rotation power of  $\sim 4$  degrees/ $\mu\text{m}$ . In  
124 a usual two rubbed surface cells, optically active texture is affected by both surfaces. These  
125 suppress the natural optical activity, and the textures are usually homogeneously planar.



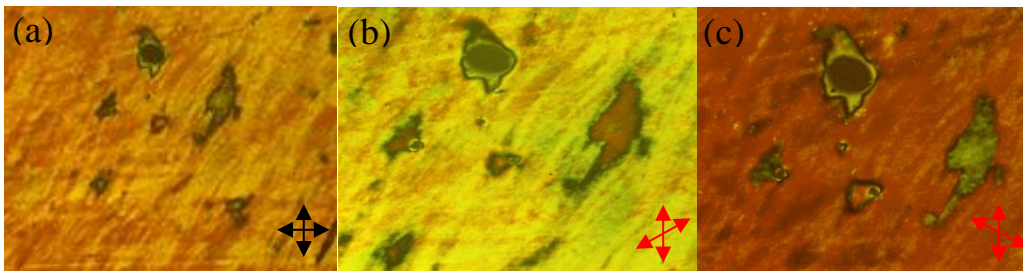
126

127 FIG. 2: Snapshots of a 5  $\mu\text{m}$  thick cell at a temperature of 170 °C in the nematic  
128 phase; one of the glass plates in the cell is rubbed for homogeneous planar  
129 alignment while the second plate is unrubbed and uncoated ITO; (a) crossed  
130 polarizers (b) the analyzer is rotated clockwise by 20°.

131 Similar chiral domains are visible in a cell made from two unrubbed, but polymer coated  
 132 ITO plates with thickness of  $8\ \mu\text{m}$  (refer fig. 3). To further confirm our results, cells are  
 133 made with untreated ITO glass plates as well, surprisingly, this cell also shows chiral  
 134 domains of opposite chirality (refer fig. 4). Chiral textures involving non-chiral molecular  
 135 systems have been reported before in different phases, such as: the bent-core (BC) smectic  
 136 LCs [15,16]; twist-bent nematics, ( $N_{\text{TB}}$ ) [17,18] and even in some isotropic liquids [19].  
 137 The symmetry breaking in the first two systems is caused by a strong non-calamitic shape  
 138 of the bent molecular core or dimers, which most likely is not the case for DIO. In DIO,  
 139 chirality of domains arises from symmetry breaking like in the isotropic liquids [19]. It is  
 140 pertinent to mention that this observation of chiral domains in the high temperature N  
 141 phase of ferronematic liquid crystals is for the first time.



142  
 143  
 144 Fig. 3. The textures of  $8\ \mu\text{m}$ , unrubbed (both surfaces) cell for different polarizer  
 145 configurations at a temperature of  $160\ ^\circ\text{C}$  in the nematic phase.  
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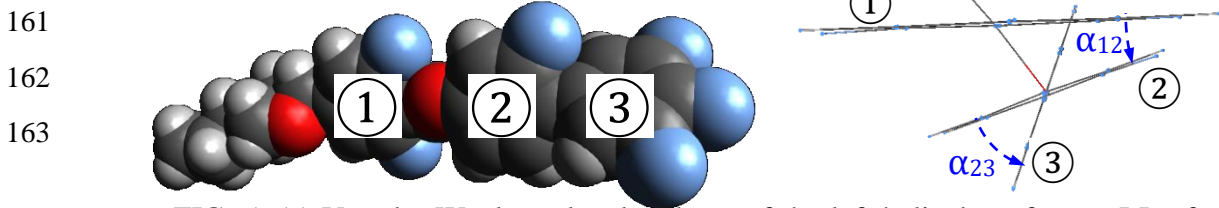


147  
 148 Fig 4. Textures of  $6\ \mu\text{m}$  cell made from two uncoated and unrubbed ITO glass  
 149 plates for different polarizer positions at  $160\ ^\circ\text{C}$  in the nematic phase.  
 150

151 The preferred features of the system DIO are: (i) large net molecular dipole moment; (ii)  
 152 the long molecular core consisting of three or more aromatic rings. The aromatic rings in  
 153 these molecules have two stable states twisted at some angle between the two neighboring  
 154 rings which can be positive for clockwise (or Right, R) or negative for anticlockwise (or  
 155 Left, L) rotations. In the case of a compound having three or more aromatic rings, the  
 156 rings may twist either in the left or the right direction forming LL...and RR... respectively  
 157 or rotate in the opposite direction consecutively to form non-chiral non-helical conformers

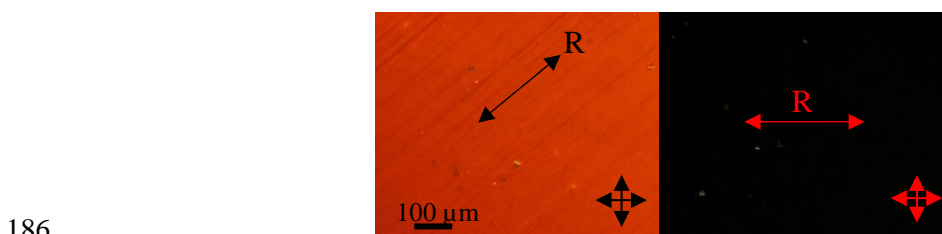


158 LR.../RL. The molecular modeling software Gaussian 09 gives global minimum energy  
 159 levels lie at  $E=192.884$  Units for helical conformers and local minimum of  $E=192.961$   
 160 units for non-helical conformers.



164 FIG. 5: (a) Van der Waals molecular shape of the left helical conformer LL of  
 165 DIO and (b) side view on the aromatic rings 1-3. Rotation angles  $\alpha_{12} \cong -20^\circ$  and  
 166  $\alpha_{23} \cong -48^\circ$ .

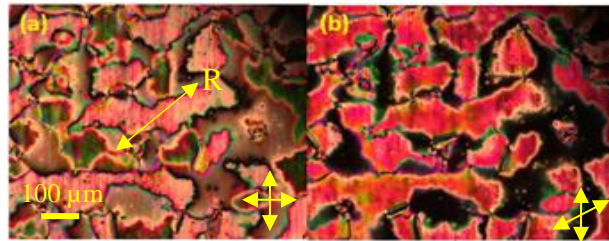
167 This implies that helical conformers of DIO (LL/RR) are more thermodynamically stable  
 168 than the non-helical conformers (LR/RL). A left-handed helical conformer LL is shown  
 169 in Figure 5(a), where three principal rings are numbered as 1-3. Figure 5(b) shows the side  
 170 view of the angular orientations of these three rings with angles of rotation  $\alpha_{12} \cong -20^\circ$  and  
 171  $\alpha_{23} \cong -48^\circ$  between them. Possible reasons may include conformers of the same chirality  
 172 having denser molecular packing, leading to a lower potential energy for the homochiral  
 173 domains and hence the gain achieved in the strength of chiral discrimination ( $-\Delta H_{cd}$ )  
 174 exceeds entropic penalty of the de-mixing process ( $T \cdot \Delta S$ ) [19,20]. Furthermore, this  
 175 twisted organization in the domains/clusters is likely to contribute to chiral segregation of  
 176 helical molecular conformers as these could stabilize helical conformations by a co-  
 177 operative coupling between the molecular and the nano structural twist sense, thus  
 178 increasing the energy gain of homochiral packing. Based on our observations, we conclude  
 179 that compound DIO under investigation in the ordinary conventional nematic phase, shows  
 180 chiral domains of the opposite chirality arising from a chiral segregation of helical  
 181 molecular conformers of opposite symmetry. These chiral domains may be suppressed by  
 182 surface interactions as in previous studies [3,5,10]. Also, to test whether molecular  
 183 structure and surface anchoring plays a role in forming these structures in DIO, similar  
 184 kind of cells are filled with the ubiquitous nematic 5CB and no chiral domains are observed  
 185 (refer Fig. 6). This result further confirms our conclusion.





187 Fig. 6. The texture of classic Nematic LC 5CB filled in only 1-rubbed cell  
188 with a cell thickness of 7  $\mu\text{m}$  recorded at 32  $^{\circ}\text{C}$ .  
189

## 190 2.2 Field induced chiral domain in the high temperature Nematic phase



191  
192 FIG. 7. Textures observed in the N phase (5 V applied across a thick cell (15  
193  $\mu\text{m}$ )) at  $T=150^{\circ}\text{C}$  with antiparallel buffed planar alignment layers (a) the image  
194 is recorded under crossed polarizers and (b) for uncrossed polarizer and analyzer  
195 by  $+12^{\circ}$ .

196 Furthermore, in cells with both ITO surfaces coated and rubbed antiparallel, a  
197 homogeneously planar texture is stabilized initially in the N phase. At the Iso-N phase  
198 transition temperature, homogeneously uniform structure in these antiparallel rubbed cells  
199 is due to the quadrupolar term ( $W_Q$ ) in the azimuthal anchoring energy (see Eq.5 in Ref.  
200 [14]) energy and this quasi-stable structure is retained in the entire temperature range of the  
201 N phase. However, on the application of an electric field greater than  $0.3 \text{ V}/\mu\text{m}$   
202 perpendicular to the ITO electrodes in the N phase, the POM images show emergence of  
203 the two sets of chiral polar domains (Fig. 7). Once formed, these domains continue to exist  
204 even after the electric field is removed. Uncrossing the polarizers by an angle  $+12^{\circ}$  in a  
205 specific direction darkens one set of domains and brightens the other, as seen in Fig.7b. The  
206 opposite is observed for rotation in the opposite direction- $12^{\circ}$  (not shown in Figure 7). The  
207 rotation of the hot stage mounted on the rotational stage however does not affect the relative  
208 brightness of these domains. This shows that the domains are chiral and are of opposite  
209 chirality with the polarization of light rotated as  $\sim 1 \text{ degree}/\mu\text{m}$ , by each domain. The value  
210 is lower than of the natural rotation power ( $\sim 4 \text{ degrees}/\mu\text{m}$ ) achieved for one-sided rubbed  
211 cell (Fig. 2). The difference in the rotation powers in these two cases can be explained by  
212 the quadrupolar term ( $W_Q$ ) in the azimuthal anchoring energy (see Eq.5 Ref. [14]) which  
213 tends to suppress or reduce the natural optical rotation power.

## 214 2.3. Electro-optical dynamics in the high temperature N phase

215 Results obtained from the POM show polarity and chirality of the domains in the  
216 high-temperature nematic phase. The domains display a strong dependence on the cell  
217 thickness, surface treatment and temperature/phase of the sample. To investigate a

218 development of the polar order with temperature, we performed electro-optical (EO)  
 219 measurements in planar-aligned cells. The electric field of varying voltages (0.1 V - 10 V)  
 220 at frequencies (6 Hz - 100 kHz) with a sine-wave dependence of voltage on time was  
 221 applied across the LC cell placed between the crossed polarizers such that the angle between  
 222 the rubbing direction, and the polarizer/analyzer axis, is  $45^\circ$  [21]. The output signal from  
 223 the photodetector was fed to the input of a DSP lock-in amplifier (SR830) and the intensity  
 224 of the transmitted light through the cell was recorded for the first and the second harmonics  
 225 of the applied signal.

226 A change in the transmittance through the cell is exclusively dependent on a change  
 227 in the macroscopic refractive index  $\Delta n_{eff}$ . The effective birefringence is dependent on the  
 228 angle  $\theta$  between the LC director and the electric field as:

229

$$230 \quad \Delta n_{eff} = \frac{n_o n_e}{\sqrt{n_e^2 \cdot \cos^2(\theta) + n_o^2 \cdot \sin^2(\theta)}} - n_o \quad (1).$$

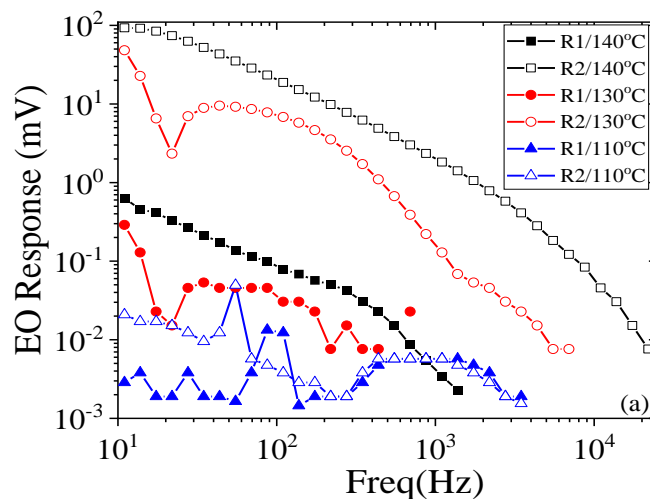
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232 The average director in the absence of the field is parallel to the substrate's plane (for  $E =$   
 233  $0$ ,  $\theta = 90^\circ$ ,  $\Delta n_{eff} = \Delta n = n_e - n_o$ ). On the application of the electric field, the director  
 234 twists away the plane of the surfaces. This results into a splay deformation (the so-called  
 235 S-effect) reducing effective birefringence  $\Delta n_{eff}$  as  $\theta < 90^\circ$ . For a sufficiently high applied  
 236 voltage to the cell the polar angle  $\theta \rightarrow 0^\circ$ ,  $\Delta n_{eff} \rightarrow 0$  and the texture becomes almost  
 237 homeotropic with a negligible light transmittance occurring in the experiment.

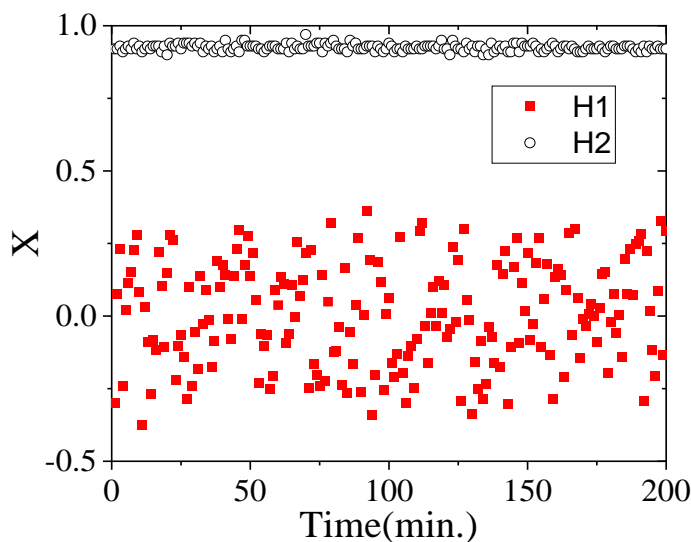
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239 For a conventional paraelectric nematic phase, the output of electro-optical signal is  
 240 only of the second harmonic and is strongly dependent on the frequency of the applied field.  
 241 For frequencies much lower than the relaxation frequency of the LC structure, the electro-  
 242 optic response gives maximal signal for the second harmonic. For frequencies much higher  
 243 than LC relaxation frequency, the electrooptic response is small. For intermediate  
 244 frequencies, the second-harmonic electrooptic response decreases with an increase in the  
 245 frequency as the 1<sup>st</sup> order low-pass filter with a slope of -20 dB/decade. This scenario is  
 246 observed in the higher temperature range of N nematic, i. e., for  $T \geq 150^\circ\text{C}$ . However, the  
 247 polarity and the chirality exist even in the paraelectric N nematic phase at lower  
 248 temperatures. Therefore, one may expect the first harmonic response to appear arising from  
 249 the polar interactions with the electric field. Figure 8a shows the frequency dependence of  
 the magnitude ( $R \cdot \exp(j\theta) = X + jY$ ) of both the first and the second harmonics for applied

250 sinusoidal signal of amplitude 5 V, for three temperatures below the benchmark  
 251 temperature of 150 °C. These are set at 140 °C, 130 °C and 110 °C. these temperatures  
 252 correspond to the higher temperature nematic phase of DIO. However, the characteristics  
 253 of the EO response are different for these three temperatures. For 140 °C, there is a finite  
 254 but a lower output of the first harmonic than of the second. The spectra for first and second  
 255 harmonics show two slopes: -20 dB/decade in the low frequency range and the -40  
 256 dB/decade in the high frequency range. At a mid-temperature in the nematic phase (130 °C)  
 257 the response is similar, but the level of noise signal is higher, especially for the 1<sup>st</sup> harmonic.  
 258 At the lowest temperature of 110 °C, the spectra are not regular but are observed to be  
 259 extremely noisy. To elucidate this feature, we plot the dependence of the real part  $X$  of the  
 260 signal  $R$  on time in Fig. 8b of the EO response for a fixed frequency (28 Hz), measured at  
 261 an interval of one minute.



262



263

264 FIG. 8: (a) Frequency dependence of the magnitude (R) of the EO response of  
 265 1<sup>st</sup> harmonic (filled symbols) R1 and the 2<sup>nd</sup> harmonic (open symbols) for 5 V  
 266 applied voltage at three temperatures of 110°C, 130 °C and 140°C. These  
 267 temperatures of the material correspond to the conventional N phase of DIO. (b)  
 268 The real part (X) of the 1<sup>st</sup> (■) [H1] and the 2<sup>nd</sup> harmonic [H2] (○), of EO  
 269 response at a temperature of 110 °C are plotted as a function of time for a fixed  
 270 frequency of 28 Hz, 5 V voltage signal applied. In each case, the data is recorded  
 271 at a time interval of 1 min.

272

273 Both the magnitude and the phase part of the 2<sup>nd</sup> harmonic signal is stable with time while  
 274 the 1<sup>st</sup> harmonic output shows no regularity with time and the output is noisy. Out of the  
 275 200 data points shown in Fig. 8b, magnitude of the signal varies roughly from  $-40 \mu\text{V}$  to  
 276  $+40 \mu\text{V}$ . The observation of the first harmonic signal R1 is not as dominant as from the  
 277 twist bend structure found before, in that case the signal was obtained from a single chiral  
 278 domain [18] unlike here. This observed phenomenon has a rather simple explanation. The  
 279 texture of the planar-aligned antiparallel rubbed cell (Fig.7) arises from two chiral domains  
 280 of the opposite polarity. The space ratio of these domain is not exactly 1:1, as seen from  
 281 Fig.7b where the total area of the right domains (appearing dark under uncrossed polarizers)  
 282 is less than of the left-handed domains. Moreover, this changes after each state of ON/OFF  
 283 applied signal. The right-handed domains produce positive response whereas the left-  
 284 handed domains lead to the opposite response. Therefore, the real part of the magnitude and  
 285 the sign of response is proportional to the enantiomer excess, defined as  $R = \frac{A_R - A_L}{A_R + A_L}$ ,  
 286 changes in which are irregular with time. The 2<sup>nd</sup> harmonic response is driven by the non-  
 287 polar interaction  $\Delta\epsilon \cdot E^2$  and it is regular and stable with time.

288 **2.4 Optical Textures and birefringence measurements of the three Nematic phases in**  
 289 **Planar-aligned cells**

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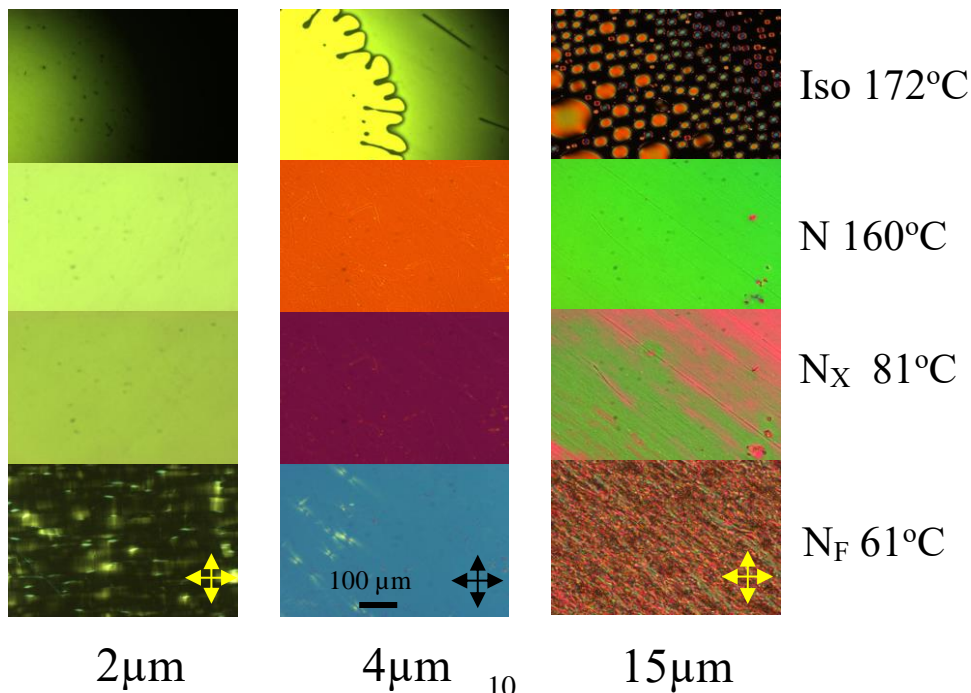
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2 μm

4 μm

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15 μm

Iso 172°C

N 160°C

N<sub>X</sub> 81°C

N<sub>F</sub> 61°C

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FIG. 9 Textures for different temperatures/phases recorded from planar-aligned cells of different cell thickness with unidirectional antiparallel buffed alignment on opposite surfaces.

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Figure 9 displays the textures of planar-aligned cells of different thicknesses with two surfaces rubbed antiparallel. The LC cell is mounted on the rotational stage of the polarizing optical microscope (POM), with polarizer and analyzer crossed. In these experiments, the rubbing direction makes an angle  $\psi=45^\circ$  with the axis of the polarizer in each of the cells. Homogeneous and uniform textures are observed in the three cells as the temperature is lowered from the Iso state. A change in the color of the texture depends on the optical retardation  $(\pi \cdot \Delta n \cdot d) / \lambda$  experience by the light, this is dependent on the cell thickness, birefringence, and the wavelength of light (see Fig. 9). The birefringence is observed to gradually grow under cooling from the Iso state, the increase in the N-phase is caused by an increase in the order parameter.

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In the two nematic phases: N and N<sub>X</sub>, the textures are observed typically homogeneous with the optical axis/director lying along the rubbing direction in thin cells. However, in a thick (15 μm) cell, at a temperature in the N<sub>X</sub> phase (81 °C), the texture though homogeneously uniform but some red colored domains of higher birefringence are superimposed on the green texture. The size of the red colored domains grows under cooling. In the N<sub>F</sub> phase however, a few yellow-colored domains are also observed even in thinner cells, and these are found chiral in nature. The total area of the chiral domains grows continuously under cooling. In a thick (15 μm) cell, the texture shows many ferroelectric domains, the emergence of these domains is sensitive to the alignment layer/s and the surface treatment of substrates [12].

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The birefringence measurements are based on measuring the transmittance spectra of a homogenous aligned 25 μm thick cell. Experimentally, the transmittance spectra from a planar-aligned cell for different temperatures are recorded using achromatic source of light, the spectral content of which contains an entire range of the visible wavelengths. In such a homogeneous cell, the transmittance  $T$  is given by

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$$T = A \cdot \sin^2 \left( \frac{\pi \cdot \Delta n_{eff} \cdot d}{\lambda} \right) + B \quad (2)$$

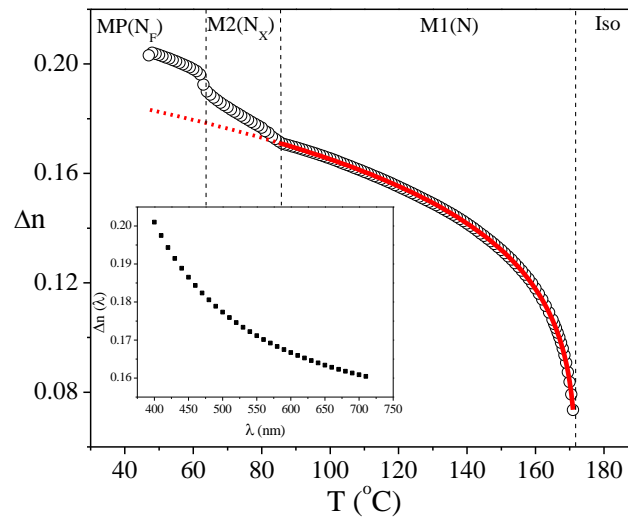
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In Eqn. (2)  $A$  is the scaling factor,  $B$  is the leakage of light through the cell,  $d$  is the cell thickness and  $\Delta n_{eff}$  is the effective birefringence, dependent on the out-of-plane angle  $\theta$  and

336 on the dispersion of the birefringence with the wavelength of light. The latter dependence  
 337 is governed by an extended Cauchy equation [Eqn. (3)] as:

$$338 \quad \Delta n(\lambda) = k \cdot \frac{\lambda^2 \lambda^{*2}}{\lambda^2 - \lambda^{*2}}, \quad (3).$$

339 Here  $k$  is proportional to the order parameter  $Q$  dependent on temperature and  $\lambda^*$  is the  
 340 temperature independent dispersion parameter. The transmittance ( $T$ ) spectra were  
 341 measured using Avantes AvaSpec-2048 fiber spectrometer from a temperature of 171 °C  
 342 (just below the isotropic to nematic transition temperature) down to 40 °C, with a  
 343 temperature step of 1°C. The experimental data are fitted to Eqn. (1), on considering  
 344 dependence of  $\Delta n$  on the wavelength given by Eqn. (2).  $\lambda^*$  is deduced as 208 nm from a  
 345 fitting of the  $T$  at 171 °C (just below the I-N transition temperature). The value of  $\lambda^*$  found  
 346 is fixed for other temperatures. Figure 10 shows the dependence of birefringence on  
 347 temperature for  $\lambda = 550$  nm, the dispersion of the refractive index on wavelength at 90 °C  
 348 in the high temperature nematic phase is given in the inset of Fig. 10. Results of the  
 349 birefringence are found to be in good agreement with the previously obtained results on  
 350 this compound [10,13].



351  
 352 FIG. 10. The birefringence ( $\Delta n$ ) measured for  $\lambda = 550$  nm is plotted as a function  
 353 of temperature for a homogeneous 25  $\mu\text{m}$  thick cell. The inset shows a plot of  
 354 the dispersion of birefringence with wavelength of light at a temperature of 90  
 355 °C.

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 357 The highest value of the birefringence in the N phase is 0.166, for which the texture of 15  
 358  $\mu\text{m}$  cell looks green. The birefringence, just below  $N_X$  - $N_F$  phase transition, temperature,  
 359 jumps to 0.195 where it looks red in POM. On cooling the sample to the temperature of

360 the intermediate  $N_X$  phase, the higher-birefringence (red) domains appear on the low-  
 361 birefringence (green) field, size of these domains grows on cooling. In the temperature  
 362 range lying in the middle of the  $N_X$  phase ( $81^\circ$ ), the texture comprises almost 50% / 50%  
 363 of the high- and the low-birefringence domains, and finally higher birefringence domains  
 364 occupy the entire area of the cell at the transition to the  $N_F$  phase, while birefringence  
 365 grows almost linearly cross the  $N_X$  phase as an average of the high- and low-birefringence  
 366 areas. This may suggest that intermediate  $N_X$  phase though thermodynamically stable  
 367 (following results of the DSC studies [3]) may have a possibility of the phase being a  
 368 mixture of the N and  $N_F$  domains under some experimental conditions, nevertheless the  
 369 quantitative studies do show that it is an antiferroelectric phase. This needs to be examined  
 370 in greater detail in future. However, we also note that structures/textures are very sensitive  
 371 to the cell parameters, as in ref [11]  $N_X$  phase has a modulated, so-called  $SmZ_A$  structure  
 372 or it is a splay modulated phase as in ref. [pre review] If the high-temperature N phase is  
 373 ordinary nematic, the temperature dependence of the birefringence should follow the  
 374 Haller equation [22]:

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$$\Delta n(T) = \Delta n_0 \cdot Q = \Delta n_0 \cdot \left(1 - \frac{T}{T_{IN}}\right)^\beta \quad (4).$$

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377 Here  $\Delta n_0$  is the maximum birefringence reached for order parameter  $Q = 1$ ,  $T_{IN}$  is Iso-N  
 378 phase transition temperature and the exponent  $\beta = 0.2 \pm 0.03$  is obtained from a fitting of  
 379 the data to Eqn. (4). Fitting of  $\Delta n(T)$  to Eqn. (4) with the exponent  $\beta$  shows a perfect match  
 380 to the experimental data (see the red line, Fig. 10) with the parameters:  $\Delta n_0=0.18$ ;  $\beta=0.18$   
 381 and  $T_{NI}=172^\circ\text{C}$ . An excellent fitting of the data to Eqn. (4) confirms that N behaves like  
 382 a conventional nematic phase under the specified surface conditions. In addition, the N  
 383 phase exhibits additional features: (a) existence of the chiral domains with the opposite  
 384 chirality and (b) observation of the linear EO response, discussed already in section 2.3.

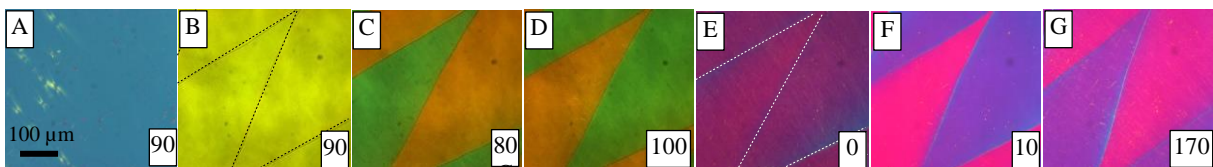
### 385 **2.5 Ferroelectric nematic phase ( $N_F$ ): Twisted structure**

386 The interesting feature involves observing unusual textures in the  $N_F$  phase in a  $4\ \mu\text{m}$   
 387 cell shown in Figure 11, marked A-G. The angle between the analyzer (A) and the polarizer  
 388 (P) is varied in this experiment.

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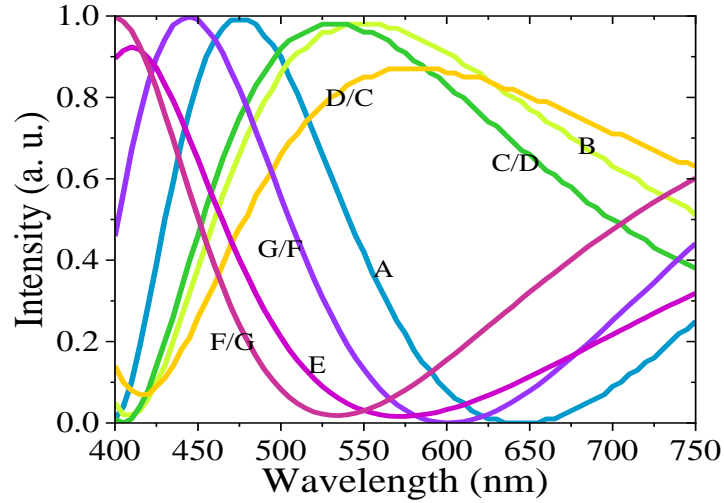
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392 FIG. 11 The POM textures from 4  $\mu\text{m}$  cell with unidirectional antiparallel  
393 rubbing of substrates at a temperature of 61  $^{\circ}\text{C}$  in the  $N_F$  phase. The  
394 homogeneous texture A transforms to the twisted texture B. The textures C to G  
395 are recorded for different angles between the  $P$  and  $A$ , the angles are shown in  
396 the righthand bottom corner of Figures 11A to 11G.

397 The homogeneous texture A is observed close to the  $N_X$ - $N_F$  transition temperature  
398 transforms to the twisted texture B as temperature within the  $N_F$  phase is reduced by 2.5  $^{\circ}\text{C}$   
399 below the  $N_X$ - $N_F$  phase transition temperature, the ‘yellow texture B’ does not show the  
400 extinction of light between the crossed polarizers (Fig. 11B), the texture from parallel  
401 polarizers (Fig. 11E) appears as uniform/monodomains. The rotation of the analyzer by  
402 angles of  $\pm 10^{\circ}$  from the crossed positions are shown (C/D) and rotations by  $\pm 10^{\circ}$  from  
403 the parallel positions of  $\mathbf{P}$  and  $\mathbf{A}$  are marked (F/G). These textures show two domains in  
404 which their colors are swapped by the opposite rotations of the analyzer from the crossed  
405 polarizers position. The twist angle between the directors from the top to the bottom of the  
406 cell is dependent on a competition between the two energy terms in Eq. (5) of reference  
407 [14]. The twist angle would exactly be  $180^{\circ}$  only in the case of a negligibly small elastic  
408 constant. In order to examine these textures quantitatively, we simulate color of the  
409 transmittance spectra for different angles between the  $\mathbf{P}$  and  $\mathbf{A}$  using the conventional  
410 Berreman’s 4 x 4 matrix method [23]. The best simulation results are achieved for planar  
411 twisted structure where the director uniformly rotates from the top to the bottom substrate  
412 of the cell by  $\pm 170^{\circ}$ . for anti-parallel rubbed substrates. In a realistic elastic medium, the  
413 twist angle is dependent on the term  $Kd/\omega W_Q$  and it may vary from  $0^{\circ}$  ( $Kd/\omega W_Q \rightarrow \infty$ ) to  
414  $180^{\circ}$  ( $Kd/\omega W_Q \rightarrow 0$ ). However, in our experimental conditions, the twist angle is found as  
415  $\sim 170^{\circ}$ . The result is of higher precision than found previously by the observation of the  
416 orientation of the disclination lines under polarized microscopy [25]. Figure 12 presents the  
417 simulated optical spectra of the textures corresponding to Figs. 11A to 11G. The colors of  
418 the simulated spectra with the twist of the directors between the top and bottom substrates  
419 for different angles between  $\mathbf{P}$  and  $\mathbf{A}$  agree completely with the observed optical texture.  
420 The twisted structure of the nematic directors is confirmed in the  $N_F$  phase. Similar domains  
421 as those observed here for DIO were seen in the other  $N_F$  compound RM734, and their  
422 director structures were found as twisted [24,25,26].



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424 FIG. 12. Simulated optical spectra corresponding to the textures A-G shown in Fig. 7.

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It is to be noted that the twisted state is achieved in the cells with antiparallel rubbing on the two opposite surfaces, while for a similar cell of the same thickness but with parallel rubbing of the alignment layers, the texture stays homogeneously planar in the entire temperature range. This phenomenon is explained by the large polar azimuthal anchoring surface energy, suggested by the Boulder group [25]. This polar in-plane anisotropy stabilizes the homogeneous planar structure for the parallel rubbing and gives twisted structure for the antiparallel rubbing.

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### 3. Conclusion

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The compound DIO with non-chiral molecules exhibits three nematic subphases. Our texture and the EO studies of this material confirm the phase sequence. However, some of these phases reveal several additional important features not reported before. N is like an ordinary nematic phase with a conventional  $\Delta n(T)$  dependence in planar-aligned cells on temperature. But it also shows chiral domains of the opposite chirality under certain conditions. This is the first example of the helical segregation having occurred of non-chiral molecules; the segregated molecules form chiral domains. The other unusual feature (related to chirality) is the polarity which is responsible for the observation of the electrooptic EO response to the fundamental frequency (linear response) as opposed to the second harmonic response in a conventional nematic phase. The ferroelectric nematic  $N_F$  exhibits a strong polar azimuthal surface interaction energy [25] which stabilizes the homogeneous structure in a planar aligned cell rubbed parallel and forms the twisted

446 structures in the cell rubbed antiparallel. Simulation of the spectra shows that the directors  
447 are twisted by  $\sim 170^\circ$  between the top and the bottom antiparallel rubbed substrates as  
448 opposed to  $180^\circ$  observed previously.

#### 449 **Acknowledgement**

450 One of the authors NY thanks the Irish Research Council for awarding the Government of  
451 Ireland PDF 2021, GOIPD/2021/858; WJ thanks the CSC, China for a PhD scholarship.

#### 452 **References:**

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- [1] M. Born, Über anisotrope Flüssigkeiten. Versuch einer Theorie der flüssigen Kristalle und des elektrischen Kerr-Effekts in Flüssigkeiten. Sitzungsber. Preuss. Akad. Wiss. **30**, 614 (1916).
- [2] R. J. Mandle, S. J. Cowling, and J. W. Goodby, Rational design of rod-like liquid crystals exhibiting two nematic phases. Chem. Eur. J. **23**, 14554 (2017).
- [3] H. Nishikawa *et al*, A fluid liquid crystal material with highly polar order. Adv. Mater. **29**, 1702354 (2017)
- [4] Y. Song, J. Li, R. Xia, H. Xu, X. Zhang, H. Lei, W. Peng, S. Dai, S. Aya and M. Huang, Development of emergent ferroelectric nematic liquid crystals with highly fluorinated and rigid mesogens. Phys. Chem. Chem. Phys. **24**, 11536 (2022).
- [5] X. Chen, E. Korblova, D. Dong *et al.*, First-principles experimental demonstration of ferroelectricity in a thermotropic nematic liquid crystal: polar domains and striking electro-optics. Proc. Natl. Acad. Sci. U.S.A. **117**, 14021 (2020).
- [6] O. D. Lavrentovich, Proc. Natl. Acad. Sci. U.S.A. **117**, 14629 (2020).
- [7] N. V. Madhusudana, Simple molecular model for ferroelectric nematic liquid crystals exhibited by small rodlike mesogens. Phys. Rev. E **104**, 014704 (2021)
- [8] M.P. Rosseto and J.V. Selinger, Theory of the splay nematic phase: Single versus double splay. Phys. Rev. E **101**, 052707 (2020).
- [9] E.I. Kats, Stability of the uniform ferroelectric nematic phase. Phys. Rev. E **103**, 012704 (2021).
- [10] A. V. Emelyanenko, V. Yu. Rudyak, S. A. Shvetsov, F. Araoka, H. Nishikawa and K. Ishikawa, Emergence of paraelectric, improper antiferroelectric, and proper ferroelectric nematic phases in a liquid crystal composed of polar molecules. Phys. Rev. E **105**, 064701 (2022).
- [11] X. Chen, V. Martinez, E. Korblova, *et al.*, Antiferroelectric Smectic Ordering as a Prelude to the Ferroelectric Nematic: Introducing the Smectic  $Z_A$  Phase. arXiv:2112.14222 [cond-mat. soft] (2021).
- [12] F. Caimi, G. Nava, R. Barboza, N. A. Clark, E. Korblova, D. M. Walba, T. Bellini, and L. Lucchetti, Surface alignment of ferroelectric nematic liquid crystals. Soft Matter **17**, 8130 (2021).

- 
- [13] S. Brown, E. Cruickshank, J.M.D. Storey, C.T. Imrie, D. Pocięcha, M. Majewska, A. Makal and E. Gorecka, Multiple polar and non-polar nematic phases. *ChemPhysChem*. **22**, 2506 (2021).
- [14] B. Basnet, M. Rajabi, H. Wang, P. Kumari, K. Thapa, S. Paul, M. O. Lavrentovich and O.D. Lavrentovich, *Nature Comms*, **13**, 3932 (2022).
- [15] T. Niori, T. Sekine, J. Watanabe, T. Furukawa, and H. Takezoe, Distinct ferroelectric smectic liquid crystals consisting of banana shaped achiral molecules. *J. Mater. Chem.*, **6**, 1231 (1996).
- [16] S. P. Sreenilayam, Y. P. Panarin, J. K. Vij, V. P. Panov, A. Lehmann, M. Poppe, M. Prehm and C. Tschierske, Spontaneous helix formation in non-chiral bent-core liquid crystals with fast linear electro-optic effect. *Nat. Commun.* **7**, 11369 (2016).
- [17] V. P. Panov, M. Nagaraj, J. K. Vij, Y. P. Panarin, A. Kohlmeier, M. G. Tamba, R. A. Lewis, and G. H. Mehl, Spontaneous Periodic Deformations in Nonchiral Planar-Aligned Bimesogens with a Nematic-Nematic Transition and a Negative Elastic Constant. *Phys. Rev. Lett.*, **105**, 167801 (2010).
- [18] V. P. Panov, R. Balachandran, M. Nagaraj, J. K. Vij, M. G. Tamba, A. Kohlmeier, and G. H. Mehl, Microsecond linear optical response in the unusual nematic phase of achiral bimesogens. *Appl. Phys. Lett.* **99**, 261903 (2011).
- [19] C. Dressel, T. Reppe, M. Prehm, M. Brautzsch, and C. Tschierske, Chiral self-sorting and amplification in isotropic liquids of achiral molecules. *Nature Chem.* **6**, 971 (2014).
- [20] S. Toxvaerd, Molecular Dynamics Simulations of Isomerization Kinetics in Condensed Fluids. *Phys. Rev. Lett.* **85**, 4747 (2000).
- [21] S. Sreenilayam, N. Yadav, Y.P. Panarin, J. K. Vij, and G. S. Shanker, Electrooptic, pyroelectric and dielectric spectroscopic studies of nematic and twist bend nematic phases of achiral hockey-shaped bent-core liquid crystal. *J. Mol. Liq.* **351**, 118632 (2022).
- [22] I. Haller, Thermodynamic and static properties of liquid crystals, *Prog. Solid State Chem.* **10**, 103–118 (1975), [https://doi.org/10.1016/0079-6786\(75\)90008-4](https://doi.org/10.1016/0079-6786(75)90008-4).
- [23] D. W. Berreman, Optics in Stratified and Anisotropic Media: 4×4-Matrix Formulation. *J. Opt. Soc. Am.* **62**, 502 (1972)
- [24] N. Sebastián, R. J. Mandle, A. Petelin, A. Eremin, and A. Mertelj, Electrooptics of mm-scale polar domains in the ferroelectric nematic phase. *Liq. Cryst.* **48**, 2055 (2021). DOI: 10.1080/02678292.2021.1955417
- [25] X. Chen, E. Korblova, M. A. Glaser, J. E. MacLennan, D. M. Walba, and N. A. Clark, Polar in-plane surface orientation of a ferroelectric nematic liquid crystal: Polar monodomains and twisted state electro-optics. *Proc. Natl. Acad. Sci. U.S.A.* **118**, e2104092118 (2021)
- [26] P. Rudquist, Revealing the polar nature of a ferroelectric nematic by means of circular alignment. *Sci. Reports* **11**, 24411 (2021).