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Development of ferroelectricity in the smectic phases of 4-cyanoresorcinol derived achiral bent core liquid crystals with long terminal alkyl chains

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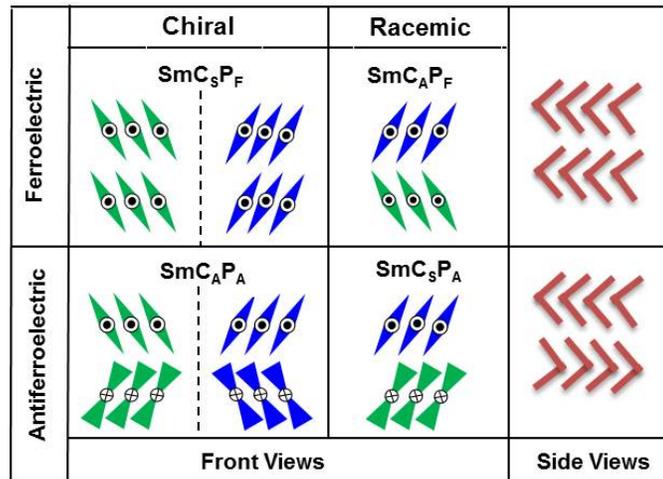
Bent-core molecules can form numerous polar and symmetry broken liquid crystalline phases with fascinating properties. Here we report the characteristics of a new smectic phase, SmC_SP_X , found in the phase sequence of an achiral bent-core material with a 4-cyanoresorcinol bisbenzoate core, terminated by long linear alkyl chains ($n=18$) on both ends. This new phase exists over a narrow range of temperatures and is sandwiched in between the polar SmC_SP_R and SmC_SP_F phases with $P_S \sim 250 \text{ nC/cm}^2$. In a planar-aligned cell it exhibits only chirality flipping on application of a conventional AC field but it also exhibits optical switching by rotation of the molecular directors on the tilt cone under a modified sequence of bipolar pulses. This changeover is discussed in terms of the model given by Nakata *et al.* (Phys. Rev. Lett. 96, 067802, 2006), involving a competition between the two forms of switching: the rotation around the long molecular axis and the switching through rotation of the molecular directors on the tilt cone. The model is modified to take account of the azimuthal pretilt and the molecular tilt angles. In addition to it, characteristics of a randomly polar synclinic smectic phase SmC_SP_R are also discussed.

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I. INTRODUCTION

Liquid crystals (LCs) characterized by fluidity and long-range order [1, 2] belong to a fascinating branch of soft condensed matter science. Bent-core LCs have recently been extensively investigated, these exhibit a large variety of phases with a set of unique properties. Some of the characteristics are: the polar order, the spontaneous breaking of the mirror symmetry and polar switching by electric fields. Bent-core LCs display a multitude of desirable properties while confined in cells with a thickness of the order of a few μm . Some of these characteristics form the basis of a range of applications currently being developed [3-12]. In

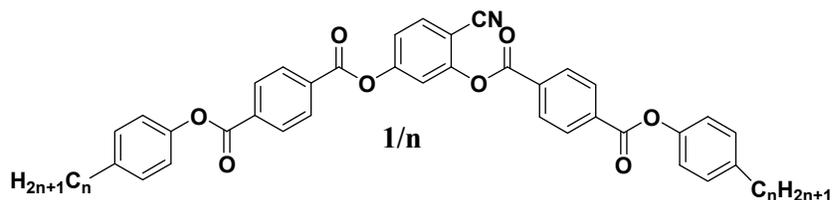
37 smectic phases of bent-core LCs, the mirror symmetry is broken by the orthogonal combination
 38 of tilt and polar direction and there exist different modes of correlations of tilt and polar
 39 direction in the neighboring layers. This in turn leads to a rich polymorphism of the polar
 40 smectic phases. These include orthogonal smectics where the plane formed by the long
 41 molecular axis and the polar director is parallel to the layer normal [13-21]. In most other
 42 smectic phases, the plane of the bent-core molecules is tilted to form smectic C (SmC) type
 43 phases, the tilt is either left or right from the layer normal and this leads to the formation of
 44 several additional sub-phases [22]. The main difference between the polar smectic phases of
 45 bent-core molecules (B2 phases) and the non-polar tilted smectic C (SmC) phase of normal rod-
 46 like molecules is that unlike the latter, different molecular configurations can exist among the
 47 neighboring layers with synclinic/ anticlinic molecular arrangements with respect to the tilt
 48 direction and syn-polar/ anti-polar with respect to the polarization vector. Furthermore these sub-
 49 phases exhibit ferroelectric (F) /antiferroelectric (A) properties. Their structures are described as:
 50 SmC_SP_F , SmC_AP_A , SmC_SP_A , and SmC_AP_F [22] (Fig. 1), where C_S stands for a synclinic and C_A
 51 for an anticlinic tilt correlation in adjacent layers: P_F and P_A indicate the same and opposite
 52 directions of polar order in adjacent layers respectively.



53

54 FIG. 1. Distinct views on the four subtypes of tilted polar smectic phases resulting
 55 from the correlation of the tilt and the polar directions (in the front views indicated
 56 by dots and crosses) of the bent-core molecules in adjacent layers [22]. The front
 57 views represent projections of bent-core molecules with the tip of the molecules in
 58 the direction ‘in’ or ‘out’ of the plane. The tip direction is coupled with the polar
 59 direction; dots and crosses indicate the polar direction pointing ‘out’ and ‘into’ the
 60 plane, respectively. An orthogonal combination of tilt and polar order leads to a
 61 reduced C_{2v} symmetry and superstructural chirality of layers (color indicates
 62 chirality sense). The notations P_A and P_F refer to the antiferroelectric and
 63 ferroelectric polar order C_A and C_S refer to the anticlinic and synclinic tilt in
 64 adjacent layers. Ferro/antiferro arrangements have two chiral domains separated by
 65 a dashed vertical line on the left of this figure.

66 The bent-core molecules **1/n**, being reported here, consists of five aromatic rings with a
 67 central 4-cyanoresorcinol core. This bent 4-cyanoresorcinol core is connected with terephthalate
 68 based arms terminated by identical alkyl chains (C_nH_{2n+1} , $n=16,18$) at both ends as shown in Fig.
 69 2 [23]. A common feature of these 4-substituted resorcinols is the ‘reduced bent angle’
 70 compared to the other bent-core mesogens without the 4-substituent [24]. In compounds **1/n**, the
 71 peripheral COO groups are reversed with respect to the previously reported series of 4-
 72 cyanoresorcinols involving 4-hydroxybenzoate rods, showing exclusively N_{Cybc} (cybotactic
 73 nematic phases composed of SmC clusters and SmC phases with larger tilt [25] compared to the
 74 compounds of the series **1/n**. This inversion of the peripheral COO groups leads to increased
 75 mesophase stability, enhanced polar order and the reduced tilt for compounds **1/n**. The lower tilt
 76 angle gives rise to unusual features and different characteristics, that result from a combination
 77 of reduced coherence length of the polar order and a weak inter-layer coupling. These special
 78 features lead to complex phase sequences with transitions between tilted and non-tilted phases.
 79 A strong influence of confinement and of sample history is found on the phases with different
 80 molecular arrangements [23, 26-29] and on the dependence of the induced tilt on the electric
 81 field [28].



Compd.	$T/^\circ\text{C}$
1/16 ($n=16$)	Cr 77 SmC _A P _A 90 SmC _S P _F ^{hel} 110 SmC _S P _R 125 SmA 162 Iso
1/18 ($n=18$)	Cr 76 SmC _A P _A 90 SmC _S P _F / SmC _S P _F ^{hel} 110.2 SmC _S P _X 110.7 SmC _S P _R 134 SmA 160 Iso

83 FIG. 2. Molecular structure of the investigated bent-core molecules; their mesophases
 84 and phase transition temperatures as observed on cooling from the isotropic liquid.
 85 Abbreviations: Iso = isotropic state, Cr = crystal; SmA = non-tilted and non-polar
 86 smectic phase, SmC_SP_R = paraelectric smectic phase with uniform (synclinc) tilt and
 87 almost randomized polar direction of ferroelectric domains; SmC_SP_F^{hel} = synclinc
 88 tilted ferroelectric smectic phase with a short pitch where the helical axis lies parallel
 89 to the layer normal; SmC_AP_A = anticlinc tilted smectic phase with antiferroelectric
 90 polar order.

91 In this paper we focus specifically on the two compounds of the series **1/n** with longest
 92 alkyl chains, synthesized so far. Figure 2 lists the phase sequences and transition temperatures of
 93 the homologues with $n = 16$ and 18 . In previous investigation of **1/16** and **1/18**, we focused on
 94 the spontaneous or field-induced development of a helical superstructure in SmC_SP_F phase and
 95 the fast electro-optical switching [30]. Herein we investigate characteristics of a complete series
 96 of distinct paraelectric and polar smectic phases in more detail and thereby find a new phase

97 which appears only in a narrow temperature range, sandwiched in between the polarization
98 randomized SmC_5P_R and the polar SmC_5P_F phases of compound **1/18**. The main focus of the
99 present manuscript will be on this new phase tentatively designated as SmC_5P_X . We demonstrate
100 switching of chirality in SmC_5P_X phase by ‘chirality flipping’ as well as by rotation of the
101 molecular director on the tilt cone depending on the form and the magnitude of the external
102 electric field applied to the cell. In the SmC_5P_R phase, both, polarization \mathbf{P} and the permittivity
103 $\Delta\epsilon$, show critical behavior on approaching SmC_5P_F , similar to those exhibited by de-Vries
104 smectics during the cooling process.

105 **II. EXPERIMENT**

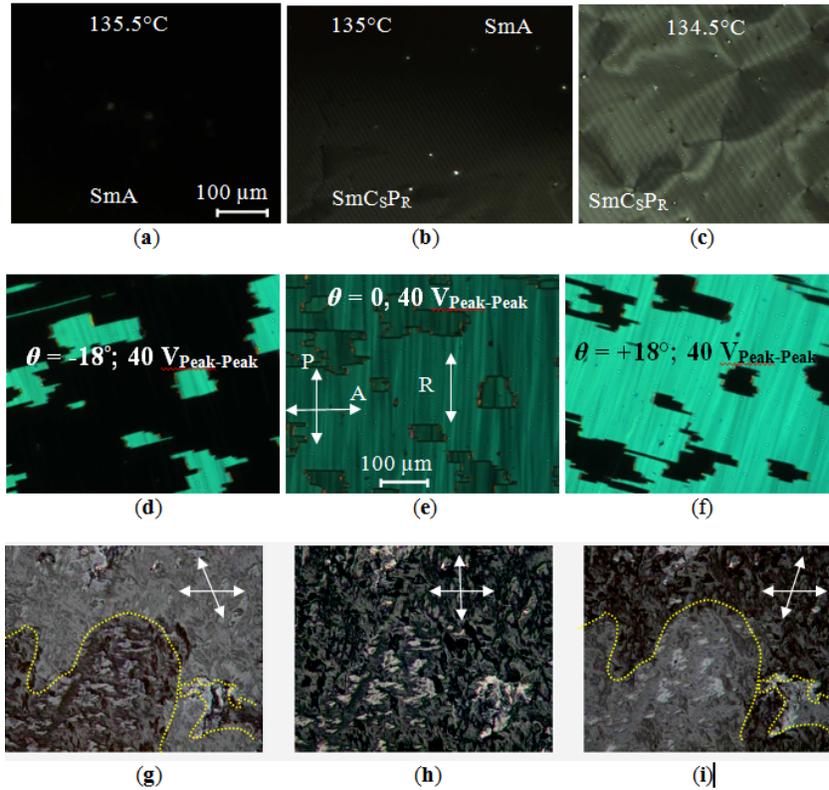
106 Experimental measurements are carried out on homeotropic and planar-aligned LC cells.
107 Homeotropic alignment in a cell is obtained by coating the polymer AL60702 (JSR Korea) on
108 the two ITO coated glass substrates. The substrates are baked at a temperature of 210 °C for 15
109 minutes each. A uniform polymer layer several ‘nm’ thick is adhered on to the substrate. ITO
110 coating on the glass substrate that forms the bottom plate of the cell is etched to form two in-
111 plane electrodes with a spacing of $\sim 80 \mu\text{m}$ in between the two electrodes. An electric field at a
112 frequency of 110 Hz is applied across these electrodes. Planar alignment in a cell is achieved by
113 coating the substrates with RN1175 polymer (Nissan Chemicals Japan) and baking these at a
114 temperature of 250 °C for 30 minutes. The cell thickness controlled by Mylar spacers is
115 measured using an optical interference technique. The cell is mounted in a hot stage, fixed on to
116 the rotating table of the polarizing optical microscope (Olympus BX 52). Temperature of the
117 hot-stage is controlled by a Eurotherm 2604 temperature controller to an accuracy better than \pm
118 0.05 °C. To investigate the electro-optic behaviour of LC phases at higher fields, an electric
119 signal from an Agilent 33120A signal generator amplified by a high voltage amplifier (TReK
120 PZD700) is applied across the electrodes. Measurements of the dielectric permittivity and
121 dielectric loss are made on a planar-aligned cell using a broadband Alpha High Resolution
122 Dielectric Analyzer (Novocontrol GmbH, Germany) in the frequency range of 1 Hz - 10 MHz
123 and by applying a weak electric field. Dielectric cells are made up of two ITO coated glass
124 substrates with a planar-alignment layer on both substrates, and a low sheet resistance of the
125 ITO layers, ($20 \Omega/\square$). A parasitic capacitance of the cell containing the compound is in series
126 with a low sheet resistance of the ITO electrodes. The product of R and C must ensure that the
127 frequency of this arrangement is shifted beyond the desired experimental window of dielectric
128 measurements.

129 III. RESULTS AND DISCUSSION

130 A. Polarizing optical microscopy and Electro-optical response study of 131 compound 1/18

132 The texture of the SmA phase of 1/18 in a homeotropic cell (at $T = 135.5$ °C), formed on cooling
133 the sample from the isotropic state is dark (Fig. 3a); this reflects uniaxiality of the phase. On
134 reducing the temperature to 135 °C (Fig. 3b), parts of the cell show Schlieren texture. At 134.5
135 °C, a fully developed low-birefringent Schlieren texture is observed in a homeotropic cell (Fig.
136 3c), indicating that the transition to an optically biaxial mesophase has occurred. There is a
137 striking pattern of equidistant stripes appearing across the developing Schlieren texture (Fig.
138 3b,c) which disappears on further cooling. This kind of stripe texture is typically observed for
139 SmA-SmA_b [31-33] and SmA to SmC_A transitions [34-35]. This could indicate that that SmA-
140 SmC_SP_R transition occurs *via* an additional small range of an intermediate randomized SmC_S
141 domain structure with predominantly anticlinic tilt correlation between the domains [36] before
142 this correlation becomes synclinic in the SmC_SP_R range. However since an additional phase
143 transition is not evident from other investigations (PM of planar samples, DSC, XRD,
144 dielectrics), at the present state of knowledge it is considered as a kind of pre-or post-transitional
145 phenomenon. A typical SmC_S domain texture in a planar cell is recorded at a temperature of 113
146 °C (Fig. 3e). The textures show dark and bright areas (Figs. 3d and 3f) due to two tilt domains
147 with director orientations being inclined at angles $\theta \approx \pm 18^\circ$ to the layer normal. In addition,
148 four-brush disclination points are dominating in the Schlieren textures in homeotropic aligned
149 cell (Fig. 4a). These observations show that the phase under discussion has a uniform molecular
150 tilt in layers. The tilt is either left or right of the layer normal and thus forming distinct chiral
151 domains belonging to a family of synclinic tilted smectic mesophases (SmC_S). When an electric
152 field is applied across the planar aligned cell at a temperature of 113 °C (Fig. 3d-f and Fig. 6a, b
153 (1)), the texture does not respond to the field, *i.e.* no optical switching occurs on the application
154 of an electric field. As is typical for the SmC_SP_R phase, chiral domains can be observed in
155 homeotropic aligned cells [34]. The transition SmA-SmC_SP_R is continuous and does not involve
156 a measurable value of the transition enthalpy [30]. The SmC_SP_R phase is often referred to as
157 SmC because both phases possess the same C_{2h} symmetry. Nevertheless, the physical
158 characteristics of SmC_SP_R and SmC phases are very different from each other. In contrast to the
159 non-chiral SmC phase, the SmC_SP_R phase shows properties related to polar phases. For example,
160 a current response to an applied electric field is due to the polar switching, [30] and electric field
161 induced polarization and soft mode like behavior of the tilt fluctuations are observed on
162 approaching the polar SmCP-phases. Some of these observations follow from results of

163 dielectric measurements to be discussed later in the section on dielectric spectroscopy in section
 164 III C. Chiral domains are observed under certain conditions in homeotropic aligned cells (see
 165 Fig. 3g-i) which may indicate that phase biaxiality is not due to a restricted molecular rotation
 166 around their long molecular axes. It is more likely to be due to the tilt of the molecules, because
 167 only in this case layer chirality can develop.



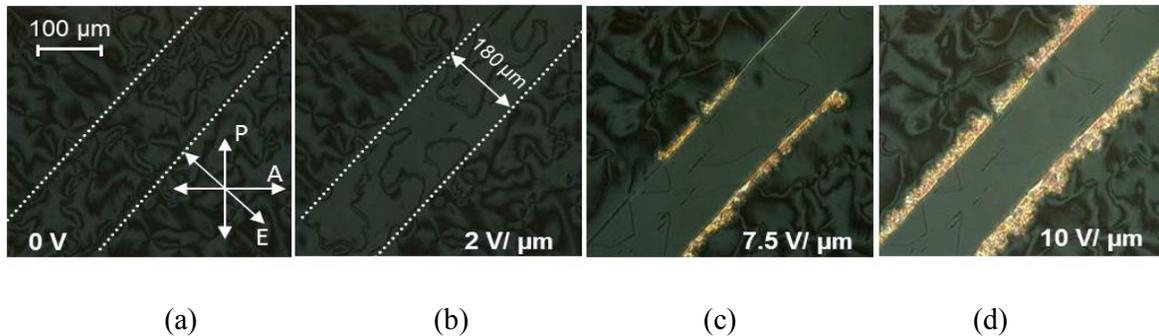
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169 FIG. 3. (a-c) Polarizing micro-photographs of the SmA and SmC_SP_R phases recorded
 170 under cooling in the absence of an external electric field in a homeotropic planar-aligned
 171 ITO cell of cell-thickness 6.5 μm filled with **1/18**. (d-f) SmC_SP_R phase at 113 °C in a 8
 172 μm planar aligned cell; the textures are recorded by application of a 40 V_{Peak-Peak} signal at
 173 a frequency of 110 Hz between the ITO coated electrodes; the rubbing direction **R** is (e)
 174 along the polarizer or is oriented at an angle θ , (d) $\theta = -18^\circ$ and (f) $\theta = +18^\circ$ to the
 175 polarizer. (g - i) SmC_SP_R phase at $T = 120^\circ\text{C}$ in a homeotropic cell between ordinary
 176 glass plates showing chiral domains with opposite handedness, (h) between crossed
 177 polarizers, (g) and (i) with the polarizer rotated by 20° off the 90° position with respect to
 178 the analyzer, either in a clockwise or an anticlockwise direction; the brightness of
 179 domains is exchanged in (g) and (i), whereas rotation of the cell between the crossed
 180 polarizers does not lead to a change in the brightness; these observations indicate a
 181 conglomerate of chiral domains with opposite sign of optical rotation in the distinct
 182 domains.

183

184 The birefringence of the Schlieren texture continuously increases under cooling and this
 185 is clearly reflected in the visual textural changes. When an in-plane electric field at a frequency

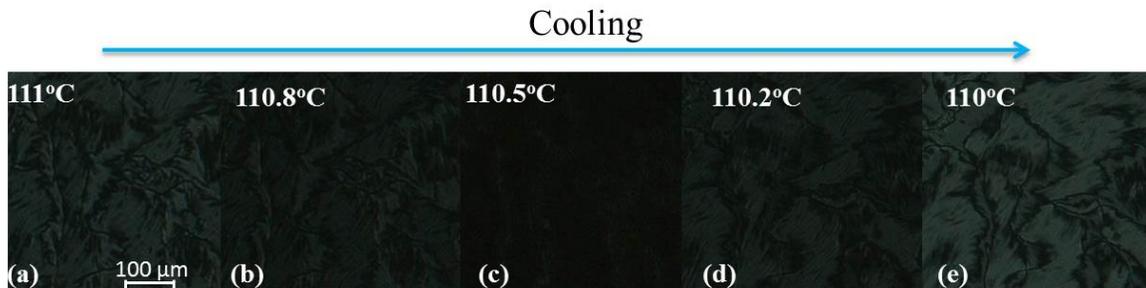
186 of 110 Hz is applied at an amplitude of 10 V/ μm in a homeotropic cell at a temperature of 113
 187 $^{\circ}\text{C}$, the initial Schlieren texture (Fig. 4a) transforms to a uniform one (Fig. 4c) and the
 188 birefringence increases with the field (Fig. 4d). On removal of the electric field, the high
 189 birefringent state (Fig. 4d) returns to a low birefringent one with Schlieren texture (Fig. 4a). This
 190 indicates that a field induced polar order parallel to the layer planes exists, and the electric field
 191 induced SmC_5P_F state relaxes to the polarization randomized SmC_5P_R one upon the removal of
 192 electric field.



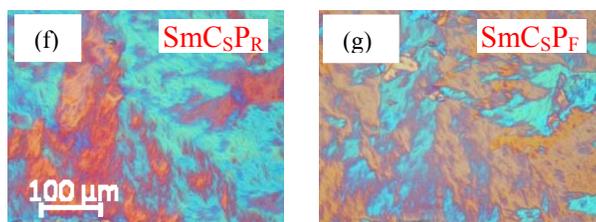
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195 **FIG. 4.** Polarizing optical microscopic textures of SmC_5P_R phase of compound **1/18** at 113
 196 $^{\circ}\text{C}$. (a - d) show the textures recorded in a 6.5 μm homeotropic aligned cell on the application
 197 of an in-plane electric field (E) at a frequency of 110 Hz, applied between the electrodes (the
 198 edges of electrodes are indicated by dashed white lines). The in-plane electrodes are fixed at
 199 an angle of 45° to the analyzer (A) / polarizer (P) as shown in (a). The distance between the
 200 two ITO electrodes is 180 μm .

201 On cooling the homeotropic cell below 113 $^{\circ}\text{C}$ the birefringence starts decreasing. The
 202 four brush Schlieren texture (Fig. 4a) at 113 $^{\circ}\text{C}$ slowly changes to a mosaic-like appearance (Fig.
 203 5a, b) at temperatures of 111 $^{\circ}\text{C}$ and 110.8 $^{\circ}\text{C}$, before reaching the optically uniaxial state (Fig.
 204 5c) at 110.5 $^{\circ}\text{C}$. On further cooling, the high temperature low biaxial phase (SmC_5P_R) transforms
 205 to a low temperature high biaxial SmC_5P_F phase at 110.2 $^{\circ}\text{C}$ (Fig. 5d) and 110.0 $^{\circ}\text{C}$ (Fig. 5f).



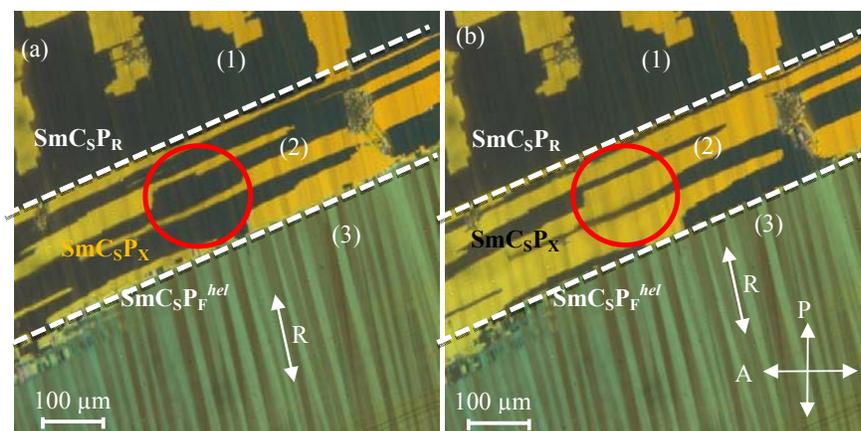
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208

209 FIG. 5. Polarizing microphotographs of the LC phases of compound **1/18** in a homeotropic
 210 aligned cell ($d=6\ \mu\text{m}$): (a) SmC_5P_R at $111\ \text{°C}$, (b) $110.8\ \text{°C}$ (c) SmC_5P_X at $110.5\ \text{°C}$ (d),
 211 SmC_5P_F at $110.2\ \text{°C}$ and (e) $110\ \text{°C}$. Textures are recorded during the cooling process. To
 212 obtain textures (f) and (g) an additional λ -retarder plate is inserted in the homeotropic cell
 213 between the crossed polarizers at temperatures of (f) $120\ \text{°C}$ and (g) at $100\ \text{°C}$, the last two
 214 figures indicate an inversion of birefringence.

215 The birefringence inversion is demonstrated by inserting an additional λ -retarder plate in
 216 between the crossed polarizers (see Figs. 5f, g). This **inversion** is due to the flipping of the
 217 secondary optical axis [29]. An appearance of the optical uniaxiality is considered as an
 218 indication of the formation of intermediate structure, provisionally labeled here as SmC_5P_X . The
 219 temperature range of this SmC_5P_X phase is narrow and is restricted to lie only within $\sim 0.5\ \text{°C}$.
 220 For this reason, three structures corresponding to SmC_5P_R , SmC_5P_X and SmC_5P_F are observed
 221 simultaneously in a small temperature gradient cell (Fig. 6a, b at $U = 0\ \text{V}$). The sequence of
 222 structures is SmC_5P_R (1), SmC_5P_X (2) and SmC_5P_F (3) as temperature decreases from the top to
 223 the bottom of the cell. The application of a conventional AC or DC voltage signal does not affect
 224 the textures in areas, (1) and (2), of the cell, corresponding to SmC_5P_R and SmC_5P_X ,
 225 respectively. On the other hand, in the SmC_5P_X temperature range, an electric current flows on
 226 reversing the electric field which demonstrates electrical switching brought about by the field. A
 227 sudden reversal of the applied field causes reorientation of the **polarization or polar** vector
 228 around the long molecular axis (the so-called “chirality flipping” [35-38]) rather than the
 229 director switching on the tilt cone.



230

231 FIG. 6. Polarizing optical microscopic textures of the LC phases of compound **1/18**
 232 recorded in a small temperature gradient in a $8\ \mu\text{m}$ planar aligned ITO coated cell in

233 between the two electrodes from higher temperature (top) to lower temperature
234 (bottom): SmC_sP_R (1) SmC_sP_X (2) and $\text{SmC}_s\text{P}_F^{hel}$ (3). The cell is kept at a temperature
235 of 110.5 °C and the area (2) in (a) and (b) corresponds to SmC_sP_X showing two
236 bistable states, switched oppositely by reversing the polarity of the applied field via an
237 intermediate short-circuited state, respectively. The red circle in (a) and (b) shows an
238 aperture/area of the cell used for the electro-optical measurements. The white dashed
239 lines in (a) and (b) separate out the SmC_sP_R , SmC_sP_X , and $\text{SmC}_s\text{P}_F^{hel}$ phases.

240 It must be stressed that the optical switching in the temperature range of SmC_sP_X can be
241 achieved only by reversing the polarity of the applied field through an intermediate state, short-
242 circuiting of the electrodes of the cell (Fig. 6a→b; region 2). A reversal in the polarity through
243 short-circuiting over a short period of 0.5 ms brings about both electrical and optical switching.
244 The latter can only occur when the director rotates around the tilt cone. On the removal of the
245 electric field, the optical texture returns to its previously switched state, thus showing bistability
246 at $\mathbf{E} = 0$ (Fig. 6b→a; region 2). Such a phenomenon of optical and electric switching under
247 special conditions has not so far been reported in the literature and is detailed below.

248 In order to investigate the electro-optical response of the sample in the SmC_sP_X phase, a
249 successful conduction of the experiment requires additional precautions to be observed since (i)
250 the temperature range of this phase is quite narrow as stated previously, and (ii) the two opposite
251 $\pm\theta$ domains coexist over an area smaller than the minimal aperture of the electro-optical set-up.
252 Nevertheless, it is possible to select an area of the cell that corresponds to an almost single
253 domain, as shown by red circles in Fig. 6a,b such that the average transmittance level over the
254 aperture of Fig. 6a is less than that of Fig. 6b. Figure 7 shows a corresponding diagram to the
255 oscilloscope screenshots that were recorded for the electro-optical response to the waveform of
256 an applied voltage signal. As already stated, the SmC_sP_X phase shows a polarization switching
257 current but does not optically react to the square-wave signal except for the short spikes that
258 appear on the polarity reversal, shown in Fig. 7a. On considering the importance of the short-
259 circuited state of optical switching, we modify the applied voltage waveform by a sequence of
260 bipolar square pulses separated by a zero-voltage signal existing over relatively short-times (*i.e.*
261 short-circuit), t_0 . Such a modified voltage waveform with a short-circuiting over a period of 0.5
262 ms causes the full electro-optical switching to occur. This waveform designed for the purpose is
263 shown in Fig. 7b with 25 ms/div time scale and is expanded to a waveform of 1 ms/div shown in
264 Fig.7c.

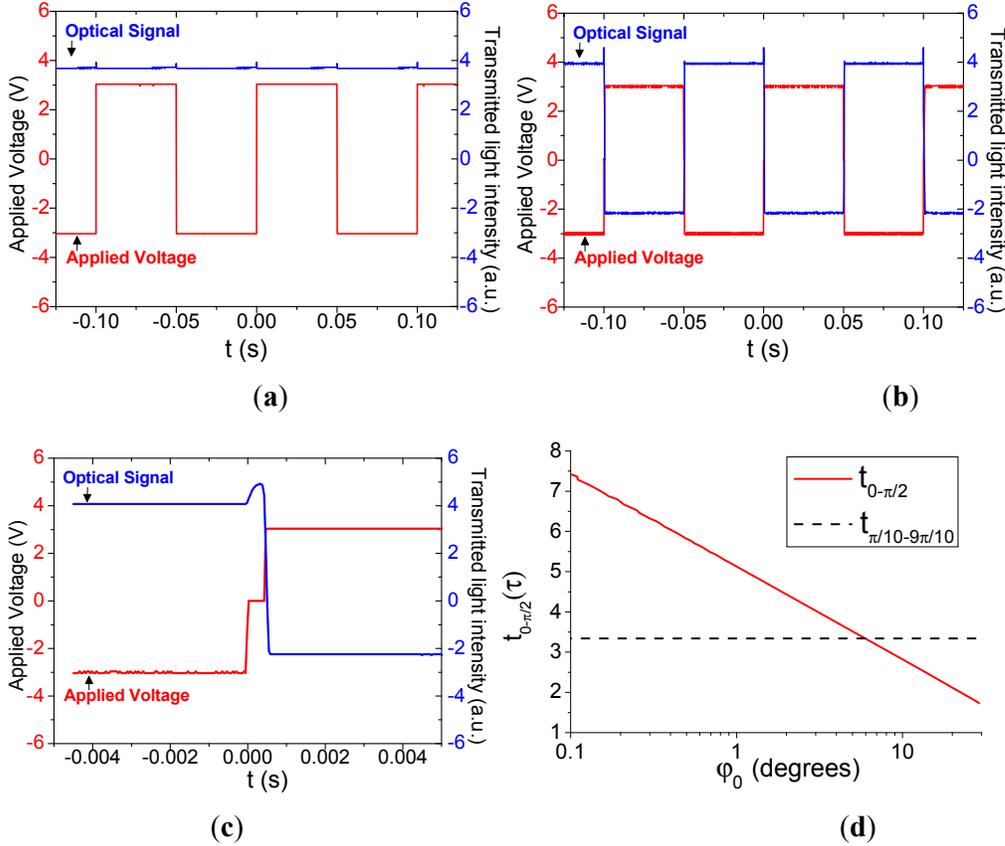


FIG. 7. Electro-optical response of a planar aligned $8 \mu\text{m}$ cell, filled with **1/18** in the SmC_5P_x phase ($T=110.5 \text{ }^\circ\text{C}$), to different applied voltage waveforms (plots of the recorded oscilloscope screen-shots): (a) 60 V square-wave; (b) 60 V bipolar square pulses, separated by zero voltage over a time duration of 0.5 ms in between the pulses; (c) the same as (b) with time scale expanded to 1 ms/div, (d) the calculated dependence of the switching time on ϕ from the initial ϕ_0 state to the critical $\pi/2$ state (solid red line) and from 10% π to 90% π (dashed black line) in the units of τ , where τ is the time constant.

The switching dynamics was modelled theoretically in bent-core LCs in B1 [38] and B2 [39] phases. They consider two competing mechanisms of ferroelectric switching: (i) collective rotation around the long molecular axis, and (ii) collective rotation around the tilt cone. The EO response in B2 phases with temperature and electric field can satisfactorily be explained by Nakata et al.'s model [39] which considers two opposite chirality states separated by an energy barrier $U_{max} \cdot \cos^2(\beta)$. This model also considers two competing mechanisms of switching: (a) chirality flipping due to the molecular rotation around its long molecular axis by an angle β and (b) the optical switching due to rotation of the molecular director on the tilt cone by an angle ϕ . The two dynamical states were modelled by a system of coupled differential equations. These are solved numerically using the Euler-Cauchy method [39]. A key feature of this solution is that both angles start changing from 0 to π on the reversal of the applied electric field. The final switching achieved either by chirality flipping or by the optical switching depends on, which one

289 of the two angles, φ or β , reaches the $\pi/2$ state first. When this angle has reached the $\pi/2$ state,
290 this continues to grow to π , while the second one goes back to its initial value/state.

291 The experimental results show that for low electric fields ($< E_c$) the optical switching by
292 φ -angle is observed. On an increase in the electric field greater than E_c , the LC sample shows β -
293 switching [35, 36, 39]. According to the model [39] the threshold field E_c depends linearly on
294 the energy barrier U_{max} . This model, however, does not explain explicitly the observed
295 temperature dependence of the threshold field. This effect can be explained by the energy barrier
296 U_{max} depending on the molecular tilt angle, θ which in turn depends on temperature. Obviously
297 it is zero for $\theta = 0$ and a maximum for $\theta = 90^\circ$, and the energy barrier can be expressed as
298 $U_{max}=U_0 \cdot \sin^2\theta$. Therefore on an increase in temperature and a consequent decrease in the tilt
299 angle, the energy barrier decreases with temperature. This assists the changeover to chirality
300 flipping (β -switching). In $SmC_S P_X$ phase, the energy barrier is low enough to initially provoke
301 ‘chirality flipping’, (due to a small tilt angle $\theta \approx 17^\circ$). However, the optical switching can also be
302 achieved by using a specially designed sequence of pulses (as shown in Figs.7b and 7c) and by
303 taking into account the azimuthal pretilt angle.

304 Earlier Xue et al. had discussed the switching of molecular directors on the cone in a
305 ferroelectric SmC^* phase consisting of chiral calamitic molecules. They derived analytical
306 solution in *implicit* form, of time t in terms of $\varphi(t)$, the azimuthal angle [40]. Valksman and
307 Panarin, [41] solved it explicitly in terms of $\varphi(t)$ and from it, they found that the delay time t_{0-10}
308 (time taken by the response to go from its initial state of zero to reach 10% of the final response)
309 depends strongly on the initial azimuthal (pretilt) angle φ_0 , while the rise time t_{10-90} (the time
310 taken by the response to go from 10% to 90%) is independent of φ_0 . In the simplest case of the
311 dielectric anisotropy, measured at low frequencies, and specifically for $\Delta\varepsilon=0$, the dynamical
312 equation has an exact analytical solution for $\varphi(t)$ [41]. The dependence of the switching of φ
313 from its initial state φ_0 to its critical $\pi/2$ state, $t_{\varphi_0 \text{ to } \varphi\pi/2} = \log(\pi/2/\tan(\varphi_0/2)) \approx \log(\pi/\varphi_0)$ was
314 found. This is plotted in Fig. 7d as a function of φ_0 . Based on such a solution, we consider two
315 cases of optical response subjected to (i) a square wave signal, and (ii) a series of bipolar
316 pulses.

317 In the first case, the switching begins by reversing the polarity of the switched state. The
318 switched state on the application of E makes the pretilt azimuthal angle φ_0 closer to zero due to
319 large polar interactions of \mathbf{P} with the field \mathbf{E} , ($\mathbf{P} \cdot \mathbf{E}$). This makes the delay time longer for
320 switching by φ (Fig. 7d) and the chirality flipping by β is the only feasible outcome at this stage.
321 In the second scenario, the optical switching by φ begins when the electric field changes from a

322 finite value of E to $E = 0$. In the latter case, the initial pre-tilt angle φ_0 grows from almost zero
 323 value to a finite value depending on the smectic layer tilt δ and the molecular tilt θ as

324 $\varphi_0 = \sin^{-1}(\tan(\delta)/\tan(\theta))$ [42]. From this equation, value of φ_0 is found to range in between $10^\circ -$
 325 20° in the bookshelf structure depending on δ and θ but it takes a finite time for the relaxation to
 326 occur. The switching delay time (Fig. 7d) in this case from φ_0 to $\pi/2$, $t_{\varphi_0-\pi/2} \approx 2 - 3 \tau$. Here φ will
 327 reach the critical value of $\pi/2$ prior to β doing the same, the optical switching through φ is then
 328 the outcome (Fig. 7b, c). Hence at the end of the negative pulse, the low initial value of φ_0
 329 relaxes to a higher value at $E = 0$ but it takes a fraction of a millisecond to achieve (see the
 330 optical response at $E = 0$, Fig. 7c). **When the duration for $E = 0$ is made longer than the**
 331 **relaxation time of φ_0 (~ 0.5 ms, for this case), the optical switching preferably occurs.** However
 332 for shorter short-circuited time periods $\ll 0.5$ ms, the chirality flipping takes precedence **and in**
 333 **that case chirality flipping is the only feasible outcome.**

334 Summarizing, the POM and the electro-optical studies find that SmC_SP_X is an
 335 intermediate uniaxial phase sandwiched in between the SmC_SP_R and SmC_SP_F phases and it has
 336 low enough energy barrier for chirality flipping and this occurs rather easily. But the optical
 337 switching can also be brought about by designing a special sequence of pulses applied to a
 338 **planar-aligned cell** and this has been demonstrated here.

339

340 **B. Birefringence (Δn) measurements**

341 For carrying out the birefringence (Δn) measurements, the transmitted intensity from a well
 342 planar-aligned cell with good alignment is recorded. The rubbing direction \mathbf{R} on the two
 343 substrates are made parallel to each other. \mathbf{R} is fixed at an angle of $\alpha = 45^\circ$ to the
 344 polarizer/analyser in a crossed polarizers system. The transmitted light (T) through a LC cell as
 345 a function of the effective birefringence (Δn_{eff}) is given by [43]:

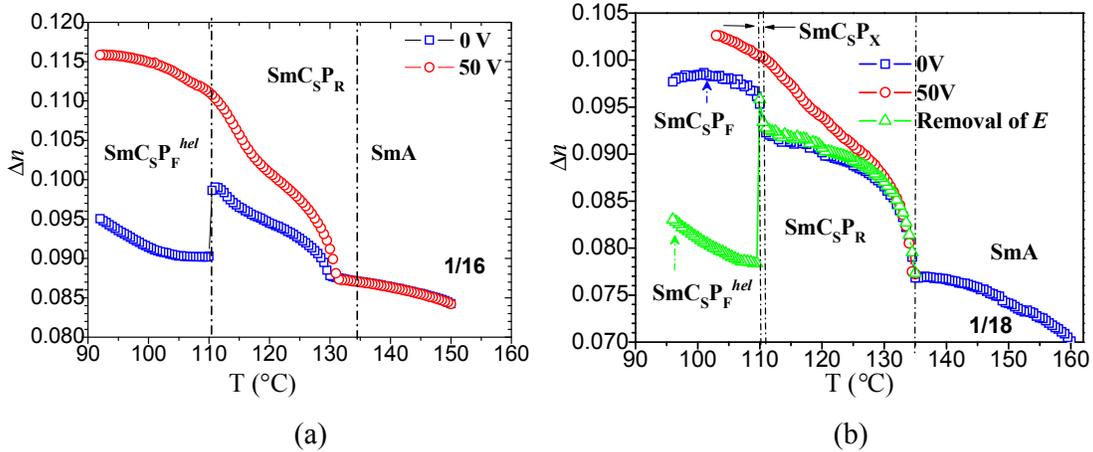
$$346 \quad T = A \sin^2 \left(\frac{\pi \Delta n_{eff} d}{\lambda} \right) + B \quad (1)$$

347 Here λ is the wavelength, d is the cell thickness. A is the scaling factor and B is the offset signal.
 348 The effective birefringence, Δn_{eff} , exhibits dispersion as a function of λ , the latter described by a
 349 modified Cauchy equation (2) [44,45].

$$350 \quad \Delta n_{eff}(\lambda) = k_{eff} \left(\frac{\lambda^2 \lambda^{*2}}{\lambda^2 - \lambda^{*2}} \right) \quad (2)$$

351

352 k_{eff} and λ^* are the parameters of the Cauchy equation. Eqn. 2 is inserted in Eqn. 1 to take in
 353 account the optical dispersion. k_{eff} and λ^* are determined from fits of the transmitted spectrum at
 354 a particular temperature. λ^* so determined is assumed to be a constant over the entire range of
 355 temperatures of investigation. The birefringence as a function of temperature is calculated from
 356 the transmittance spectra by using this determined value of λ^* . Figure 8 shows Δn , calculated as
 357 functions of temperature and voltage from the transmittance data of planar-aligned cells filled
 358 with the bent core LC materials **1/16** (a) and **1/18** (b) both as functions of temperature.



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361 FIG. 8. Temperature and the voltage dependencies of Δn of the LCs (a) **1/16** and (b)
 362 **1/18**. The two substrates are rubbed parallel (**R** on the cell substrates are parallel to
 363 each other). **R** is fixed at an angle of $\alpha = 45^\circ$ to the crossed polarizer/analyzer
 364 directions. Measurements are carried out on planar-aligned cells under cooling for
 365 three different conditions: (i) a virgin state of the cell (\square), (ii) under applied field (\square)
 366 for both **1/16** and **1/18** and (iii) on the removal of the applied electric field (Δ) [green
 367 triangle symbol] for **1/18**.

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The magnitude of Δn increases on cooling from SmA to the SmC₅P_F phase with
 characteristic jumps in Δn occurring at each of the phase transition temperatures. Under a square
 wave voltage of 50 V_{Peak-Peak} ($f = 110$ Hz), the magnitude of Δn , for both samples **1/16** and **1/18**,
 increases in the SmC₅P_R and SmC₅P_F phases. In the SmC₅P_R phase, Δn on removal of the
 electric field is almost equal to the magnitude prior to the field having been applied, for both
 compounds as in the textures recorded. In **1/16**, on further cooling from the SmC₅P_R phase, a
 low birefringent state is observed and it increases with a decrease in temperature. This phase is
 assigned as ‘helical SmC₅P_F’ (SmC₅P_F^{helical}) with a very short helical pitch [30]. It is identical
 with the previously observed, but not fully investigated, helical SmCP _{α} phase found for the
 related compounds with alkoxy chains [29]. It is also related to the weakly tilted or non-tilted
 uniaxial smectic phase with helical rotation of the polar vector, observed for a shorter
 homologue of the series **1/n** with $n = 14$ (also known as PAL 30). In that case, it had been
 designated as SmAP _{α} , because the tilt was not measurable [17]. The observed low values of

381 birefringence in a planar-aligned cell [Figs. 8a, b] arise from the helical structure that gives rise
 382 to a ‘uniaxial homeotropic texture’ [30]. In the SmC_SP_R and SmC_SP_X phases of **1/18** the
 383 magnitude of Δn on removal of the electric field is almost equal to its magnitude prior to the
 384 application of the field. In the SmC_SP_F phase of **1/18**, the Δn values after removal of the field are
 385 much lower than Δn measured prior to the application of the field, in line with the formation of a
 386 helix in SmC_SP_F after the cell has been treated by the electric field. This can be due to the field-
 387 induced [weakening/breaking](#) of the synclinic smectic inter-layer molecular interactions, which
 388 turn out to be stronger in the SmC_SP_F phase of **1/18** (tilt, 23°) than in the same phase of **1/16**
 389 (with a smaller tilt, 17°). For the latter, the helix is spontaneously formed at the transition to the
 390 polar phase, whereas for **1/18** the polar smectic phase requires electric field treatment and in
 391 consequence the helical structure is induced in the latter. The helical state once [formed/induced](#)
 392 is retained even after the field has been removed. This implies that the SmC_SP_F phase of **1/18** on
 393 transition from SmC_SP_X temporarily retains a quasi-stable (surface stabilized) non-helical,
 394 uniformly polar structure which then transforms to the thermodynamically stable helical state
 395 with [a short helical pitch](#). Once formed the helical state of SmC_SP_F does not return or relax back
 396 to its initial uniformly polar SmC_SP_F state.

397 The helical state arises as a consequence of the minimization of the electrostatic energy
 398 from a large in-layers spontaneous polarization P_S in the SmC_SP_F phase. According to a simple
 399 phenomenological theory given by Pikin and Indenbom [46], the helical structure in tilted
 400 smectics is formed by a large spontaneous polarization and is independent of chirality. The latter
 401 determines the sense of the helical winding. For non-chiral LCs, formation of a helical structure
 402 reduces the electrostatic energy but at the same time it increases the elastic energy. Stabilization
 403 of a helical structure is thus a compromise in between these two competing energies:
 404 electrostatic and elastic. The helical pitch is expressed as [46]:

$$405 \quad p_0 = \frac{2\pi K\theta}{\mu P_S} \quad (3)$$

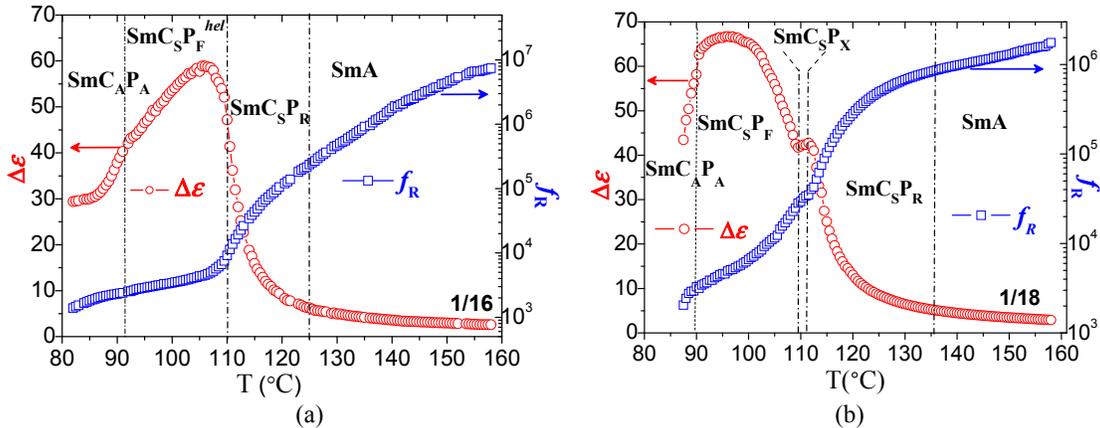
406 where, K is elastic constant, μ is the flexoelectric coefficient, θ is the tilt angle and P_S is the
 407 spontaneous polarisation. The relatively small molecular bend angle in the polar smectic phases
 408 of compound **1/18** provides a weak polar coupling between the layers e.g. a lower elastic
 409 constant K . Therefore, in weakly tilted and weakly coupled polar smectics with large
 410 polarization ($\sim 400 \text{ nC/cm}^2$) the ratio K/P_S is very low when compared to the conventional SmC^*
 411 phase of chiral calamitic molecules. This explains the existence of an anomalously short helical
 412 pitch ($\sim 15 \text{ nm}$) in **1/18** determined using Atomic Force Microscopy (AFM) [30].

413 C. Dielectric spectroscopy

414 The complex permittivity $\epsilon^* = \epsilon' - i\epsilon''$; (i is the imaginary number) is measured as a
 415 function of frequency and temperature by applying a weak probe electric field to a planar-
 416 aligned cell. The experimental values of the dielectric strength ($\Delta\epsilon$) and the relaxation frequency
 417 (f_R) are obtained for samples, **1/16** and **1/18**, by fitting the experimental dielectric spectra to the
 418 Havriliak-Negami equation [47],

$$419 \quad \epsilon^*(\omega) = \epsilon' - i\epsilon'' = \epsilon_\infty + \sum_{j=1}^n \frac{\Delta\epsilon_j}{[1 + (i\omega\tau_j)^{\alpha_j}]^{\beta_j}} - \frac{i\sigma_{dc}}{\epsilon_0\omega} \quad (4)$$

420 where ϵ_∞ is the high frequency dielectric permittivity, j varies from 1 to n (where n is the number
 421 of relaxation process), $\omega = 2\pi f$ is the angular frequency, ϵ_0 is the permittivity of free space, τ_j is
 422 the relaxation time, $\Delta\epsilon_j$ is the corresponding dielectric relaxation strength, α_j and β_j are the
 423 respective symmetric and asymmetric broadening parameters corresponding to the j^{th} process.
 424 $\sigma_{dc}/\epsilon_0\omega$ is the contribution of dc conductivity to ϵ'' . The relaxation frequency, f_j , of the j^{th} process



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427 FIG. 9. Dielectric relaxation strength $\Delta\epsilon$ (o) and corresponding relaxation frequency
 428 f_R (□) for the two samples (a) **1/16** ($d= 8 \mu\text{m}$) and (b) **1/18** ($d= 6.6 \mu\text{m}$) in planar-
 429 aligned cells as a function of temperature. Measurements are carried out under the
 430 cooling process.

431 is related to τ_j [48] as

$$432 \quad f_j = \frac{1}{2\pi\tau_j} \left[\frac{\sin(\alpha_j\pi)}{2+2\beta_j} \right]^{1/\alpha_j} \left[\frac{\sin(\alpha_j\beta_j\pi)}{2+2\beta_j} \right]^{-1/\alpha_j} \quad (5)$$

433 The temperature dependencies of $\Delta\epsilon$ and f_R for the main relaxation process are fitted to Eqn. 4,
 434 results from which are shown in Figs. 9a (**1/16**) and 9b (**1/18**) respectively.

435 The dielectric strength $\Delta\epsilon$ of the SmC_SP_R phase for both **1/16** and **1/18** samples increases
 436 gradually with decreasing temperature. This implies a soft mode-like increase in the correlations

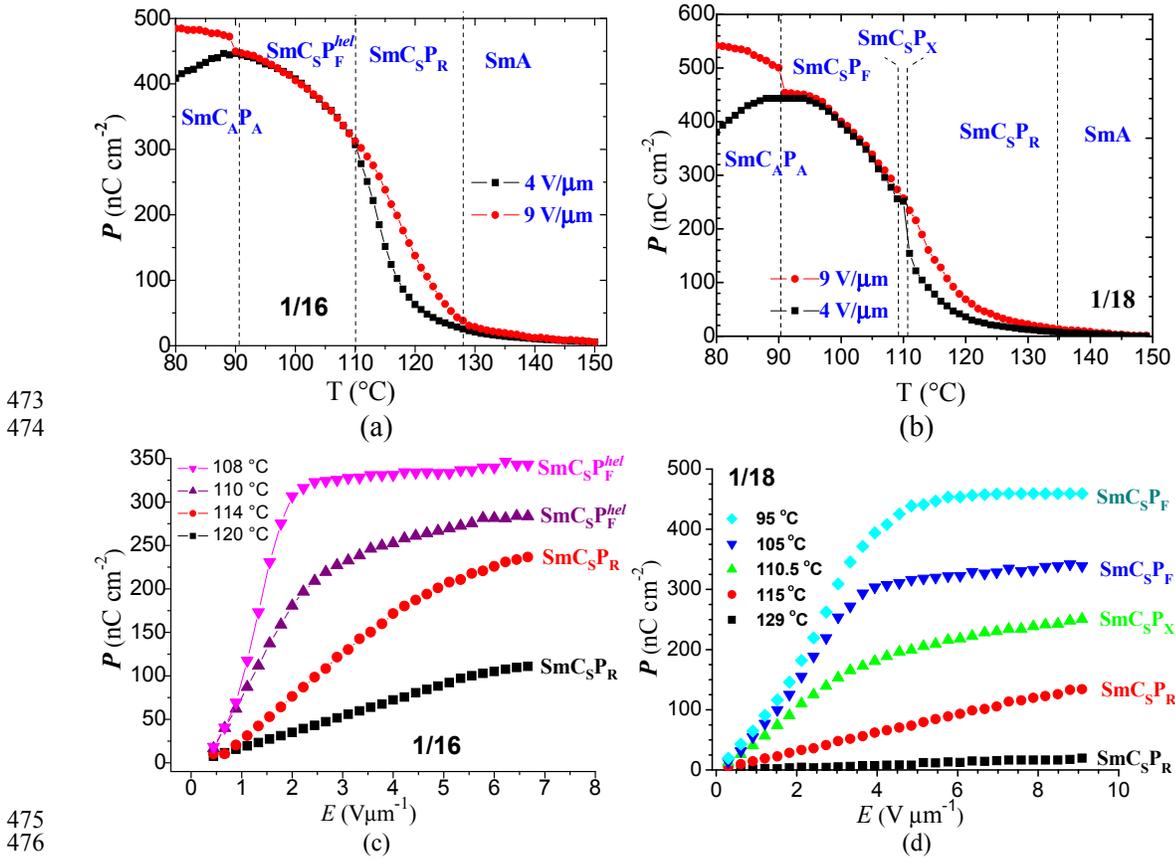
437 of the neighboring molecules on transition to the polar SmCP phase. The corresponding f_R of the
438 relaxation process decreases with decreasing temperature. In the SmC_SP_R phase close to the
439 transition temperature of the SmC_SP_F^{hel} (in **1/16**)/ SmC_SP_F (in **1/18**) phase, the soft mode $\Delta\epsilon$
440 sharply increases and f_R sharply decreases. The temperature dependencies of $\Delta\epsilon$ at the SmC_SP_R to
441 SmC_SP_F are fitted to a power law equation $\Delta\epsilon = k / (T - T_c)^\gamma$; exponent γ is found as 1.5 for **1/16**,
442 and 1.55 for **1/18**, both larger than the typical value of ~ 1.3 found for a conventional SmA –
443 SmC phase transition. Magnitude of the exponent is reminiscent of the de Vries scenario at the
444 SmA* to SmC* transition [49-51]. On further cooling of **1/18** in a planar-aligned cell, we
445 observe a small step-like behavior in a narrow range of temperatures 110.7 °C–110.2 °C
446 (SmC_SP_X) with a magnitude of $\Delta\epsilon \sim 42.3$ (Fig. 9b). However, in the **1/16** sample (Fig. 9a), $\Delta\epsilon$
447 increases with a characteristic jump at the SmC_SP_R to SmC_SP_F^{hel} phase transition at 110 °C and
448 then decreases slowly on the formation of a helix. In the SmC_SP_F^{hel} phase of **1/16** sample, the
449 helix can easily be distorted by a weak external electric field and a change in the macroscopic
450 polarization with the applied field is very significant and the relative permittivity is also large.
451 The rise of $\Delta\epsilon$ in the SmC_SP_X and SmC_SP_F phases of **1/18** can be explained by a competition
452 between the increase in the polarization and a corresponding escape from the polar order through
453 formation of a helical structure as well as forming anti-polar correlations on approaching the
454 SmC_AP_A phase. The latter is also composed of polar layers with polar directions alternating
455 from layer to layer thus resulting in a decrease in $\Delta\epsilon$. The dielectric behavior both in the
456 dielectric strength and the relaxation frequency is characteristically different from the SmA* and
457 SmC* phases of calamitic chiral LCs [52, 53].

458 **D. Polarization measurements**

459 Figure 10 shows the temperature and field dependencies of the induced polarization P
460 measured using planar-aligned cells, filled with compounds **1/16** and **1/18**. Measurements are
461 carried out in the cooling process under application of a square voltage waveform of frequency
462 110 Hz using the method reported previously [41,42].

463 The shape of the polarization curves (Fig. 10a, b) as a function of temperature at electric
464 fields up to 9 V/ μm is similar to the observed temperature dependencies of dielectric strength $\Delta\epsilon$
465 (Fig. 9a, b). In SmC_SP_R, both P and $\Delta\epsilon$, show critical behavior similar to the de Vries SmA* to
466 SmC* transition but different from the conventional SmA* to SmC* transition. In this phase, the
467 measured polarization is electric field–induced and hence is field dependent. However, in the
468 SmC_SP_X ($\sim 250 \text{ nC cm}^{-2}$) and SmC_SP_F phases of **1/18** and in the SmC_SP_F^{hel} phase of **1/16** the P
469 value is independent of the field, hence it is the spontaneous polarization. In the SmC_AP_A phase
470 P decreases for low electric fields ($\sim 390 \text{ nC cm}^{-2}$ at 80 °C) due to the formation of

471 antiferroelectric order, while at higher electric fields, the ferroelectric state is induced and P
 472 grows to $\sim 450 \text{ nC cm}^{-2}$.



477 FIG. 10. Temperature and field dependencies of P measured in planar-aligned cells (a)
 478 and (c) filled with compound **1/16** ($9 \mu\text{m}$) and (b) and (d) filled with compound **1/18**
 479 ($6.3 \mu\text{m}$). Measurements are carried out by applying a square wave AC voltage
 480 waveform at a frequency of 110 Hz.

481 The field dependencies of P are shown in Fig. 10c, d. There is a linear increase with the
 482 field in the temperature range of SmC_SP_R phase with its slope increasing with decreasing field, in
 483 line with that observed for paraelectric switching. In the SmC_SP_F phase however, there is
 484 saturation at a field of $4 \text{ V } \mu\text{m}^{-1}$ followed by a plateau. These are the typical features of polar
 485 switching. In the intermediate state i.e. in the SmC_SP_X range of **1/18**, the field dependency of P
 486 is intermediate in between SmC_SP_R and SmC_SP_F . In the temperature range of this phase an initial
 487 increasing trend in slope of P with temperature registers a decrease at $\sim 4 \text{ V } \mu\text{m}^{-1}$ but up to ~ 9
 488 $\text{V } \mu\text{m}^{-1}$ the $P(E)$ curve does not appear to reach a plateau in P .

489 IV. CONCLUSIONS

490 A detailed investigation of 4-cyanoresorcinol bisbenzoate bent-core LCs terminated by
 491 long alkyl chains, $n = 16, 18$ has been carried out by using a range of experimental methods: such

492 as polarizing microscopy, electro-optics, birefringence, dielectric and polarization
493 measurements. Here we present results of a new intermediate SmC_SP_X phase in **1/18** material at
494 the transition from the short to the long-range polar order in the layers. This phase is an
495 intermediate state in the transition in between SmC_SP_R and SmC_SP_F and is uniaxial with a low
496 energy barrier for chirality flipping. Due to such a low barrier, the application of an electric field
497 enables chirality flipping to occur, rather than electro-optical switching on the tilt cone, as
498 observed for the majority of other polar smectic phases. Nevertheless, the SmC_SP_X phase also
499 shows optical switching on application of bipolar pulses separated by short-circuited pulses. This
500 transition from chirality flipping to optical switching is explained by the dynamic model given
501 by Nakata *et al.* [39] where additionally the initial pre-tilt angle, φ_0 , is taken into account. The
502 energy barrier [depending](#) on the molecular tilt angle is also taken into consideration. Switching
503 by rotation of the director on a tilt cone is a signature of the transition from the Langevin-type
504 switching in SmC_SP_R to the polar optical switching in SmC_SP_F .

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