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Novel Ferroelectric and Antiferroelectric Smectic and Columnar Mesophases in Fluorinated Symmetrical Bent-Core Compounds

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We report the synthesis and mesomorphic properties of new bent-core (BC) mesogens exhibiting novel antiferroelectric switching columnar phases with rectangular as well as oblique lattices. The homologues with short chains show typical nonswitchable rectangular columnar (B_1) phase and a ferroelectric switching smectic phase is obtained for the middle homologues. Interestingly, with increasing chain length, the switchable columnar phases are induced and the X-ray diffraction pattern with well-oriented samples indicates the presence of rectangular and oblique lattices. On the basis of the experimental observations, possible models have been proposed for these phases. Field-induced SmC_SP_F and M_x phases are also observed in the ferroelectric and antiferroelectric rectangular columnar phases, at high and low temperatures, respectively. Switching chiral domains of opposite handedness as well as a change in the sense of chirality within a domain could also be observed for the first time for the ferroelectric phase. Two different switching mechanisms in the ferroelectric and antiferroelectric columnar phases have also been observed. In the presently investigated two series of compounds, the electrooptical switching changes from ferroelectric to antiferroelectric behavior with increasing chain length.

Introduction

Banana liquid crystals (liquid crystals formed by compounds whose constituent molecules have a bent core) have gained considerable importance over the past few years. This is due to such compounds forming polar smectics,[1−3] viz., ferro- and antiferro-electric phases as also a wide variety of polar columnar mesophases.[4] In addition, very careful high resolution experiments carried out recently[5] in establishing new structures, namely, modulated smectic phases with splay polarization, have enhanced further growth. Among the various liquid crystalline phases, the ferroelectric liquid crystals have attracted more interest because of the piezo-, pyroelectric, and second-order nonlinear optical properties that they exhibit. Ferroelectricity was first observed[6] in crystals with a noncentrosymmetric structure. The discovery of ferroelectricity in liquid crystals is due to the pioneering work of Meyer et al.[7] who showed that one of the requirements for this phenomenon to occur is compounds composed of enantiomerically rich lath-like molecules which tilt in the smectic layers. A large number of such ferroelectric liquid crystals have already been synthesized and investigated for various physical properties and applications. However, in 1996, Niori et al.[1] reported ferroelectric switching behavior in compounds composed of achiral banana-shaped molecules (later, the mesophase has been proved to be antiferroelectric[2]). The origin of ferro- and antiferro-electricity in these compounds was attributed to the efficient packing of the bent-core (BC) molecules into smectic layers or columns, which restrict the rotation around the long molecular axis. As a result of this kind of arrangement of the molecules in the mesophase, a polarization along the bend direction is induced. This induced polarization can be reversed by the application of an external electric field. Further, the tilt of BC molecules wrt the layer normal induces the layer chirality[2] in the mesophase which can be either right-handed (H+) or left-handed (H−) depending on the directions of tilt and polar axis wrt the layer normal. This is because the tilt and polarity are independent unlike in chiral calamitic liquid crystals. Depending on the direction of polarization in adjacent layers or columns, the mesophase can have either ferro- and/or

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antiferroelectric ground-state structure. Further, depending on the tilt sense of molecules in adjacent layers/columns, the mesophase obtained could be chiral [C_SP_F, synclinic (uniform) tilt of molecules with ferroelectric polarization in adjacent layers or columns; C_AP_A, anticlinic (alternating) tilt of molecules with an antiferroelectric polarization in adjacent layers or columns] or racemic [C_AP_F, anticlinic (alternating) tilt of molecules with ferroelectric polarization in adjacent layers or columns; C_SP_A, synclinic (uniform) tilt of molecules with an antiferroelectric polarization in adjacent layers or columns], or a mixture of both.[2] In other words, in the SmC_AP_A and SmC_SP_F structures the uniform chirality of all the layers leads to a homogeneously chiral state, whereas in the SmC_SP_A and SmC_AP_F structures the chirality alternates from layer to layer producing a macroscopically racemic state.

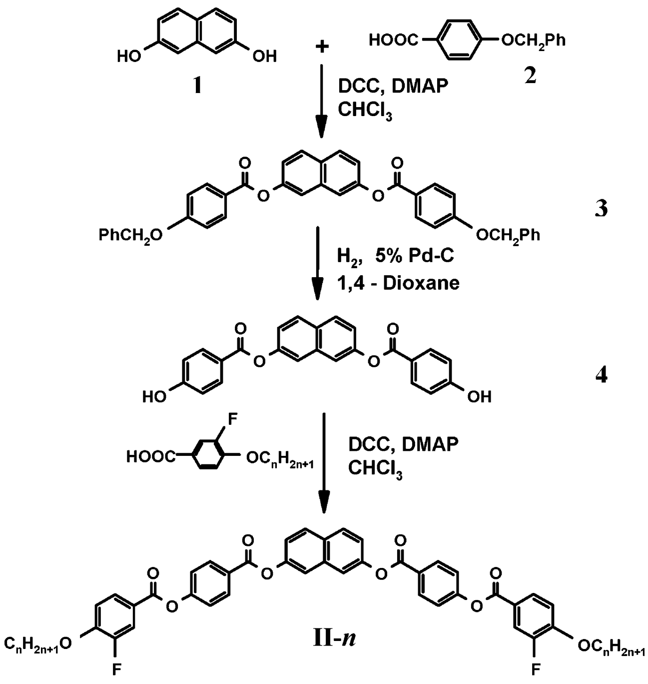
However, from the available data reported so far, it is known that most of the chiral mesophases exhibited by bent-core compounds have an antiferroelectric interlayer structure. There are exceptions to these general observations, such as the brilliant approach by Walba et al.[8] who introduced a racemic octan-2-ol moiety in one of the terminal positions of a bent-core structure. Similarly, the introduction of a fluorine substituent *ortho* to the terminal *n*-alkoxy chains also results in a ferroelectric switching phase.[9] Several attempts have been made to understand the occurrence of ferroelectricity in BC compounds. Recently, Tschierske et al.[10] designed and synthesized a new class of BC molecules in which one of the terminal positions contains an oligosiloxane unit and such compounds do show ferroelectric switching behavior. On the basis of these experimental observations, they have speculated that the occurrence of ferro- and anti-ferroelectricity in banana liquid crystals may strongly depend on the interlayer interactions. However, this may not be applicable to the columnar phases due to the presence of the frustrated layer structures which provide the most efficient escape from the macroscopic polarization.

Herein we report a new homologous series of BC compounds in which the influence of a fluorine substituent, as well as the length of the terminal chain, on the liquid crystalline properties have been investigated. All these compounds are symmetrical six-ring esters containing a fluorine on the outer phenyl ring *ortho* to the *n*-alkoxy chain and are derived from a 2,7-dihydroxynaphthalene central unit. These results have been compared with the previously reported[4b] compounds containing a resorcinol central unit.

Results and Discussion

(a) Synthesis. The bent-core compounds belonging to the two homologous series, viz. series **I-*n*** and **II-*n*** (*n* indicates the aliphatic chain length) were prepared following a general synthetic pathway shown in Scheme 1. The detailed synthesis and characterization of compounds of series **I-*n*** are reported in an earlier publication.[4b] Compounds of series **II-*n*** were synthesized as follows. The commercial 2,7-dihydroxynaphthalene obtained was purified by column chromatography and crystallized. 4-Benzyloxybenzoic acid was prepared following a procedure described earlier.[4b] 3-Fluoro-4-*n*-alkoxybenzoic acids were prepared as reported[4b] previously. The phenol **4** was obtained in two steps: first by the esterification reaction of 2,7-dihydroxynaphthalene, **1**, with 4-benzyloxybenzoic acid, **2**, in the presence of *N*,*N*′-dicyclohexylcarbodiimide as dehydrating agent and 4-(*N*,*N*-dimethylamino)pyridine as a catalyst, followed by hydrogenolysis of the product **3** thus obtained using 5% Pd−C in 1,4-dioxane under an atmosphere of hydrogen. The bisphenol **4** obtained was condensed with two equiv of an appropriate 3-fluoro-4-*n*-alkoxybenzoic acid following the esterification reaction described above to obtain the target compounds, **II-*n***.

Scheme 1. Synthetic Route Employed for the Preparation of New Banana-Shaped Mesogens



n=4,7,9,10………16,18,20

(b) Mesomorphic Properties of the Compounds of Series I-*n*. The mesomorphic properties of all the compounds were investigated using classical techniques. The transition temperatures and the associated enthalpy values obtained for the compounds of series **I-*n*** and **II-*n*** are summarized in Tables 1 and 2, respectively. The mesomorphic properties of compounds **I-*n*** have already been reported in an earlier publication.[4b] As described, compounds **I-7** to **I-11** are not liquid crystalline and the mesophase of compounds **I-12** to **I-16** is smectic with dark textures that show chiral domains of opposite handedness on rotating either the polarizer or analyzer. This mesophase shows ferroelectric switching characteristics and has been designated as SmC_SP_F. Interestingly, compounds **I-18** and **I-20** showed very interesting mesomorphic behavior. A detailed electrooptical investigation of the ferroelectric switching phase of compound **I-18**

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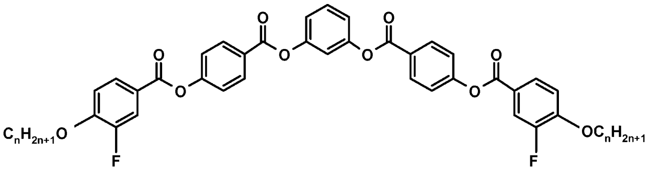
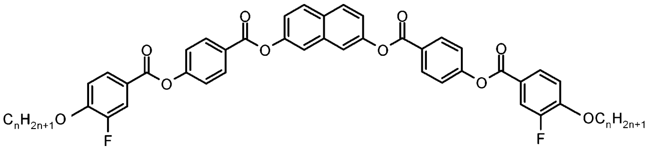
Table 1. Transition Temperatures (T/°C) and Enthalpies (ΔH/kJ mol^{-1}) (in brackets) for Compounds I-n[b]



compound	n	phase transition temperature °C (enthalpy, kJ mol^{-1})
I-7	7	Cr 130.0 (73.3) I
I-9	9	Cr 130.0 (47.6) I
I-10	10	Cr 129.0 (85.7) I
I-11	11	Cr 129.0 (111) I
I-12	12	Cr 128.0 (110) (SmC$_S$P$_F$ 127.5) (21.8) I
I-14	14	Cr 124.0 (97.9) SmC$_S$P$_F$ 128.5 (23.3) I
I-16	16	Cr 121.0 (104.9) SmC$_S$P$_F$ 129.0 (24.3) I
I-18	18	Cr 118.0 (125.7) Col$_{rF}$ 128.5 (24.4) I
I-20	20	Cr 117.5 (95.8) Col$_{rAF}$ 127.0 (24.5) I
I-20[a]	20	Cr 117.5 M$_X$ $\leftarrow$ Col$_{rAF}$ 127.0 I

[a] Phase transitions under an electric field. [b] Abbreviations (applicable to Tables 1 and 2): Cr, crystalline phase; Col$_r$, rectangular columnar mesophase (B$_1$ phase); SmC$_S$P$_F$, ferroelectric polar synclinic correlated smectic C phase; Col$_{rF}$, ferroelectric switching columnar phase with a rectangular centered lattice; Col$_{rAF}$, antiferroelectric switching novel columnar phase with a rectangular centered lattice; Col$_{obAF}$, =antiferroelectric switching novel columnar phase with an oblique lattice; M$_x$, unidentified mesophase with a smectic type structure; I, isotropic phase.

Table 2. Transition Temperatures (T/°C) and Enthalpies (ΔH/kJ mol^{-1}) (in brackets) for Compounds II-n[b]



compound	n	phase transition temperature °C (enthalpy, kJ mol^{-1})
II-4	4	Cr 170.0 (29.5) Col$_r$ 207.0 (12.9) I
II-7	7	Cr 164.0 (51.7) Col$_r$ 189.5 (18.9) I
II-9	9	Cr 156.0 (57.6) Col$_r$ 183.0 (19.2) I
II-10	10	Cr 156.5 (58.4) SmC$_S$P$_F$ 183.5 (19.4) I
II-11	11	Cr 154.5 (81.8) SmC$_S$P$_F$ 183.5 (20.3) I
II-12	12	Cr 155.0 (84.9) SmC$_S$P$_F$ 184.0 (20.7) I
II-13	13	Cr 155.0 (102.0) Col$_{rF}$ 184.5 (22.7) I
II-13[a]	13	Cr 155.0 Col$_{rF}$ 179.0 SmC$_S$P$_F$ 184.5 I
II-14	14	Cr 155.5 (94.7) Col$_{rF}$ 184.0 (22.0) I
II-14[a]	14	Cr 155.5 Col$_{rF}$ 175.0 SmC$_S$P$_F$ 184.0 I
II-15	15	Cr 152.5 (105.5) Col$_{rAF}$ 184.0 (23.5) I
II-15[a]	15	Cr 152.5 M$_x$ $\leftarrow$ Col$_{rAF}$ 184.0 I
II-16	16	Cr 152.5 (99.8) Col$_{rAF}$ 184.0 (22.1) I
II-16[a]	16	Cr 152.5 M$_x$ $\leftarrow$ Col$_{rAF}$ 184.0 I
II-18	18	Cr 151.0 (112.0) Col$_{obAF}$ 182.5 (21.9) I
II-20	20	Cr 149.5 (92.3) Col$_{obAF}$ 180.0 (22.6) I

[a] Phase transitions under an electric field. [b] Abbreviations are the same as those listed for Table 1.

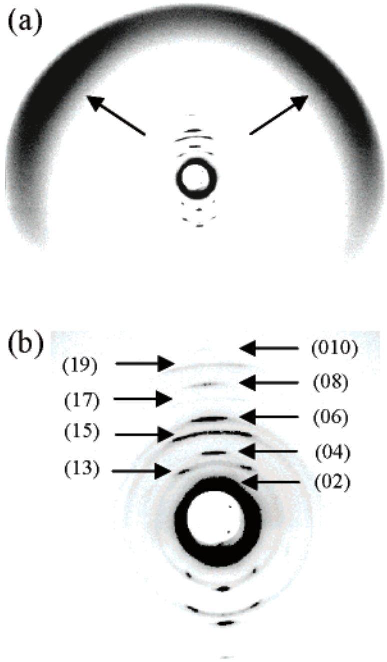


Figure 1. (a) X-ray diffraction pattern of an aligned sample of the Col$_{rF}$ phase of compound **I-18** at 120 °C; arrows indicate the preferred orientation direction of aliphatic/aromatic parts in the wide angle region; (b) expanded small angle region of (a) together with the Miller indices.

has already been reported.[4b] As described, this mesophase shows bistable (ferroelectric) switching and has been designated as B$_{X2}$ phase. The X-ray diffraction (XRD) pattern of an aligned sample (Figure 1) shows strong reflections in the small angle region indicating a two-dimensional structure for the mesophase. The XRD data together with the Miller indices confirm the columnar phase with a centered rectangular lattice. The calculated tilt angle of molecules from the oriented pattern is about 35°. The lattice parameter values as well as the Miller indices obtained are recorded in Table 3. The value of the lattice parameter b is almost double the molecular length by assuming a tilt of the molecules. The total number of molecules estimated is about 14 per unit cell. On the basis of these X-ray and electrooptical investigations, now this mesophase has been designated as Col$_{rF}$ phase. The bistable switching domains[4b] with tilted extinction cross or dark brushes (obtained when the orientation direction of the long axes of the bent-core molecules coincides with the position of the optical axes) in the ground state clearly indicate a synclinic tilt of the molecules in adjacent clusters or fragments. The bistable switching process suggests that the polarization reversal takes place around a tilt cone of the molecules as often observed in the classical SmC* materials (see Figure 7 later for more details about the switching mechanism).

The mesophase of compound **I-20** showed the following features. On cooling the isotropic liquid under a polarizing microscope, the mesophase exhibited a fan-shaped texture. The electrooptical investigations were carried out by sandwiching a sample between two ITO-coated conducting glass plates (thickness 11.4 μm). On cooling the isotropic liquid to the mesophase and applying a triangular-wave electric field of about ±13 Vμm^{-1} at 30 Hz, two polarization current peaks appeared and the switching current response obtained is shown in Figure 2b. The calculated polarization value is about 810 nC cm^{-2}. The textural patterns obtained under these conditions are shown below the current response traces. Based on these, the mesophase has been abbreviated as Col$_{rAF}$ (see XRD studies for more details). No optical switching could be observed under these conditions and the polarization reversal that takes place by a collective rotation of molecules around the long axis.[4c] On lowering the temperature, one of the polarization peaks gradually disappeared and the remaining peak grew sharply and saturated as shown in Figure 2a. However, no change in the polarization value could be

Table 3. *d*-Spacings (Å) Obtained in the Mesophases of Some Compounds of Series I-*n* and II-*n*[a]

compound	*d*-spacings/Å	phase type	*T*/°C
I-18	46.7 (02), 26.6 (13), 23.5 (04), 17.8 (15), 15.9 (06), 13.0 (17), 11.9 (08), 10.3 (19), 9.4 (010); Calcd: 23.8 (04), 17.5 (15), 15.6 (06), 12.9 (17), 11.7 (08), 10.2 (19), 9.3 (010); $a = 51.2$ and $b = 93.4$.	Col_{rF}	120
I-20	48.7 (02), 27.7 (13), 24.9 (04), 18.7 (15), 16.6 (06), 13.7 (17), 12.4 (08), 11.0 (19); Calcd: 24.4 (04), 18.3 (15), 16.2 (06), 13.5 (17), 12.2 (08), 10.6 (19); $a = 53.1$ and $b = 97.4$.	Col_{rAF}	119
II-14	42.8 (02), 24.2 (13), 21.2 (04), 16.3 (15), 14.1 (06), 12.0 (17), 10.7 (08), 9.5 (19); Calcd: 21.4 (04), 16.0 (15), 14.2 (06), 11.8 (17), 10.7 (08), 9.3 (19); $a = 45.6$ and $b = 85.7$.	Col_{rF}	162
II-15	44.5 (02), 25.7 (13), 22.3 (04), 17.2 (15), 15.0 (06), 12.9 (17), 10.0 (19); Calcd: 22.2 (04), 16.8 (15), 14.8 (06), 12.3 (17), 9.7 (19); $a = 51.4$ and $b = 89.0$.	Col_{rAF}	160
II-16	45.0 (02), 26.6 (13), 22.4 (04), 17.7 (15), 15.0 (06), 10.2 (19); Calcd: 22.5 (04), 17.2 (15), 15.0 (06), 9.8 (19); $a = 57.5$ and $b = 90.0$.	Col_{rAF}	160
II-18	46.5 (01), 35.1 (10), 29.4 (11), 26.9 ($\bar{1}$1), 23.2 (02), 18.6 ($\bar{1}$2), 15.7 ($\bar{2}$1), 10.9 ($\bar{3}$1); Calcd: 26.8 ($\bar{1}$1), 23.2 (02), 18.6 ($\bar{1}$2), 15.9 ($\bar{2}$1), 11.1 ($\bar{3}$1); $a = 35.3$, $b = 46.7$; $\beta = 84.6°$.	Col_{obAF}	165
II-20	48.8 (01), 31.4 (10), 27.0 (11), 24.3 (02), 19.8 (12), 16.4 (03), 11.9 (14); Calcd: 24.4 (02), 19.8 (12), 16.3 (03), 11.6 (14); $a = 31.4$, $b = 48.8$; $\beta = 87.2°$.	Col_{obAF}	160

[a] XRD measurements have been carried out on mesophases obtained on cooling.

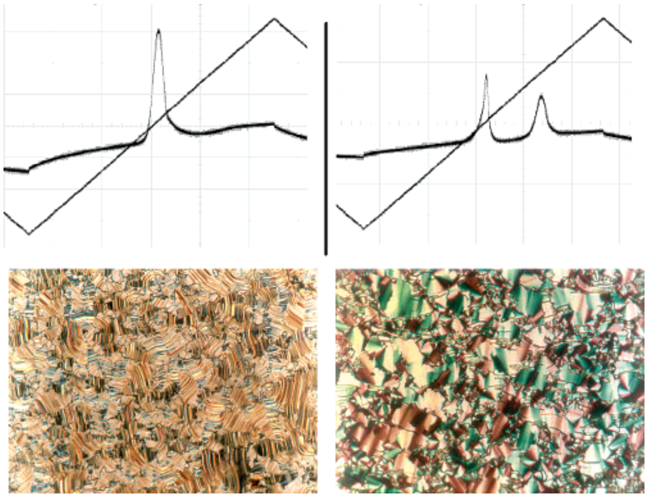

(a) (b)

Figure 2. Switching current response traces to a triangular-wave field and the corresponding optical photomicrographs obtained for the mesophase of compound **I-20**: (a) at 118 °C, and (b) at 124 °C.

observed at the transition, except for a small shift in the position of the polarization peak. Also, a complete change in the textural pattern took place at the transition and a photomicrograph of this is shown below the corresponding current response trace (Figure 2a). The field induced phase and texture are stable even on terminating the applied field. However, at this temperature neither a change in transition enthalpy nor a change in the XRD pattern could be observed in the absence of electric field. Furthermore, the phase transition temperature depends on the experimental conditions such as frequency and applied voltage. An increase in the voltage or the frequency stabilizes the low-temperature ferroelectric switching phase, which means that the phase transition temperature increases. The field induced texture at low temperature is indicative of a smectic phase and the striped pattern suggests a synclinic tilt of the molecules. These observations suggest the following. (1) The phase is antiferroelectric over the entire thermal range of the mesophase and due to the high viscosity the higher switching voltage required favors a direct switching between the two ferroelectric states which results in a single polarization peak with decreasing temperature. (2) The organization of fragments in the columnar phase (clusters of molecules are induced from smectic layers) is such that with decreasing temperature, frustration between the fragments decreases which leads to the formation of smectic structure under the field. In addition, a continuous decrease in the threshold voltage with decreasing temperature further supports such a phase transition. This is somewhat similar to a phase transition observed[11,12] between B_1 and B_2 phases with an applied electric field and without a field. However, we have not succeeded as yet in carrying out the XRD measurements under the electric field to prove the smectic structure of the low-temperature phase. Hence, the low-temperature ferroelectric switching phase has been designated as M_X phase. The XRD data of an oriented sample of the columnar phase can be indexed to a centered rectangular lattice as obtained for the mesophase of compound **I-18**. The small angle XRD data together with the Miller indices obtained for the mesophase of compound **I-20** are recorded in Table 3. The outer scattering is diffuse with a maximum at 4.7 Å indicating a mesophase structure without long-range positional order within the columns. It is located out of the equatorial plane, which confirms a tilted arrangement of the molecules (38°).

It should be noted that the oriented XRD patterns obtained for the mesophases of compounds **I-18** and **I-20** are indicative of a centered rectangular lattice. As reported[4b] by us, the mesophase of compound **I-18** shows only ferroelectric (bistable) switching, whereas that of compound **I-20** shows antiferroelectric switching characteristics.

(c) Mesomorphic Properties of the Compounds of Series II-*n*. The new set of compounds **II-*n*** were obtained by replacing the 1,3-phenylene central unit with a 2,7-naphthylene system. The transition temperatures and the associated enthalpy values obtained for these compounds are recorded in Table 2. A total of 12 compounds were synthesized and investigated and they exhibit six different mesophases including the field induced phases which are described below.

The mesophase of compounds **II-4** to **II-9** shows textural features that are normally observed for a rectangular columnar (Col_r) B_1 phase. This phase assignment was further confirmed by XRD studies. The X-ray diffraction pattern

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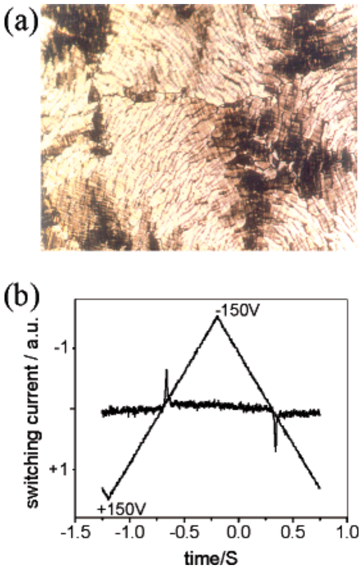

Figure 3. (a) Birefringent fan-shaped texture obtained in SmC_SP_F phase of compound **II-11** under a triangular-wave electric field. (b) Ferroelectric switching current response trace obtained on application of a triangular-wave electric field (±25 Vμm^{-1}, 0.2 Hz).

obtained for compound **II-9** is described as an example. The powder diffraction pattern shows four sharp reflections in the small angle region corresponding to $d_1 = 34.9$ Å (11), $d_2 = 21.2$ Å (02), $d_3 = 17.4$ Å (22), and $d_4 = 13.9$ Å (13) which could be indexed on to a centered rectangular lattice. The lattice parameter values obtained are $a = 60.9$ Å and $b = 42.4$ Å. The lattice parameter b corresponds to the length of the molecule. We have also recorded the XRD pattern of an aligned sample which confirms the indexing of the small angle region. In addition, the wide-angle diffuse region aligned in the perpendicular direction wrt the (02) reflection in the meridian suggests no tilt of the molecules.[4e,g] On the basis of these observations, a molecular model for the Col_r phase with an orthogonal arrangement of molecules has been proposed.[4e,g] The calculated number of molecules was found to be about 9 per unit cell and 4−5 molecules in each cluster or a ribbon. Because of slow response time to an applied electric field coupled with high viscosity, no electrooptical current response was recorded in this mesophase.

On increasing the chain length, compounds **II-10** to **II-12** were obtained. The mesophases of these showed dark textures and the domains of opposite chirality could be visualized by rotating the polarizer or analyzer. The textural features, as well as the switching characteristics, are similar to those observed for a B_{X1} phase.[4b] XRD investigations suggested a smectic phase without in-plane positional order. For example, compound **II-11** showed two sharp reflections in the small angle region, corresponding to $d_1 = 40.5$ Å (01) and $d_2 = 20.3$ Å (02) and an outer diffuse maximum at $d = 4.7$ Å. Electrooptical switching characteristics were determined on an 11-μm thick sample. A triangular-wave voltage was applied to the mesophase below the clearing temperature. At lower voltages (below threshold) the mesophase appeared dark, while above the threshold it exhibited a birefringent texture as shown in Figure 3a. Simultaneously, a single polarization current peak appeared in the triangular-wave indicating a ferroelectric switching for the smectic phase. Only ferroelectric switching was observed down to a frequency of 0.1 Hz (see Figure 3b) over the entire range of temperature even at different voltages. The switching current response obtained in modified triangular-wave[3d,9] (plateau is introduced at zero voltage) is a further indication for the ferroelectric switching. The spontaneous polarization value obtained was about 600 nC cm^{-2} (close to the clearing temperature) which increased to 675 nC cm^{-2} with decreasing temperature. The birefringent texture obtained under the field was retained even on terminating the applied field. Furthermore, bistable switching states obtained under a dc electric field (110 V, 5 μm) confirmed the ferroelectric switching for the mesophase. As mentioned above, this mesophase shows dark textures with chiral domains of opposite handedness (on rotating polarizer or analyzer) on cooling the isotropic liquid in the absence of an electric field. Similarly, on slow cooling the isotropic liquid under dc electric field, switching circular domains of opposite handedness [H(+) and H(−)] with a characteristic feature of extinction crosses oriented in opposite directions in which the tilted molecules are arranged in concentric circular smectic layers (Figure 4 a−d) are obtained. The extinction crosses of these domains rotate in opposite directions on reversing the polarity of the applied field which is a further indication of opposite chirality of these domains. On switching off the field, the position of the extinction crosses is retained, thus showing bistability. Furthermore, some other switching domains (Figure 4 e and f) in which the sense of chirality alternates from inner to outer part of the domains, which is due to the alternating tilt of molecules occurs at the macroscopic level and can be visualized as boundaries. The chirality of the inner switching domain [H(−)] is different from that of the outer [H(+)] domain and vice-versa as indicated with models in Figure 4f. Such a behavior has so far been observed only for the mesophase with antiferroelectric switching by Link et al.[2] Similar XRD pattern and electrooptical switching characteristics were observed for the remaining two compounds exhibiting SmC_SP_F phase. Recently, Dantlgraber et al.[10] reported a similar type of smectic ferroelectric liquid crystal formed by achiral polyphilic bent-core molecules.

On ascending the homologous series further, the mesophase of compounds **II-13** and **II-14** showed a kind of fan-shaped texture as shown in Figure S1 (see Supporting Information). On applying a triangular-wave voltage (± 15 Vμm^{-1}, 30 Hz) to the mesophase (compound **II-14**) obtained on heating and close to the melting point, a sharp single current peak appeared for each half period indicating a ferroelectric switching for the mesophase. The single polarization peak is retained down to a frequency of 0.1 Hz, which further supports the ferroelectric switching for the mesophase. This mesophase has been designated as Col_{rF} (see X-ray investigations for further details). When the mesophase was heated to about 175°C, under the same conditions of electric field, the polarization peak which was present in the columnar phase slowly disappeared, while the birefringent texture became dark and remained so until the clearing temperature. Interestingly, the dark texture obtained showed chiral domains of opposite handedness (on rotating polarizer

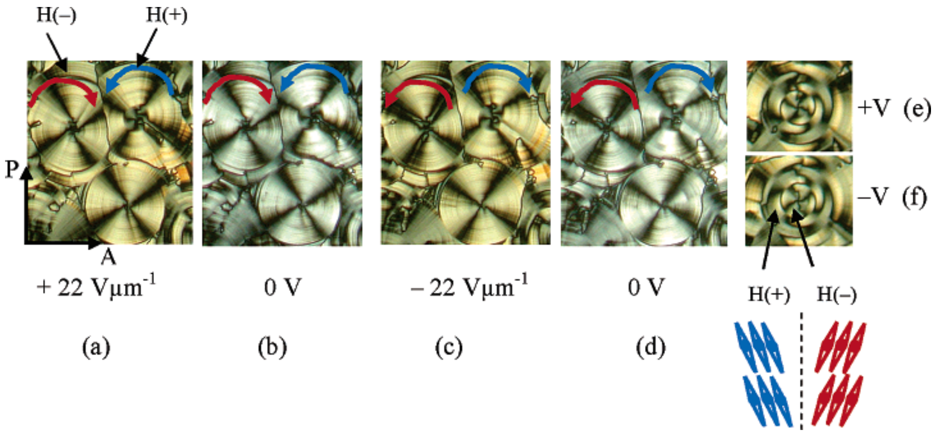

Figure 4. Ferroelectric conglomerates (switching domains of opposite handedness, H+ and H−, indicated using red and blue directional arrows) obtained (a−d) on cooling the mesophase of compound **II-11** under a dc electric field. The figures at extreme right (e and f) show the alternating chirality (H+ and H− shown with molecular models) within the switching ferroelectric domain as separated by boundaries. They differ from each other only by the tilt direction of molecules as indicated, as a result, the extinction crosses are oriented in opposite directions suggesting opposite chirality. In all the cases switching mechanism takes place around a tilt cone of the molecules as in the case of conventional SmC* materials.

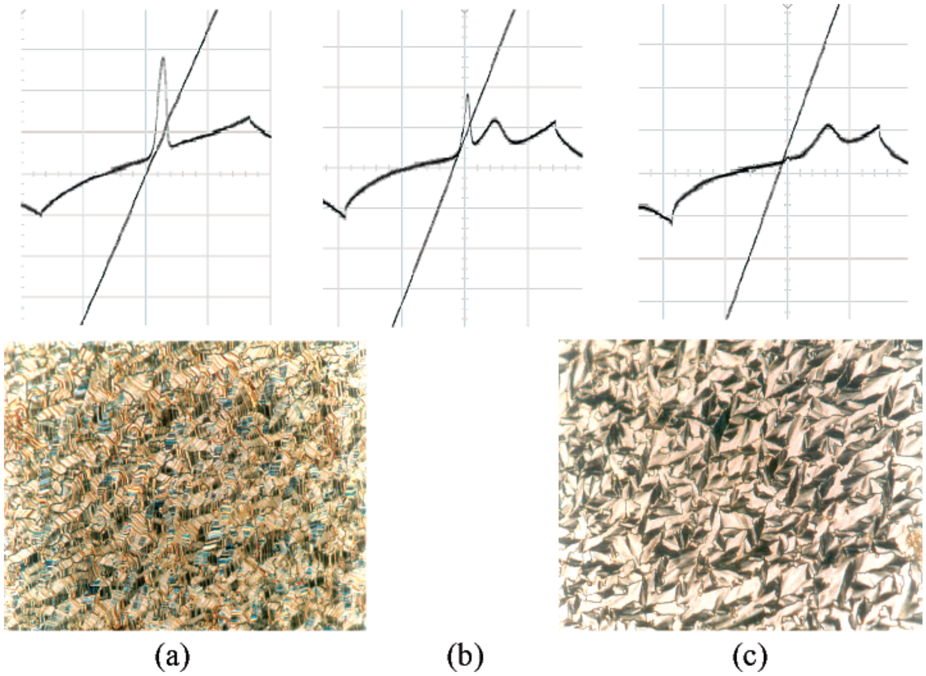

Figure 5. Switching current response traces obtained in the mesophases of compound **II-14** under a triangular-wave electric field: (a) ferroelectric switching current response in the Col_{rF} phase, (c) field induced ferroelectric switching SmC_SP_F phase, and (b) the transient state between Col_{rF} and SmC_SP_F phases. The corresponding textural changes obtained under these conditions are given below the traces (a and c).

or analyzer) as observed for the SmC_SP_F mesophase of lower homologues. On cooling the sample from the isotropic liquid under the same conditions of electric field, the mesophase appeared dark and remained like that until the sample crystallized. However, on heating the crystal to the mesophase under a higher electric field of about ± 30 Vμm^{-1}, a single polarization peak was observed in the Col_{rF} phase as shown in Figure 5a. The calculated polarization value was 850 nC cm^{-2}. On heating the sample further under the same conditions to a temperature of about 175 °C, an additional polarization peak appeared at a different position and the original peak slowly disappeared. This transition was accompanied by a textural change and photomicrographs of these are shown below the current response traces in Figure 5a and c. The fan-shaped texture observed at high temperature is suggestive of a smectic structure and is similar to textures of SmC_SP_F phase exhibited by compounds **II-10** to **II-12**. The field induced phase and texture are stable even on terminating the applied field. The transition temperature is almost independent of field strength (±1 °C). The polarization value obtained in this SmC_SP_F mesophase is about 240 nC cm^{-2}. The transient switching state between Col_{rF} and SmC_SP_F phases is shown in Figure 5b. It should be noted that no transition enthalpy or a textural change could be observed at this temperature (175 °C) without the electric field. Possibly, with increasing temperature under the field, the entropy of the fragments increases, thus the modulated structure (sinusoidal) present in the columnar phase which is perpendicular to the polar plane may be suppressed. This results in the formation of flat smectic layers which are probably stabilized by the surface upon removal of the electric field. Perhaps these observations remind us of the phase transition between a SmC and a Col phase obtained in polycatenars,[13] except for the fact that polar switching in

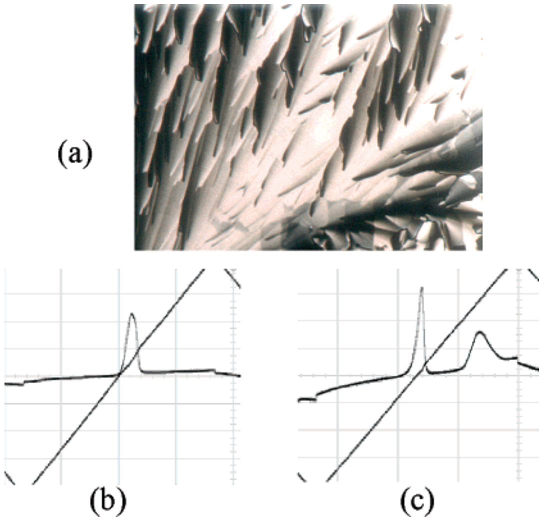

Figure 6. Optical photomicrograph obtained (a) at 175 °C in the Col$_{rAF}$ phase of compound **II-16.** The current response traces obtained on applying a triangular-wave voltage (± 24 Vμm^{-1}, 30 Hz); (b) ferroelectric type switching in the M$_x$ phase at 158 °C, and (c) the antiferroelectric switching in the Col$_{rAF}$ phase at 175 °C.

banana liquid crystals is due to the specific shape of the constituent molecules. The proposed models for these phase transitions (see Figure 7 later) are consistent with the models proposed for such phase transitions in polycatenars.

The XRD pattern of a nonoriented sample of compound **II-14** shows many sharp reflections in the small angle region. These reflections can be indexed on to a hexagonal lattice. However, the XRD pattern of an aligned sample is indicative of a centered rectangular symmetry and was indexed as such, and the data are shown in Table 3. The value of the lattice parameter *b* obtained is comparable to twice the molecular length by assuming a tilt of the molecules. Similar textural change as well as switching behavior was observed for the mesophase of compound **II-13**.

The mesomorphic behaviors of compounds **II-15** and **II-16** are different compared to those of the lower homologues but are similar to the behavior of the mesophase of compound **I-20**. On slow cooling the isotropic liquid of compound **II-16**, a type of fan-shaped texture was obtained (Figure 6a). The two polarization current peaks (antiferroelectric) that were observed in the higher temperature columnar phase gradually changed to a single peak as the temperature was lowered, which was accompanied by a textural change as observed for the mesophase of compound **I-20**. The polarization value obtained is about 720 nC cm^{-2} and is almost temperature independent even at the phase transition. If it is due to change in the switching behavior from AFE to FE, this cannot explain the change in the textural pattern at the phase transition. These observations suggest a continuous change from a columnar to a smectic structure under the electric field as shown schematically in Figure 7. This is due to a continuous increase in the segregation of aromatic and aliphatic parts on lowering the temperature with decreasing steric interactions which favors the formation of a smectic phase. This inherent property of the mesophase is perhaps favored under the electric field which is due to a synclinic tilt of the molecules in adjacent clusters. However, at present it is not clear as to the mechanism of the occurrence of two different phases under the field, one at high temperature (SmC$_S$P$_F$) in the Col$_{rF}$ phase and the other at low temperature (M$_x$) in the Col$_{rAF}$ phase. Oriented circular domains obtained under a dc electric field (125 V, 5 μm) of Col$_{rAF}$ phase of compound **II-16**, in which the extinction crosses orient at an angle wrt the directions of the crossed polarizers is independent of field reversal. On terminating the applied field, the circular domains relax such that the extinction crosses in some domains rotate in a clockwise direction while the remaining rotate in an anticlockwise direction (shown by arrow in Figure 8 with a schematic of the molecular orientation) with respect to the directions of the crossed polarizers. These domains differ in their tilt direction of molecules with respect to the layer normal resulting in domains of opposite chirality. The orientation of tilted

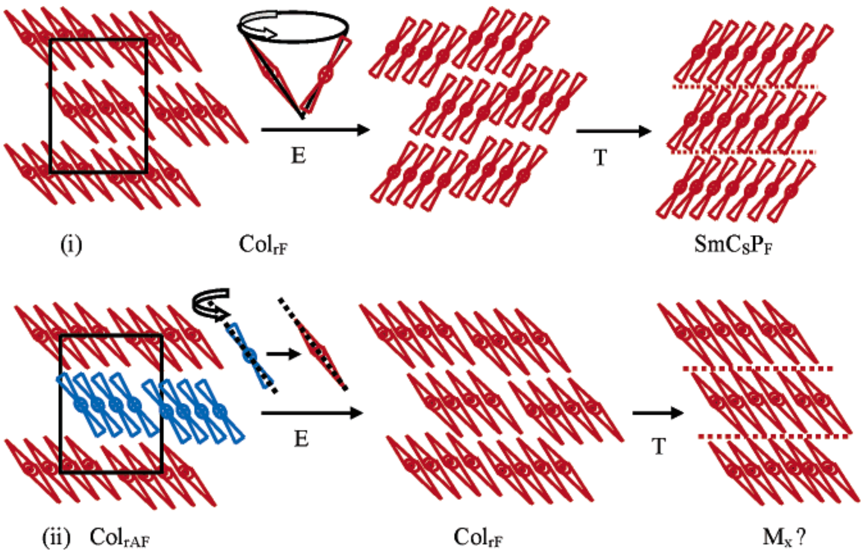

Figure 7. (i) One of the possible models for the Col$_{rF}$ phase and the bistable ferroelectric switching by the reversal of polarization around a tilt cone (retains the macroscopic chirality). (ii) The possible model for the Col$_{rAF}$ phase and the polarization reversal takes place by rotation around the long axis of the molecules (field induced switching of macroscopic chirality). Polarization direction indicated using points (up) and crosses (down) which is along the bent direction. Different colors indicate opposite chiralty. E, applied electric field; T, temperature.

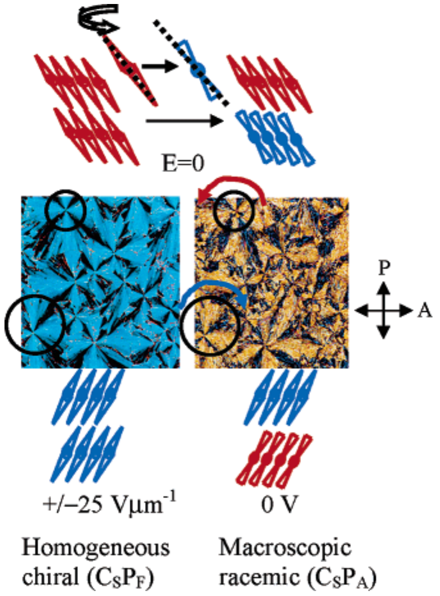

Figure 8. Circular domains obtained under a dc electric field for the Col_{rAF} phase of compound **II-16**. In the presence of electric field, extinction crosses orient between the crossed polarizers and tilt in opposite directions in different domains on terminating the field (shown by blue and red directional arrows) indicating the domains of opposite chirality in the ground state; a schematic of the arrangement of molecules in each domain is also shown. The synclinic tilt of molecules with and without the field clearly indicates the relaxation by a rotation of molecules around their long axes as shown schematically. The field induced switching of macroscopic chirality has also been demonstrated.

extinction crosses with and without field of these domains clearly indicates the synclinic tilt of molecules in adjacent clusters. This is a clear indication that the polarization reversal, as well as the relaxation, must occur around the molecular long axis in alternate clusters. However, it can be clearly seen that the angle of tilted extinction crosses wrt the directions of the crossed polarizers with the field (∼45°) is different from that in the absence of field (∼35°). This may be due to the differences in the local layer structure of the circular domains with and without the electric field as discussed by Takanishi et al.,[16] which obviously influences the position of the extinction crosses. If it is due to the relaxation of molecules around a tilt cone (on terminating the field), then the resulting extinction crosses must align along the directions of the crossed polarizers due to the anticlinic tilt of molecules in the ground state. On the basis of these experimental observations, two possible switching mechanisms, namely the polarization reversal by rotation of the molecules around the tilt cone (Col_{rF}) or around molecular long axes[4c,14] (Col_{rAF}), have been proposed (Figure 7). It is important to mention that the polar switching of molecules around a tilt cone reverses only the polarization direction, whereas the switching around the long molecular axes reverses not only the polarization direction but also the chirality. The differences in the switching mechanism between the ferroelectric and antiferroelectric phases may strongly depend on the type of interaction between the clusters or fragments present in the columnar phase. The uniform polarization direction in the adjacent clusters of the Col_{rF} phase favors the switching on a tilt cone, while in the case of antiferroelectric phase polarization reversal takes place only in alternative clusters resulting from a collective rotation of molecules around the long axis. Similar polarization current response and electrooptical switching behavior were observed for compound **II-15** also.

The synclinic tilt of molecules in adjacent columns can be realized from XRD and electric field measurements, and based on these, structural models for Col_{rF} and Col_{rAF} phases have been proposed (Figure 7). As can be seen from these models, the synclinic tilt of molecules cannot maintain the rectangular symmetry and in a real sense they are monoclinic/oblique with a layer group *P*112/*n* as discussed in the literature[4e,17] although the XRD measurements indicated a rectangular cell ($\beta \approx 90°$). The angle between the lattice parameters (β) also depends on the tilt angle of adjacent columns and the domain size, and these factors lead to a pseudo-rectangular cell. The XRD patterns of aligned samples of both the compounds **II-15** and **II-16** are comparable to the oriented XRD pattern of compounds **II-13** and **II-14** as they differ only in the direction of polarization in adjacent clusters (C_SP_F and C_SP_A). The diffraction pattern obtained is the same over the entire temperature range of the mesophase. The calculated number of molecules per unit cell amounts to 12 for compound **II-14** and around 15 for compound **II-16**. The outer diffuse maxima oriented at an angle wrt the direction of reflections in the meridian indicate a tilt of the molecules. The obtained value of the lattice parameter *b* corresponds to twice the molecular length by assuming a tilt of the molecules.

On increasing the chain length further, compounds **II-18** and **II-20** were obtained which show a completely different behavior. On slow cooling of a thin film of a sample of compound **II-20** observed under a polarizing microscope, very long colorful banana leaf-like patterns as well as spherulitic domains could be seen to grow (see Figure 9a) suggesting a two-dimensional structure for the mesophase.

The XRD data of a nonoriented sample of compound **II-20** could not be indexed on to a rectangular lattice as shown earlier for compounds **II-15** and **II-16**. However, they can be indexed on to an oblique lattice as recorded in Table 3. The resulting Miller indices agree well with the oriented XRD pattern of this compound which is shown in Figure 9b. Similarly, the XRD data obtained for compound **II-18** could be indexed to an oblique lattice. The lattice parameter *b* is comparable to the full molecular length (unlike in the case of Col_{rF} and Col_{rAF} phases in which the *b* value was twice that of the molecular length) by assuming a tilt of molecules. The value of β obtained for compound **II-18** is

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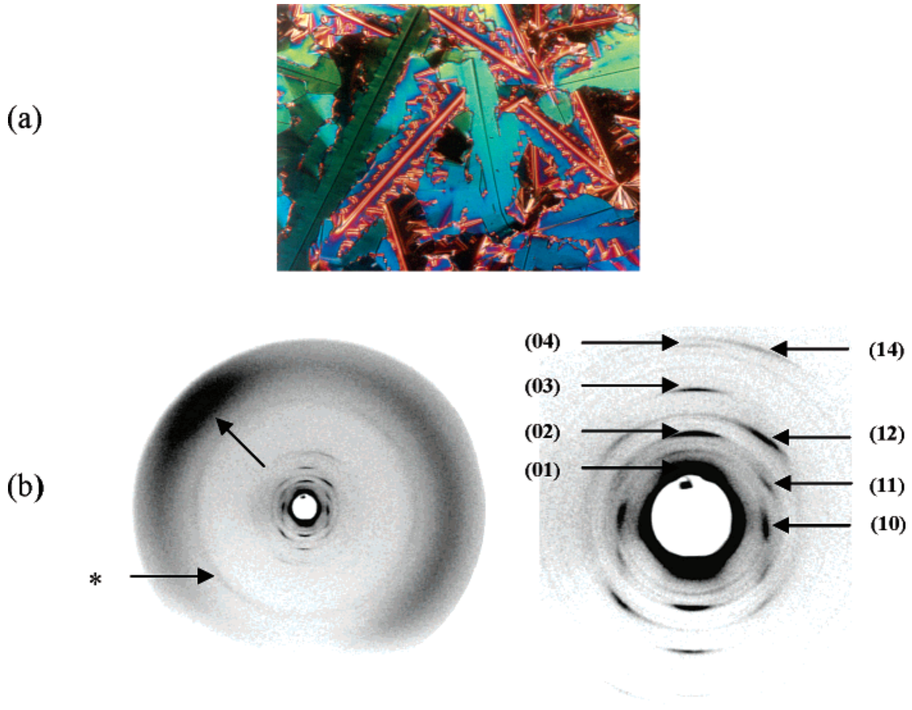

Figure 9. (a) Optical photomicrograph obtained in the $\mathrm{Col_{obAF}}$ phase of compound **II-20.** (b) XRD pattern of an aligned sample of the same compound at 160 °C; the oriented wide-angle region (shown by arrow) suggests a synclinic tilt of molecules. On the right side the expanded small angle region as well as the Miller indices are shown. *: reflection is due to the Mylar windows of the sample chamber.

84° and increases to 87° for compound **II-20** as a result of four additional methylene units in the aliphatic chains. The calculated number of molecules that exist in each unit cell amounts to 5. The outer diffuse region obtained in both the cases indicates the fluidity of the mesophase, and the preferred orientation direction points toward a synclinic tilt of the molecules (∼42°). The change in the structure of the lattice from rectangular to oblique with increasing chain length may be attributed to an increase in the tilt angle of molecules in adjacent columns which makes a deviation from the rectangular lattice.

Two polarization current peaks within one-half period of a triangular wave in Figure 10a indicates an antiferroelectric ground structure for the mesophase of compound **II-18** and similar current response was obtained for the mesophase of compound **II-20** also. Hence, this mesophase has been identified as $\mathrm{Col_{obAF}}$. The polarization value obtained is about 550 nC $\mathrm{cm^{-2}}$ for the mesophase of compound **II-18**. No field induced smectic phases could be observed in $\mathrm{Col_{obAF}}$ phase due to a large deviation between the clusters which makes it difficult to reorganize. As can be seen, the number of molecules in each cluster of the unit cell increase with increasing chain length, which is reflected in the values of the lattice parameters *a* and *b*. On the basis of these experimental observations, a possible model for $\mathrm{Col_{obAF}}$ phase has been proposed (shown in Figure 10b). The proposed models for rectangular and oblique lattices are similar to those recently proposed by Keith et al.[17] In summary, shown graphically in Figure 11, an achiral columnar mesophase with orthogonal arrangement of molecules without electrooptical switching was obtained for short chain members. However, on increasing the chain length, the molecules tilt, inducing chirality as well as the electrooptical switching for smectic and columnar phases accompanied by a change from homogeneously chiral to macroscopic racemic structures. Apart from other influences reported in the literature,[3,4,8−10] we find that the length of the hydrocarbon chain at the terminal positions of the bent-core also plays an important role either in generating new phase structures or a change in the nature of polar switching.

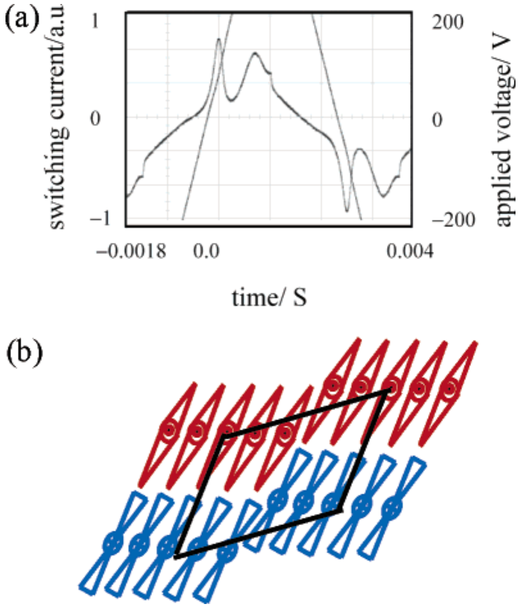

Figure 10. (a) Antiferroelectric switching current response obtained on applying a triangular-wave voltage of ±40 Vμm^{-1}, 200 Hz at 162 ° C for the $\mathrm{Col_{obAF}}$ phase of compound **II-18**. (b) Proposed model based on XRD and electrooptical studies. Note that the projected electron density of the columns is the same whether the molecules point up or down along the column.

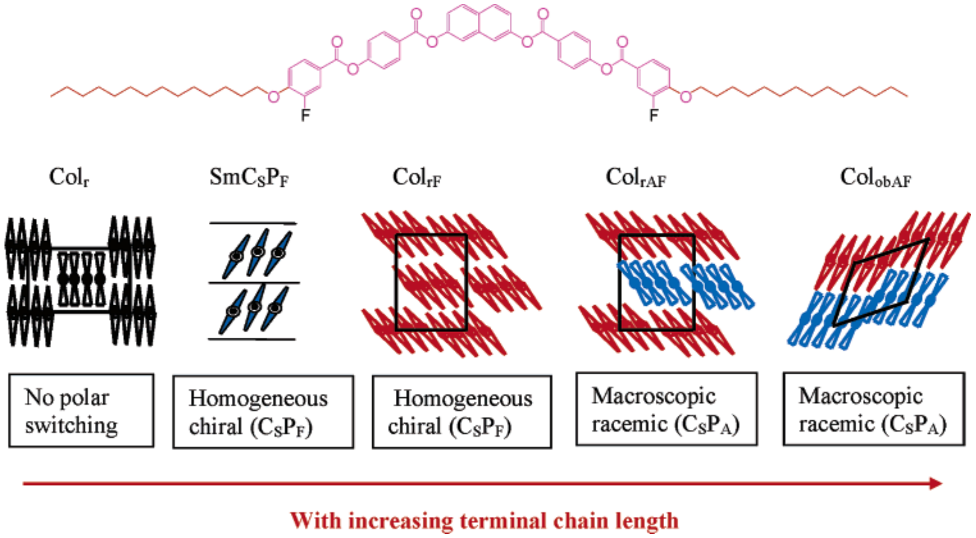

Figure 11. New phase sequence and proposed models for the mesophases obtained in a new homologous series of bent-core compounds with increasing hydrocarbon chain length. A change from achiral to chiral phases followed by a change from homogeneously chiral to macroscopic racemic structures has been observed on increasing the chain length. Different colors indicate opposite chirality of the domains.

Conclusions

The synthesis and mesomorphic properties of a new homologous series of compounds derived from 2,7-dihydroxynaphthalene with a fluorine substituent on the outer phenyl rings *ortho* to the *n*-alkoxy chain have been investigated using classical techniques. The mesomorphic properties of these compounds have been compared with those derived from 1,3-dihydroxybenzene. A wide variety of electrooptically switchable mesophases have been obtained by varying the *n*-alkoxy chain length (Figure 11). Especially, the compounds with long aliphatic chains suppose to stabilize the layer structure, but in contrast only columnar phases are obtained which is due to the effect of space filling within the segregated regions. However, the increase or decrease in the segregation between aromatic and aliphatic parts also depends on the temperature. This is the first example of a series of compounds in which ferroelectric, antiferroelectric switching smectic and columnar phases are obtained with increasing chain length, which gives a new phase sequence in banana liquid crystals. Change in the sense of macroscopic chirality within the ferroelectric switching domain (reversal of chirality along the layer normal) is reported for the first time in the ferroelectric smectic phase. Careful electrooptical investigations indicated two different switching mechanisms; (i) switching around a tilt cone in the ferroelectric phase which reverses only the polarization direction, and (ii) switching around the long axis of the molecules in the antiferroelectric phases which reverses not only the polarization direction but also the sense of chirality. It should be noted that the corresponding parent compounds without F-substitution[15] show only N to $\mathrm{Col_r}$, $\mathrm{Col_r}$, and $\mathrm{SmCP_A}$ phases with increasing chain length. In other words, fluorine substitution at this position (*ortho* to terminal *n*-alkoxy chain) not only suppresses the nematic phase but also induces the ferroelectric smectic and the novel antiferroelectric columnar phases. It can also be seen[15] that fluorine substitution only at this position induces the switchable columnar phases and not at any other position in these compounds with isomeric structures, which also suggests the importance of the position of the electronegative fluorine substituent.

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Supporting Information Available: Textural photomicrograph of compound **II-14** (Figure S1); experimental details and analytical data for compounds of series **II-*n*** (pdf). This material is available free of charge via the Internet at http://pubs.acs.org.

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