Frustration of polarity and chirality in a binary mixture of bent-core

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In order to investigate polar order and chiral layer structures in bent-core mesogens, mixtures of synclinic antiferroelectric (achiral P-8-OPIMB) and anticlinic ferroelectric (chiral P-8-OPIMB6*) liquid crystals were studied. The binary phase diagram of these materials was produced based on detailed texture observations and measurements of the dielectric response and polarization-reversal current. A synclinic ferroelectric state is found to dominate in mixtures having 38% chiral content in 6 µm thick cells. This structure is a hybrid of the structures of the two parent materials taking the synclinic tilt from P-8-OPIMB and the ferroelectric polar order from P-8-OPIMB6*. Intermolecular steric interactions at the interface of adjacent smectic layers are thought to play a role in determining the ground state structure in the mixtures.

Introduction

As predicted and observed by Meyer *et al.* in 1975,¹ the C_{2h} symmetry of the SmC phase can be reduced to C_2 through the introduction of molecular chirality (either chiral mesogens or a chiral dopant) to remove mirror symmetry. The result of this reduction in symmetry is that a spontaneous polarization P is allowed along the direction perpendicular to the plane containing the layer normal z and director n, thus making the chiral SmC phase (SmC*) ferroelectric. At a given temperature, the sign of P, i.e. whether P points along the direction given by $z \times n$ or $-z \times n$, is then completely fixed, being governed by the handedness of the chirality. The implication of this symmetry property is that in the case of the anticlinic structure (adjacent layers tilt in opposite directions) of the SmCA* phase the direction of the polarization is required by symmetry to alternate from layer to layer and the phase is thus antiferroelectric.² The relation between the tilt direction (n with respect to z) and P does not change even under application of an electric field. Namely, when P reorients in an electric field, n is also required to reorient to maintain the chirality, i.e., the orientational relationship between P and $z \times n$ is fixed. There have been numerous studies of the mixing of ferroelectric (synclinic) SmC* phase materials with antiferroelectric (anticlinic) SmCA* materials. In these studies it is possible to observe a crossover between the ferroelectric and antiferroelectric states mediated by ferrielectric phases that are thought to consist of a mixture of synclinic and anticlinic layer interfaces.³ The relative clinicity of adjacent layers and the relative polar order between adjacent layers is, however, directly connected and it is not possible for the polar order to change from ferroelectric to antiferroelectric without the layers simultaneously changing from synclinic to anticlinic.

This situation is markedly different in the polar smectic phases of bent-core (banana-shaped) mesogens. The discovery of electro-optic switching by Niori et al.4 in a fluid achiral smectic phase, the B_2 phase, of bent-core mesogens opened a new era in the study of polar order and chiral superstructures in liquid crystals. In these materials the polar order within the smectic layers is not dependent upon the relative tilt of adjacent layers. This was made clear in the work of Link et al.⁵ who found that two distinct types of domains coexist in the $B_{\rm 2}$ phase, one that is anticlinic antiferroelectric and one that is synclinic antiferroelectric, with the synclinic antiferroelectric state being the ground state structure. It was also pointed out that although the mesogens that make up the B_2 phase may be achiral, there is a chiral relationship between the layer normal z, the direction of the molecular bend b, and director n. As such, it is possible to define the layer chirality to be either + or depending respectively on whether $z \times n$ points in the direction along b or -b as shown schematically in Fig. 1(a). Since the molecules are closely packed to form smectic layers and the rotation about their long axis is strongly hindered, each layer has a spontaneous polarization P parallel or antiparallel to **b**. In this article, **b** is taken to be parallel to the polarization.

Allowing synclinic and anticlinic stacking of tilted polar smectic layers with C_2 symmetry, there are then four distinct possible arrangements of the polar order and layer chirality [see Fig. 1(b)].⁶ In these structures two successive layers define the polar order (ferroelectric or antiferroelectric) and the overall layer chirality (homochiral or racemic). The term homochiral is used to indicate that all layers in the domain have layer chirality of the same sign and racemic is used to indicate a layer-by-layer alternation of the layer chirality. The suffix S or A added to SmC in the nomenclature $SmC_{S,A}P_{F,A}$ defines whether the relative tilt sense of adjacent layers is synclinic or anticlinic and the suffix F or A added to P specifies whether the polar ordering is ferroelectric or antiferroelectric. Since the tilt and polarization directions define the layer chirality, the given combination of these suffixes defines whether the overall layer chirality is racemic or homochiral, *i.e.*, the $SmC_{s}P_{F}$ and SmC_AP_A layer structures are homochiral while the SmC_SP_A and SmC_AP_F structures are racemic [see Fig. 1(b)]. The presence of chiral carbons in the structures is indicated by an asterisk, SmC_{S,A}P_{F,A}*.

Almost all of the bent-core molecules synthesized so far exhibit antiferroelectric ground state structures.⁷ Recently, however, we synthesized the chiral bent-core mesogen P-8-OPIMB6*, which is a chiral analogue of the prototypical achiral bent-core mesogen P-8-OPIMB (see Fig. 2). From the

mesogens[†]

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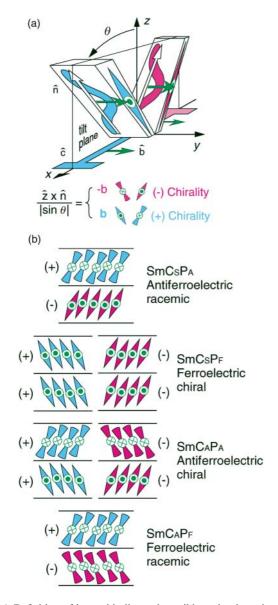


Fig. 1 Definition of layer chirality and possible molecular orientation arrangements in bent-core mesogens. (a) In a smectic layer with layer normal along the *z*-axis and polar order along **b** parallel to the *y*-axis, two possible chiral layer structures are defined by the director **n** tilting by θ either along the positive (blue) or negative *x*-axis (red). (b) The suffix S or A added to SmC in the nomenclature SmC_{S,A}P_{F,A} indicates either a synclinic or anticlinic tilt structure and suffix F or A added to P specifies either ferroelectric or antiferroelectric polar ordering in adjacent layers. Two racemic layer structures are also specified by the combinations of ferroelectric or antiferroelectric in polar order and synclinic or anticlinic in layer tilt (taken after ref. 6).

dielectric response, polarization-reversal current and secondharmonic generation (SHG) measurements, we concluded that the highest temperature smectic phase of P-8-OPIMB6* is ferroelectric.⁸ Detailed texture observation helped us to conclude that the layer structure of this phase is $SmC_AP_F^*$, though the molecules take a twisted orientation from the top to bottom surfaces in the absence of an electric field (see Fig. 3).⁹

Here we present experimental results of the binary mixtures of P-8-OPIMB having a synclinic antiferroelectric ground state and P-8-OPIMB6* having an anticlinic ferroelectric ground state. Unlike the mixing experiments in rod-like mesogens, here the polar order is independent of the layer clinicity, allowing for crossover from the synclinic structure to the anticlinic structure to take place at a different mixing ratio from the crossover from ferroelectric polar order to antiferroelectric polar order. In fact, we have found that there is a frustrated region in which the dominant structure is synclinic ferroelectric. This structure is a hybrid of the structures of the two parent materials, having the synclinic layer tilt of P-8-OPIMB and ferroelectric ordering of P-8-OPIMB6*.

Experimental

Homogeneous mixtures of the liquid crystals P-8-OPIMB and P-8-OPIMB6* were prepared from chloroform solutions by evaporating the chloroform under conditions of darkness to prevent photochemical reactions. The mixtures were studied in sandwich-type capacitor cells consisting of two indium-tinoxide-coated glass plates without surface alignment layers or rubbing. The permittivity measurements were made using an impedance analyzer (HP4192) and the polarization reversal current was measured by applying a triangle-wave voltage. The texture observations were made using a polarizing optical microscope and the birefringence was estimated using a compensator together with band pass filters.

Results

Polar order in the SmCP phase

As reported previously,8 P-8-OPIMB6* exhibits a strong dielectric relaxation at a frequency of the order of several tens of kHz and a single polarization reversal current peak under application of a triangle-wave voltage (20 Hz, $\pm 10 \text{ V} \mu \text{m}^{-1}$; features that were utilized for the identification of ferroelectricity. When P-8-OPIMB6* is added as a dopant to antiferroelectric P-8-OPIMB, there are distinct changes in both the dielectric response and polarization reversal current. Shown in Fig. 4 is the temperature dependence of the dielectric response at 5 kHz and the polarization-reversal current curves for (a) pure P-8-OPIMB (0% P-8-OPIMB6*), (b) 73% P-8-OPIMB-27% P-8-OPIMB6*, (c) 67% P-8-OPIMB-33% P-8-OPIMB6*, (d) 62% P-8-OPIMB-38% P-8-OPIMB6* and (e) the 50:50 mixture in 6 µm thick cells. The tilted polar smectic phase (designated here as SmCP) shows a large dielectric response (20–200) in comparison to the isotropic, B_3 and B_4 phases (~ 3) and continuously exists in all the mixing ratios including the B₂ phase of pure P-8-OPIMB.

While the change in the relative permittivity in the SmCP phase is minimal in mixtures having less than 33% of the chiral P-8-OPIMB6* dopant, it increases by roughly a factor of 10 in the mixtures with high dopant content (38% and 50%). In addition, the polarization-reversal current in these two mixtures shows only a single peak. Combined, these results strongly suggest that the 38% and 50% mixtures are ferro-electric. There is, however, a continuous drop in the relative permittivity of the 38% mixture with temperature, suggesting that this material has both ferroelectric and antiferroelectric domains with the antiferroelectric domain size growing as the temperature decreases.

In the lower concentration mixtures (27% and 33%), the dielectric response is similar to that in the antiferroelectric B_2 phase of pure P-8-OPIMB. These mixtures exhibit double polarization reversal current peaks, but the area of the second current peak is dramatically reduced from that of the pure material. Texture observations under application of low frequency electric fields confirm that these mixtures are antiferroelectric and the threshold field of the field-induced transition to the ferroelectric state decreases with increasing chiral dopant content. These results suggest that the reduction of the area of the second polarization reversal current peak is due to the dominance of the direct switching from one fieldinduced ferroelectric state to the other because of increased stability of the ferroelectric state when dopant is added. Thus, the phase boundary between the ferroelectric and antiferroelectric phases seems to exist between 33% and 50% chiral

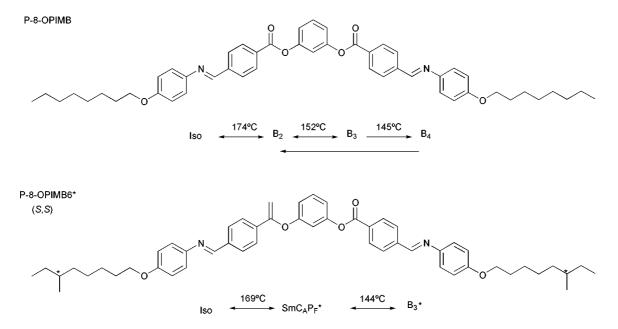


Fig. 2 Molecular structures and transition temperatures of achiral P-8-OPIMB and chiral P-8-OPIMB6*.

content with the 38% mixture exhibiting a continuous change from ferroelectric to antiferroelectric polar order with temperature.

The seemingly single switching current peak observed in Figs. 4(b) and 4(c) warns us against easily identifying ferroelectric phases based only on measurements of the polarization reversal current. In fact, Niori *et al.*,⁴ Shen *et al.*,¹⁰ Walba *et al.*,⁶ and Bedel *et al.*,¹¹ have all reported ferroelectric phases in bent-core mesogens as a result of observation of a single polarization reversal current peak. The findings of Niori and Shen were later amended to be antiferroelectric.^{5,12,13} Although those of Walba and Bedel are currently accepted, further experiments such as SHG are required to unambiguously confirm the ferroelectric phases.

Overall layer chirality in the SmCP phase

While polarization reversal current and permittivity measurements provide information about the polar order within the mixtures, optical microscopy observations are necessary for the determination of whether the layers are synclinic or anticlinic. Such layer clinicity together with the polar order (ferroelectric or antiferroelectric) defines the overall layer chirality. As both of the original components of the mixtures exhibit multiple types of domains, it is to be expected that texture observations of switching in the mixtures should be complex. In addition to the ground-state structure of pure P-8-OPIMB, synclinic antiferroelectric SmC_sP_A (racemic layer chirality), metastable domains of anticlinic antiferroelectric SmC_AP_A (homochiral layer chirality) are also observed.⁵ The ground-state structure of the dopant material, P-8-OPIMB6*, is anticlinic ferroelectric SmC_AP_F* (racemic layer chirality) and has two additional

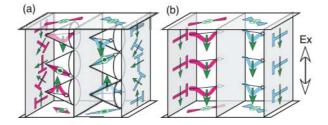


Fig. 3 Molecular orientation structures of $SmC_AP_F^*$ (a) in a twisted state in the absence of an electric field and in the uniform states under a field (b) perpendicular to the substrate surfaces.

types of metastable domains, synclinic ferroelectric $SmC_sP_F^*$ (homochiral layer chirality) and synclinic antiferroelectric $SmC_sP_A^*$ (racemic layer chirality).⁶ Despite the seeming complexity of the variety of domains observed in the pure materials, texture observation of the mixtures is straightforward.

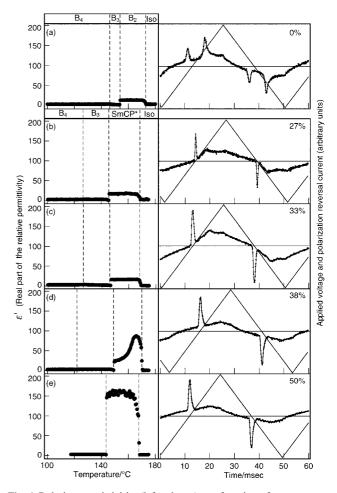


Fig. 4 Relative permittivities (left column) as a function of temperature and polarization-reversal current profiles (right column) under the application of a triangle-wave field in (a) pure P-8-OPIMB (0% P-8-OPIMB6*), (b) 73:27 P-8-OPIMB–P-8-OPIMB6*, (c) 67:33, (d) 62:38 and (e) the 50:50 mixture in 6 µm thick cells.

The switching characteristics exhibited in the mixtures with a low concentration of dopant, 27% and 33% chiral dopant, are essentially the same as those found in the pure material, *i.e.*, we observe both $SmC_SP_A^*$ and $SmC_AP_A^*$ domains with $SmC_SP_A^*$ being the ground state. The most significant difference between the mixtures and pure material is that with increasing concentration of dopant, the field-induced ferroelectric states become increasingly stable and it takes an increasingly long time to switch back to an antiferroelectric structure after the field is removed. This property results in the reduction of the area of the second polarization-reversal current peak as described in the previous section.

The most interesting properties are found in the 38% mixture. On cooling from the isotropic phase, we observe three types of domains in 6 μ m thick cells, those being the SmC_AP_A* (homochiral layer chirality), SmC_SP_A* (racemic layer chirality) and SmC_SP_F* (homochiral layer chirality) states. The switching characteristics of these domains are shown in Fig. 5. The largest part of the texture is occupied by a fan texture (region enclosed by red dashed line) shown in the middle of Figs. 5(a)–5(c). A yellowish region in this fan texture was found to be in the SmC_SP_F* twist state (ground state). Consistent with this interpretation, in the absence of a field, there is no extinction condition for these domains when rotating the microscope stage under crossed polarizers. In addition, uniformly tilted SmC_SP_F* states were obtained by applying a field (see Figs. 5(a) and 5(c)).

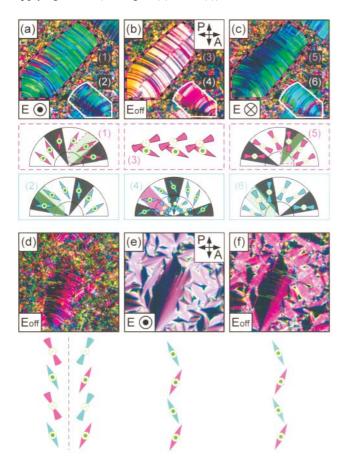


Fig. 5 Photomicrographs of the domains in the SmCP* phase of a 38% chiral mixture in a 6 µm thick cell. Most of the region inside the white solid line in (b) is assigned as a homochiral SmC_AP_A* state and the yellowish region inside the red dashed line in (b) a twisted homochiral SmC_SP_F* state (see sketches below the photomicrographs in (b)). Both domains change to uniform SmC_SP_F* states with opposite layer chirality under the application of a field (see sketches below the photomicrographs in (a) and (c)). Small domains of racemic SmC_SP_A* state are also observed (see photomicrograph in (d)). These domains switch to the SmC_AP_F* state (e) and remain in that state (f) after removing the field.

A second type of domain observed in this mixture is the SmC_AP_A* state. A typical SmC_AP_A* state domain is shown in Figs. 5(a)-5(c). This domain (region inside white solid line) has an extinction direction along the layer normal in the absence of a field, though it is not clearly seen in Fig. 5(b). As shown in Figs. 5(a) and 5(c), this domain can be switched into the fieldinduced $SmC_{S}P_{F}^{*}$ state having extinction directions tilted from the layer normal. The extinction direction is apparent in (a), though it is not in (c) because of the opposite rotation with respect to (a). The birefringence color changes from pink $(\Delta n \approx 0.1)$ to blue green $(\Delta n \approx 0.2)$ upon the application of a field, consistent with this assignment, i.e., anticlinic (4) to synclinic (2). Note that the molecular tilt directions in the two fan textures (blue and red boxes) are opposite, so that the brushes rotate in opposite senses. This means that these two domains are homochiral SmC_SP_F* state domains having opposite signs of layer chirality, despite being composed of chiral mesogens. It is also noted that the $SmC_AP_A^*$ domains are slowly converted into the SmC_SP_F* ground state with continued application of the field.

The third type of domain observed is the $SmC_SP_A^*$ state in a small portion of the cell, as recognized by the typical fine stripes shown in Fig. 5(d). The $SmC_SP_A^*$ state switched into a field-induced $SmC_AP_F^*$ state, Fig. 5(e), with the extinction direction along the layer normal. The domain remains in the $SmC_AP_F^*$ state, Fig. 5(f), after the field is removed. A slight color change was associated with the field removal and is attributed to the change to the twist structure (see Fig. 3).⁹

One of the interesting features of the SmC_SP_F* domains is that under application of large electric fields these domains can also be switched into the SmCAPF* state. Unlike the case of the 33% mixture, if the voltage is carefully adjusted, it is possible to observe the situation where under application of a trianglewave field the domains switch between the zero field SmC_SP_F* and high field SmC_AP_F* states. This process is shown in detail in Fig. 6. In the absence of an electric field the $SmC_{s}P_{F}^{*}$ twist domains stand out as bright white bands, indicated by the blue and red arrowheads in Fig. 6(a). These bands have no extinction direction when viewed between crossed polarizers, but by uncrossing the polarizer and analyzer clear extinction brushes are obtained, as shown in Figs. 6(b) and 6(c), indicating the twist structure. Between crossed polarizers at low electric fields, shown in Figs. 6(d) and 6(e), extinction brushes rotate from the layer normal with opposite sign of rotation in the two bands. Schematics below Figs. 6(d) and 6(e) show how this rotation of the extinction direction can be understood in terms of homochiral, synclinic ferroelectric domains of opposite handedness. On increasing the field strength, there is a field-induced transition to the SmC_AP_F* state having an extinction direction along the layer normal as shown in Fig. 6(f). Consistent with this interpretation, the birefringence drops from $\Delta n \approx 0.2$ to $\Delta n \approx 0.1$. The arrowheads in the polarization-reversal current plot in Fig. 6(g) show the sequence of the states as they appear during application of a triangle-wave field.

In mixtures with even higher concentrations of dopant, 50% or larger, there is little difference between the mixture and the pure dopant material. The ground state is $SmC_AP_F^*$ (racemic layer chirality) with a minority of domains that are synclinic ferroelectric. These minority domains are rapidly converted to $SmC_AP_F^*$ under application of a field.

Discussion

The measurement of the dielectric response and polarizationreversal current combined with detailed texture observations as described above lead to the binary mixture phase diagram of achiral P-8-OPIMB and chiral P-8-OPIMB6* bent-core mesogens, as shown in Fig. 7. The highest temperature smectic phase

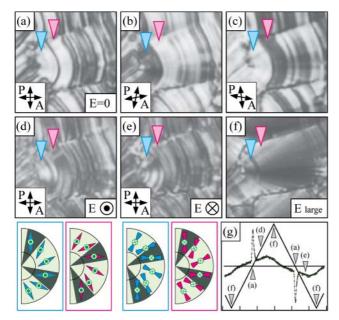


Fig. 6 Photomicrographs of $SmC_{S}P_{F}^{*}$ domains in the SmCP* phase of a 38% chiral mixture in a 6 µm thick cell. Under crossed polarizers, the domains indicated by the red and blue arrowheads appear white (a). The emergence of dark extinction brushes when the polarizers are uncrossed indicates that these domains are twisted states. The two domains specified by the red and blue arrows exhibit dark brushes by the opposite rotation of the polarizer and analyzer, as shown in (b) and (c), indicating opposite twist senses. With crossed polarizers, under application of a low electric field clear extinction brushes are observed in these domains, (d) and (e). The opposite rotation senses under an applied field indicate that while both of these domains are homochiral, they have opposite signs of layer chirality. The schematics under the photomicrographs in (d) and (e) indicate how the brushes rotate in the applied field. The domains indicated by the red and blue arrowheads in (d) or (e) differ slightly in birefringence color. The domain with low birefringence (red arrowhead) is thus not pure SmC_SP_F* but contains some anticlinic layers.¹³ Application of a larger electric field induces a transition to the $SmC_AP_F^*$ state as shown in (f). Repeatable switching between these states can be observed by applying a large triangle-wave electric field as indicated by the arrowheads in the polarization-reversal current graph of (g).

of this diagram consists of all of the four SmCP* states. In the 38% chiral mixture, a particularly rich variety of SmCP* states appear. The stability of these four states depends on the chiral content and temperature, resulting in the large temperature dependence of the relative permittivity observed in the 38% chiral mixture. In general, we find that the ferroelectric states are dominant in the high chiral content and high temperature range and occupy the majority of the cell, while antiferroelectric domains are a minority. A broken line at about 38% chiral content roughly gives the boundary on which the ferroelectric and antiferroelectric states are frustrated. Shown in Fig. 8 is the change in the SmCP* phase structures with increase in chiral P-8-OPIMB6* dopant. All of the structures observed in the absence of a field at a given weight percentage of dopant are sketched with a box indicating the ground state structure. It should be noted that at no specific temperature is there a clear transition between these states.

The structures of the B_3 and B_4 phases did not change their appearances in any of the compositions. However, the addition of the chiral material stabilized the B_3 phase with respect to the B_4 phase. The B_4 phase disappeared completely when the concentration of chiral content exceeded 50%.

Finally, we want to make a comment on the origin of the emergence of the ferroelectric polar order. The spontaneous polarization in each layer originates from a close packing of strongly rotation-hindered bent-core molecules, so that the major contribution to the polarization comes from two

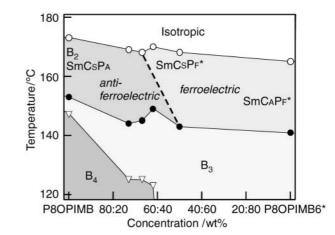


Fig. 7 Phase diagram of the binary mixture of achiral P-8-OPIMB and chiral P-8-OPIMB6* mesogens. Frustration between ferroelectric and antiferroelectric polar order as well as frustration between chiral and racemic layer chirality occurs near the 38% chiral mixture. The ferroelectric phase dominates the antiferroelectric phase at higher temperatures and in higher chiral content mixtures.

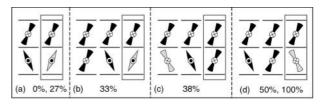


Fig. 8 Structures in the SmCP* phase in the binary mixture of P-8-OPIMB and P-8-OPIMB6*. All structures observed are drawn, with a box indicating the ground state structure.

carbonyls in the core. Hence, the in-layer polarization in P-8-OPIMB and P-8-OPIMB6* should be almost the same, indicating negligible difference between polar interlayer interactions in these compounds. Therefore, we suspect that intermolecular steric interactions play an important role in choosing the clinicity and polar order, as suggested by Walba *et al.*^{6,14}

Conclusion

Binary mixtures of P-8-OPIMB/P-8-OPIMB6* were studied using permittivity and switching current measurements as well as texture observations. The achiral bent-core material P-8-OPIMB exhibits two antiferroelectric states, SmC_SP_A and SmC_AP_A, while the chiral bent-core mesogen, P-8-OPIMB6*, exhibits the ground state $\mbox{Sm}\mbox{C}_{A}\mbox{P}_{F}{}^{*},$ that has a racemic layer composed of alternate + and - chiral layers. The mixtures of chiral and achiral bent-core mesogens exhibit all of the four SmCP* state structures, i.e., SmC_SP_A*, SmC_SP_F*, SmC_AP_A* and SmC_AP_F*. Particularly, in the 38% chiral mixture, the $SmC_{S}P_{F}^{*}$, $SmC_{A}P_{F}^{*}$ and $SmC_{S}P_{A}^{*}$ states seem to have almost the same stability. At high temperature in this mixture the SmC_SP_F* state is clearly the ground state. Such a structure is a hybrid of the structures of the two component materials taking the synclinic layer tilt from P-8-OPIMB and the ferroelectric polar ordering from P-8-OPIMB6*. In general, we observe frustration between the ferroelectric and antiferroelectric states and between the racemic and homochiral layer structures in the SmCP* phase with this chiral content. The ferroelectric phase is dominant to the antiferroelectric phase at higher temperatures and in higher chiral content mixtures.

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