Liquid Crystals

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Bent-Core Mesogens with Branched Carbosilane Termini: Flipping Suprastructural Chirality without Reversing Polarity[**]

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Dedicated to Professor Keith H. Pannell on the occasion of his 68th birthday

Materials with macroscopic polar order have widespread potential applications in molecular electronics and photonics. The discovery that achiral bent-core (bow- or banana-shaped) molecules can organize into fluid phases with polar order[1] and macroscopic chirality[2] opened an intriguing new area in the field of liquid-crystal (LC) research.[3] The polar order in these mesophases results from the restricted rotation of these closely packing bent-core molecules around their long axes (Figure 1 a), while the chirality arises from the tilted organization of these molecules in polar layers. The relationship between three vectors—layer normal, tilt direction, and bend direction—defines a right- or left-handed system (Figures S1 and S2 in the Supporting Information),[4] by which the four basic structures, SmC_sP_A (racemic), SmC_aP_A (chiral), SmC_sP_F (chiral), and SmC_aP_F (racemic), are described (Figure S3 in the Supporting Information). Most bent-core molecules possess antiferroelectric ($AF = P_A$) layer structures owing to the favorable antiparallel organization of bent-core molecules.[3a] The AF states can be switched to the corresponding ferroelectric states ($FE = P_F$) upon the application of a sufficiently strong external electric field (Figure 1 a). Usually a tristable (AF) switching with a relaxation of the FE states to an AF ground state (at 0 V) is observed.[2] This switching process is characterized by the presence of two polarization current peaks in each half period of an applied triangular wave voltage (see for example Figure 2 h). In some cases a bistable switching between the FE states of opposite polarity also takes place without relaxation to the AF state ("FE switching"); this is characterized by only one polarization current peak per half period (see for example Figure 2 i).[5]

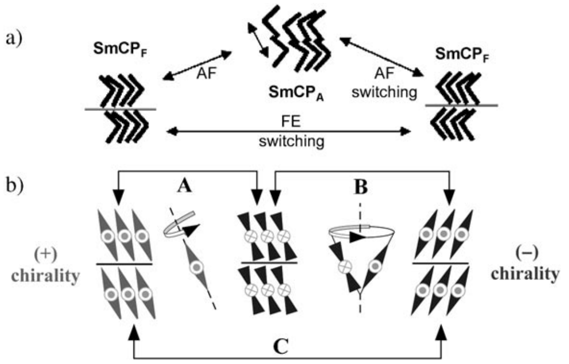

Figure 1. a) Polar order in smectic phases formed by bent-core molecules and molecular reorganization during an FE and AF switching process. b) Distinct switching mechanisms: A = switching around the long axis reverses layer chirality, B = switching about a cone retains layer chirality, and C = switching tilt direction with retention of polar direction would reverse chirality (the combination of A and B). The views are along the polar axis, and the sign of handedness is defined in Figure S1 in the Supporting Information.

Two switching mechanisms have been observed for FE and AF switching: 1) rotation of the molecules around their long axes,[6,7] (Figure 1 b, A) and 2) rotation of the molecules about a tilt cone (Figure 1 b, B).[2]) The first switching mechanism changes the polarity of the layers while retaining their chirality, while the second changes both polarity and chirality (chirality switching).[8]

Herein, we report a new, multistep type of field-induced chirality switching which takes place between oppositely tilted structures without reversing polarity (Figure 1 b, C). This was observed with a bent-core molecule that incorporates a highly branched carbosilane terminus (compound **3**, see Scheme 1). The molecular design is based on the observation that incorporation of siloxanes into the termini of tails of bent-core molecules (e.g. compound **1**) has a strong effect on molecular self-assembly.[9,10] The bulkiness of such groups could lead to a transition from switching about a cone to switching around the long axis and to a change of the mesophase structure.[7] Moreover, the capability of siloxanes to generate microsegregated sublayers leads to a transition from antiferroelectricity to ferroelectricity.[9] As far as practical applications are concerned, carbosilanes have significant advantages over siloxanes owing to their greater chemical stability. However, previously reported carbosilane-substituted bent-core molecules have three CH_2 units between two adjacent silicon atoms.[11,12] Hence, the dimethylsilane units in the carbosilane mesogens are further apart than in their

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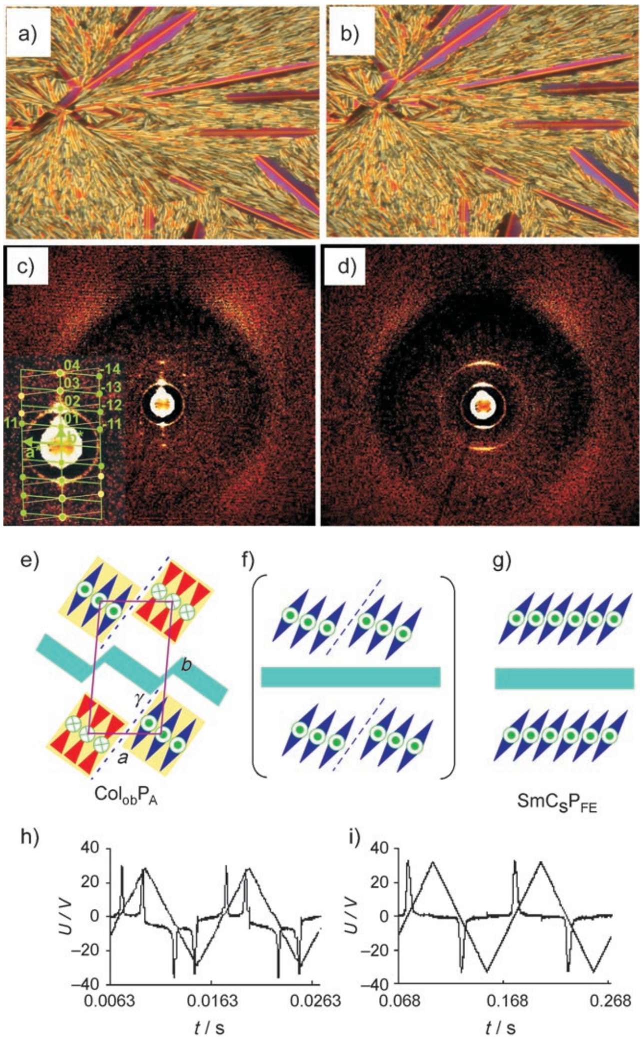
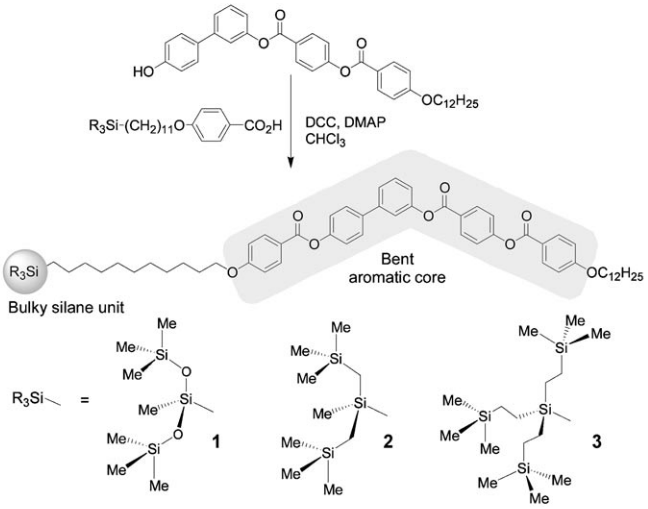


Figure 2. Investigation of compound **3**: left column: $\mathrm{Col_{ob}P_A}$ phase; right column: $\mathrm{SmC_sP_{FE}}$ phase. Textures as seen upon cooling the isotropic liquid in a 6.0 μm ITO cell: a) $\mathrm{Col_{ob}P_A}$ phase at $T = 99\,°\mathrm{C}$, b) $\mathrm{SmC_sP_{FE}}$ phase at $T = 80\,°\mathrm{C}$. X-ray diffraction patterns ($I(T) - I(115\,°\mathrm{C}$, isotropic liquid)) of an aligned sample: c) $\mathrm{Col_{ob}P_A}$ phase at $T = 99\,°\mathrm{C}$ (the inset shows the indexation of the small-angle reflections), d) $\mathrm{SmC_sP_{FE}}$ phase at $T = 80\,°\mathrm{C}$. Models showing the organization of the molecules: e) $\mathrm{Col_{ob}P_A}$ phase (magenta = 2D columnar lattice with relative ratio of X-ray lattice parameters a, b, and γ, blue dotted line = interribbon interfaces, and indigo = carbosilane layers); f) field-induced $\mathrm{Col_{ob}P_F}$ structure (unstable); g) $\mathrm{SmC_sP_F}$ structure as proposed for the $\mathrm{SmC_sP_{FE}}$ phase. Switching current response curves as obtained under a triangular wave field (±30 V, 10 Hz) in a 1.2 μm ITO cell with parallel nylon alignment layers: h) AF switching at $T = 100\,°\mathrm{C}$, i) FE switching at $T = 75\,°\mathrm{C}$.



Scheme 1. Synthesis of compounds **2** and **3**. Compound **1** was synthesized following a hydrosilylation route. DCC = N,N'-dicyclohexylcarbodiimide, DMAP = 4-dimethylaminopyridine.[9a]

Table 1: Mesophases, transition temperatures, enthalpy values, and lattice parameters for compounds **1**–**3**.[a]

Cmpd.	T °C [ΔH kJ mol^{-1}][b]							Lattice parameters [nm] (T [°C])[c]
1[d]	Cr	63 [8.9]	$\mathrm{SmCP_{FE}}$[*]	116 [21.1]	Iso			$d = 4.4$ (100)
2	$\mathrm{Cr_1}$	67 [4.3]	$\mathrm{Cr_2}$	74 [7.7]	$\mathrm{SmCP_{FE}}$[*]	107 [21.5]	Iso	$d = 4.39$ (100)
3	Cr	76 [17.9]	$\mathrm{SmC_sP_{FE}}$	91 [2.3]	$\mathrm{Col_{ob}P_A}$	107 [17.4]	Iso	$d = 4.56$ (80) $a = 2.22$, $b = 4.64$, $\gamma = 95°$ (99)

[a] Abbreviations: Cr = crystalline solid state; $\mathrm{SmC_sP_{FE}}$ = FE switching polar smectic phase with the synclinic tilted organization of molecules; $\mathrm{Col_{ob}P_A}$ = AF switching oblique columnar phase; $\mathrm{SmCP_{FE}}$[*] = FE switching dark conglomerate phase, [*] indicates the formation of optically active domains, though the molecules themselves are achiral; Iso = isotropic liquid state. [b] 10 K min^{-1}, first heating scan. [c] X-ray diffraction data (T/°C); see Tables S1 and S2 in the Supporting information for details. [d] Data from Ref. [9a].

siloxane analogues, which might reduce the effect of microsegregation. We describe here the first examples of bent-core molecules that incorporate branched carbosilane termini with only one (**2**) or two CH_2 units (**3**) between silicon atoms. Compounds **2** and **3** were synthesized by esterification of 3,4′-biphenol[9a] with benzoic acids containing carbosilane termini (Scheme 1, see the Supporting Information). The mesophases and transition temperatures are summarized in Table 1.

Compound **2** is a direct analogue of the siloxane derivative **1** in which the SiOSi units are replaced by $SiCH_2Si$ units. This compound exhibits an FE switching dark conglomerate type smectic phase ($\mathrm{SmC_sP_{FE}}$[*],see Figures S4 and S5 in the Supporting Information), which is similar to that reported previously for its siloxane analogue **1**.[9a]

For **3**, which has a bulkier carbosilane unit, two LC phases, $\mathrm{Col_{ob}P_A}$ and $\mathrm{SmC_sP_{FE}}$,[13] were identified. The high-temperature phase has a texture typical of columnar mesophases (Figure 2a). The X-ray diffraction (XRD) pattern of a surface-aligned sample (Figure 2c) confirms a columnar mesophase with an oblique lattice with lattice parameters $a = 2.22$ nm, $b = 4.64$ nm, and an oblique angle of $\gamma = 95°$ ($T = 99\,°\mathrm{C}$). In the wide-angle region, the diffuse maximum at 0.48 nm, assigned to the mean distance within the aromatic/

aliphatic parts, is split into two crescent like halos which are inclined with meridian and equator, indicating a tilted organization of the molecules. The intensities of the two inclined maxima are unequal (see also Figure S6 in the Supporting Information), consistent with a synclinic tilted organization of the molecules.[14] The columnar mesophase is a modulated smectic phase (ribbon phase) with a ribbon size of about three molecules (Figure 2e, see Table S2 in the Supporting Information). The modulation can be attributed to the bulky tertiary carbosilane unit that requires additional space, and the ribbon-type organization of molecules can overcome this steric frustration. Within the ribbons the molecules are tilted, and the angle between the director (the molecular long axis) and the *b* direction of the oblique cell is about 42°; this is deduced from the direction of the maxima of the wide-angle diffuse scattering with respect to the position and distribution of the small-angle reflections of the oblique lattice (see Figure S6 in the Supporting Information). Based on X-ray observations, we propose a ribbon structure ($\mathrm{Col_{ob}P_A}$ phase) with partial overlapping of the rodlike wings of the bent-core molecules in adjacent ribbons, as shown in Figure 2e (see also Figure S7 in the Supporting Information).

A phase transition was observed at 86 °C (cooling) by differential scanning calorimetry (DSC). No change in texture (Figure 2b) was observed at this transition, which suggests that the synclinic tilted organization of the columnar phase is retained in the low-temperature phase. The 2D XRD pattern shows that, at this temperature, reflections corresponding to the 2D lattice completely disappear with the exception of the layer reflections (d = 4.54 nm at 80 °C). These are retained as shown in Figure 2d, indicating the smectic nature of this low-temperature mesophase. The position and intensity distribution of the wide-angle diffuse scattering does not change, confirming a synclinic tilted organization of the molecules with a tilt angle of about 46°.[15] This smectic mesophase showed only one single polarization current peak in the half period of the applied triangular wave field at both high (10 Hz, Figure 2i) and low frequency (0.1 Hz), suggesting FE switching. The measured polarization is about 700 nC cm^{-2} (T = 80 °C) and bistable switching by rotation about a cone was confirmed by electrooptical investigations (Figure S8 in the Supporting Information). Hence, this smectic phase is assigned as $\mathrm{SmC_sP_{FE}}$ (Figure 2g) and its behavior is very similar to that of the $\mathrm{SmC_sP_{FE}}$[*] phase of compound **2**.

In the high-temperature phase, the switching current curve shows two well-resolved current peaks in the half period of the applied triangular electric field (Figure 2h), which clearly confirms the AF ground-state structure of the $\mathrm{Col_{ob}P_A}$ phase. The measured polarization is about 670 nC cm^{-2} (T = 100 °C). The threshold voltage required for this switching process is much higher than that observed for the $\mathrm{SmC_sP_{FE}}$ phases of **1**–**3**.[9,10] It is thought that an AF switching from the $\mathrm{Col_{ob}P_A}$ ground state to a FE field-induced $\mathrm{Col_{ob}P_F}$ state requires a high energy owing to the strong steric interactions at the interribbon interfaces between synpolar ribbons in the field-induced $\mathrm{Col_{ob}P_F}$ state (Figure 2 f, and Figure S7 in the Supporting Information). As these steric interactions would be removed in nonmodulated $\mathrm{SmC_sP_F}$ layers, it appears likely that in the field-induced FE state the layer modulation could be partly or completely removed (Figure 2 g). The synclinic FE structure induced from the $\mathrm{Col_{ob}P_A}$ phase is assigned as (+)- or (−)-$\mathrm{SmC_sP_F}$-like.[16]

Circular domains with extinction crosses inclined with polarizer and analyzer were developed for electrooptical

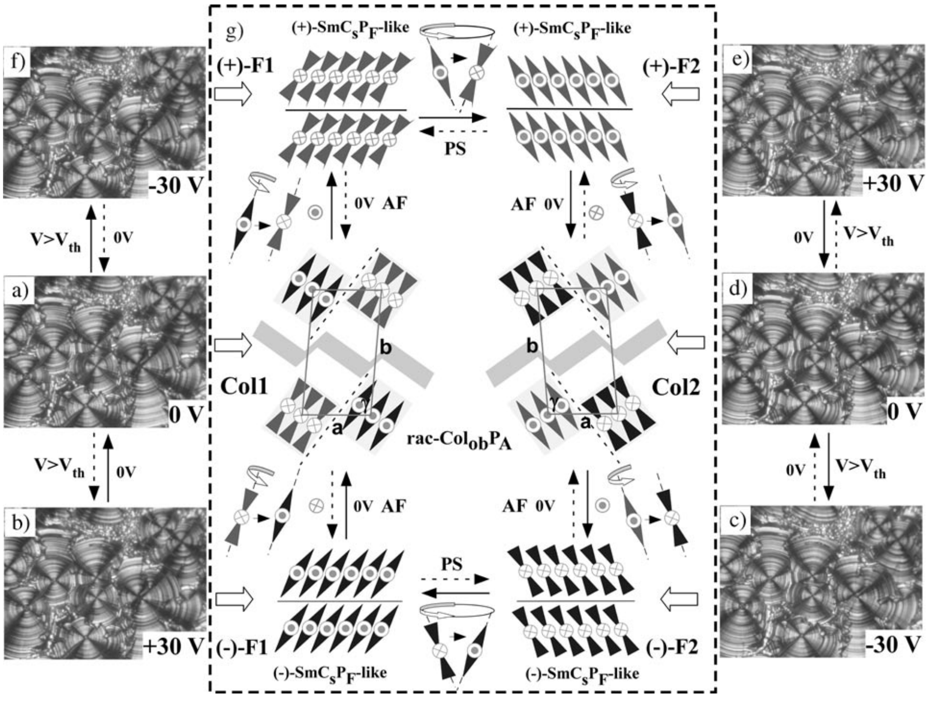


Figure 3. Investigation of compound **3** under a square-wave electric field (1.2 μm ITO cell with parallel nylon alignment layer) at 100 °C (cooling): a–f) Textures as seen under the polarizing microscope between crossed polarizers (polarizers are vertical and horizontal); g) the proposed structural models reflecting the organization of molecules in (a–f); Col1 and Col2 represent the two oppositely tilted orientations of the $\mathrm{Col_{ob}P_A}$ racemate at 0 V; (−)-F1 and (−)-F2 are the two oppositely tilted synclinic orientations of the field-induced (−)-$\mathrm{SmC_sP_F}$-like structures, and (+)-F1 and (+)-F2 are their enantiomers, that is, (+)- and (−)-F1 (as well as (+)- and (−)-F2) have the same tilt direction but opposite chirality. The fact that only one enantiomer is observed in (b, c) and (f, e) does not mean that the symmetry is broken, since the other enantiomer was observed in other areas; the molecular polar direction (indicated by dots and crosses) is from positive to negative charges as used in chemistry and it is assumed that the molecular polar vector is parallel to the bend direction (see also discussion in Figure S2 in the Supporting Information); PS = polar switching;[18] V_{th} = threshold voltage. Carbosilane sublayers, possible interribbon interfaces, and modulation are omitted in F1 and F2 (see detailed drawings in Figure 2 f) for clarity only.

investigations (Figure 3a).[17] Under the applied triangular wave electric field, two polarization peaks were observed, though extinction crosses did not move; this suggests that AF switching occurs around the molecular long axis. When a square-wave voltage (±30 V, 1 Hz) was applied, rotation of extinction crosses from one synclinic orientation state to the other one with an opposite tilt direction was observed (Figure 3b–c, or f–e), indicating that polar switching about a cone takes place.[18] However, switching off the square electric field did not result in any rotation of extinction crosses (Figure 3a and d), suggesting that under these conditions the molecules relax to the ground state Col$_{\text{ob}}$P$_{\text{A}}$ phase by rotation around the molecular long axis (Figure 3g).[19]

By applying a modified low-frequency square-wave field (0.1 Hz) where additional breaks at 0 V were introduced after each period (Figure 4), it was possible to realize transformations among the two SmC$_{\text{s}}$P$_{\text{F}}$-like structures and their two oppositely titled orientations, abbreviated here as (+)-F1, (+)-F2, (−)-F1, and (−)-F2, and between the two oppositely tilted AF orientations of the Col$_{\text{ob}}$P$_{\text{A}}$ structure, abbreviated as Col1 and Col2 (Figure 3g). Starting with the Col$_{\text{ob}}$P$_{\text{A}}$ ground-state orientation Col1 (by switching on a positive electric field), the FE orientation state (−)-F1 was achieved by rotation around the long axis (extinction brushes did not move but birefringence increased slightly). Switching off the field after the field reversal (i.e. after switching about a cone from (−)-F1 to (−)-F2, extinction brushes rotated) makes (−)-F2 relax to Col2 by rotation around the molecular long axis (extinction brushes did not move). After a pause at 0 V the reversed field (positive) was turned on to switch Col2 to (+)-F2 via rotation around the molecular long axis (extinction brushes did not move). The field was switched on until (after field reversal) the rotation of extinction brushes indicates that (+)-F2 was switched to (+)-F1 by rotation on a cone. Switching off the field makes (+)-F1 relax to the starting structure Col1 (extinction brushes did not move). Thus, the complete counterclockwise cycle shown in Figure 3g with dashed arrows (Col1 to (−)-F1 to (−)-F2 to Col2 to (+)-F2 to (+)-F1 to Col1) was realized. If the cycle starts instead with the opposite field direction, the sequence is reversed (shown with solid arrows in Figure 3g).

Previously reported AF switching processes in columnar phases involved either switching from (+)-F1 to (−)-F1 via Col1 or from (+)-F2 to (−)-F2 via Col2 (chirality switching by flipping only the polar direction).[6e] Although reversible or irreversible changes between homochiral and racemic structures in SmCP$_{\text{A}}$[20,21] and SmCP$_{\text{FE}}$ phases[9b,22] have been reported (for example, by using either rectangular or square-wave fields[21]), these processes involve transitions between diastereomeric superstructures with different free energies rather than transitions between enantiomeric superstructures as reported here. The transformations from (+)-F1 to (−)-F2 or from (+)-F2 to (−)-F1 (between the oppositely tilted states with identical free energy and opposite chirality), and even from Col1 to Col2 (between the two oppositely tilted orientations of a racemic structure) have not previously been reported.[23]

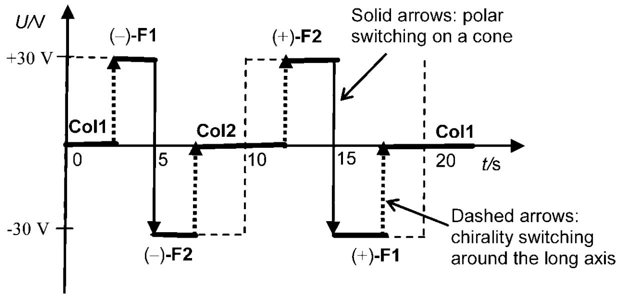


Figure 4. The application of a modified low-frequency (0.1 Hz) square-wave field results in the transformation along the cycle indicated by the dashed arrows in Figure 3g from Col1 via [(−)-F1], [(−)-F2], Col2, [(+)-F2], and [(+)-F1] to Col1.

This new mode of chirality flipping is enabled by competition between two switching mechanisms. When driven by a slowly changing voltage (triangle wave), compound **3** has time to relax to its antiferroelectric ground state (Col$_{\text{ob}}$P$_{\text{A}}$) by rotation about the long axis before a transition to the other field-induced state (e.g. (−)-F2→Col2→(+)-F2). In this case chirality is reversed without a change in tilt direction. We speculate that rotation about the tilt cone is inhibited by strong interactions generated at Col$_{\text{ob}}$P$_{\text{A}}$ interribbon interfaces (high energy barrier) during switching. When driven by a square wave (with abrupt voltage changes) compound **3** appears to switch directly from one SmC$_{\text{S}}$P$_{\text{F}}$-like orientation to another by rotation around the tilt cone (e.g. (+)-F1→(+)-F2). The tilt direction is reversed and chirality is unchanged. In this case molecules do not have time to relax to the Col$_{\text{ob}}$P$_{\text{A}}$ ground state within the short duration of the switching event. Interactions at the interribbon interfaces of field-induced SmC$_{\text{s}}$P$_{\text{F}}$-like states are therefore reduced (Figure S7 in the Supporting Information), and rotation around the tilt cone becomes the favored switching pathway. The multistep drive was designed to combine both fast and slow response modes within a single sequence, creating a series of transformations not attainable with the simpler waveforms. In contrast to the use of the simple square-wave drive, a relaxation period at 0 V was introduced as a new element. The response to this is the same as that seen for the slow −30 V→+30 V transition of the triangle wave. In principle, the effect of the multistep drive waveform should also be obtainable with a sawtooth waveform which intersperses abrupt +30 V→−30 V steps (see Figure 4) with slow linear changes of −30 V→+30 V.

In summary, we have reported the first examples of bent-core molecules with branched carbosilane termini. Compound **3**, with the bulkiest carbosilane unit, exhibits a columnar Col$_{\text{ob}}$P$_{\text{A}}$ phase (ribbon phase) at high temperature and an FE smectic phase with synclinic organization at low temperature. We have demonstrated for the first time the field-induced transformation between the two homogeneously chiral (+)- or (−)-SmC$_{\text{s}}$P$_{\text{F}}$-like enantiomers with opposite orientations and between the two oppositely tilted orientations of the Col$_{\text{ob}}$P$_{\text{A}}$ racemate. These transformations involve the combination of two switching mechanisms which allows the unexpected flipping of superstructural chirality by changing tilt direction without reversing polar direction (see Figure 1b, C). Compound **2** having a less bulky carbosilane unit shows only an FE switching smectic phase.

These investigations indicate that the combination of steric frustration and interlayer segregation by careful molecular design can lead to interesting response characteristics of stimuli-responsive functional materials. Studies on a series of bent-core molecules with other carbosilane termini in are currently in progress.

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[8] Switching about a cone is usually observed in smectic phases with undistorted layers, whereas switching around the long axis is typically found in modulated smectic phases in which the layers are broken into ribbons. In the smectic phases the type of switching depends on molecular structural parameters, but also voltage-, frequency-, and temperature-dependent transitions between the two switching mechanisms have been reported and quantitatively described by a nonequilibrium dissipative model.[6d]

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[13] The phases for **1** and **2** were designated as SmCP$_{\mathrm{FE}}$[*] in Table 1 as cooling the isotropic liquid without an applied field gives a conglomerate of optically active domains typical for dark conglomerate phases, and single-peak FE switching is observed experimentally but the ground-state structure is not exactly determined (either SmCP$_{\mathrm{A}}$ or SmCP$_{\mathrm{F}}$).[10] No chiral domains are observed for the low-temperature smectic phase of compound **3** and hence, this was designated as SmC$_{\mathrm{s}}$P$_{\mathrm{FE}}$. Note that SmCP$_{\mathrm{FE}}$ might differ from the well-defined SmCP$_{\mathrm{F}}$ that describes a specific state/phase structure.

[14] Note that only synclinic organization was reported for columnar phases with an oblique lattice presumably due to the strong interribbon frustration in an anticlinic organization. See Ref. [6b].

[15] Calculated using $\cos\theta = d/L$, $\theta = 43^\circ$; the molecular geometry was optimized by the employment of MOPAC calculations using the AM1 Hamiltonian. The molecular length ($L = 6.18$ nm) is equal to the sum of the length of the molecular long axis from the molecular modeling (5.94 nm) and two times of the van der Waals radius (0.12 nm) of the hydrogen atom.

[16] It is possible that in the field-induced FE state the layer modulation could be not completely removed. Therefore, the synclinic FE structure induced from the Col$_{\mathrm{ob}}$P$_{\mathrm{A}}$ phase is assigned as (+)- or (−)-SmC$_{\mathrm{s}}$P$_{\mathrm{F}}$-like so that it can be distinguished from (+)- or (−)-SmC$_{\mathrm{s}}$P$_{\mathrm{F}}$ structures, induced in the nonmodulated smectic phases (SmC$_{\mathrm{s}}$P$_{\mathrm{FE}}$ phases of compounds **1** and **2**), where such layer modulations can be excluded.

[17] This is achieved by cooling the isotropic liquid under a square electric field (±30 V, 10 Hz) and then switching to a triangular electric field (±30 Vpp, 10 Hz).

[18] The application of a square-wave field always results in single-peak switching since there is no time (at 0 V) to allow polar states to relax to the ground-state AF structure. Hence, under a square-wave field ferroelectric and antiferroelectric switching cannot be distinguished, and therefore the term polar switching (PS) is used here.

[19] It should be noted that the initial application of a square-wave electric field leads to AF switching from Col$_{\mathrm{ob}}$P$_{\mathrm{A}}$ to SmC$_{\mathrm{s}}$P$_{\mathrm{F}}$-like structures by rotation around the molecular long axis, and polar switching by rotation about a cone occurs subsequently as the sign of the electric field is changed.

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