Liquid Crystals

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Liquid-Crystalline Quaternary Block Molecules Incorporating Bent-Core Units**

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Dedicated to Professor Siegfried Hünig
on the occasion on his 85th birthday

The design of functional supramolecular systems by the self-organization of single molecules to give complex superstructures is a contemporary challenge. Whereas classical supramolecular chemistry focuses on assemblies formed by a limited number of molecules (host–guest chemistry),[1] the design of self-organized bulk materials with special properties is also an important task. The design of materials with polar order, for example, is of importance for piezoelectric, pyroelectric, and nonlinear optical applications. Polar ordered liquid-crystalline (LC) soft matter, in which the configuration of polar order can be switched by means of electric fields, can be used in fast-switching electrooptical microdisplays and light modulators.

Chiral rodlike molecules organized in a tilted configuration in layers (SmC* phases) were initially used as ferroelectric (FE) and antiferroelectric (AF) switchable liquid-crystalline materials.[2] In the last decade, achiral bent-core molecules were found to provide a novel class of AF switching LC materials.[3–5] Here, the polar order is due to the shape of the molecules which restricts the rotation around the long axis and leads to a spontaneous polarization (P) parallel to the layer planes (see Figure 1 a). In most of these mesophases, the bent direction in adjacent layers is antiparallel so that the layer polarization alternates from layer to layer, which leads to a macroscopic apolar AF structure ($\mathrm{SmCP_A}$ phases).[4] More recently, FE switching mesophases ($\mathrm{SmCP_F}$) also have been reported for such materials.[6–13] In such cases, the bent direction in adjacent layers is parallel and switching takes place between two energetically equivalent polar structures (see Figure 1 a).

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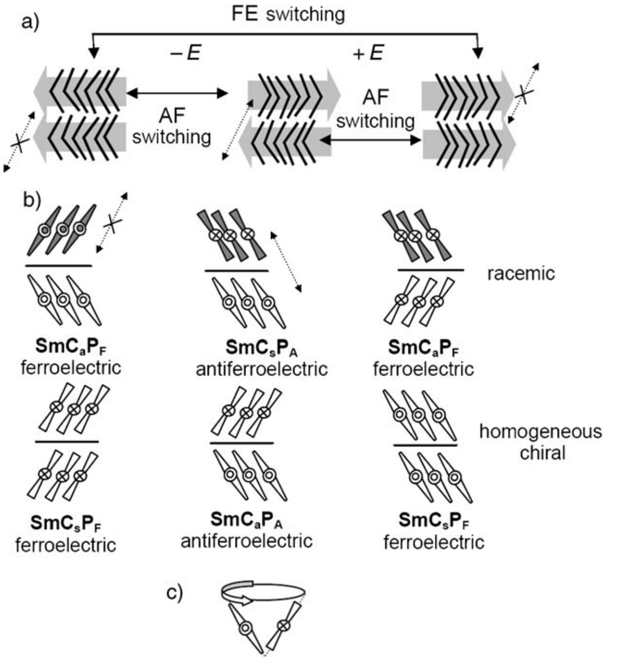


Figure 1. Modes of organization of bent-core molecules in polar smectic LC phases. a) Side views: gray arrows indicate the polar directions; dotted arrows indicate out-of-plane interlayer fluctuations, which are easier in the SmCP$_A$ structure than in the SmCP$_F$ structure.[4] b) Views parallel to the bend direction: subscript s denotes synclinic organization (the tilt direction is the same in adjacent layers); subscript a denotes anticlinic (the tilt direction changes from layer to layer); subscript F denotes ferroelectric (synpolar); subscript A denotes antiferroelectric (antipolar). The chirality of the layers is indicated by the gray or white color of the molecules (see Supporting Information for an explanation of layer chirality). SmC$_a$P$_F$ and SmC$_s$P$_A$ represent racemic structures (chirality sense changes in adjacent layers); SmC$_s$P$_F$ and SmC$_a$P$_A$ are homogeneous chiral structures (chirality sense is identical in the layers). Dotted arrows indicate out-of-plane interlayer fluctuations, which are easier in the SmC$_s$P structures than in the SmC$_a$P structures. c) Switching on a cone changes both the polar and tilt directions, that is, layer chirality is retained.[4]

Note that the molecules are tilted relative to the layer normal in most of these smectic phases which gives rise to chirality in their LC superstructures (the layer normal, tilt direction, and polar axis define a chiral system; see Supporting Information).[4] As with organic molecules where the covalent connection of stereogenic centers leads to diastereomers, the combination of chiral layers in liquid-crystalline phases leads to diastereomeric superstructures. As shown in Figure 1 b, the chirality sense can be either identical in adjacent layers, leading to homogeneously chiral structures (SmC$_s$P$_F$ and SmC$_a$P$_A$), or opposite, leading to macroscopic racemic superstructures (SmC$_a$P$_F$ and SmC$_s$P$_A$).[4] These structures can be distinguished by means of their distinct optical properties using a polarizing microscope.

As mentioned above, in soft matter systems macroscopic polar structures are unstable and therefore ferroelectric switching materials are rare. One group of compounds that have a pronounced tendency to form such FE switching smectic phases incorporate oligo(dimethylsiloxane)[6,7] or carbosilane units[10] (see, for example, compounds **H*n*** in Figure 2). This observation indicates that a polyphilic molecular structure and the segregation of oligo(dimethylsiloxane) units into separate sublayers is a successful way to generate new bulk properties.[5b,6,7,10] Whereas the majority of bent-core molecules are built up of only two distinct parts, namely, the rigid bent core and the terminal alkyl chains, these oligo(dimethylsiloxane)-substituted molecules are composed of three distinct and incompatible units and therefore represent ternary block molecules (Figure 2).

Herein, we report the first examples of bent-core molecules composed of four distinct units. As shown in Figure 2, these quaternary block molecules **F*n*** combine two different end chains—an oligo(dimethylsiloxane) and a perfluoroalkyl chain—as well as alkyl spacers and aromatic bent-core units. As a result of their special structure, these molecules show interesting properties, such as a temperature-dependent transition from ferroelectric to antiferroelectric switching and a temperature-dependent transition between diastereomeric superstructures. In addition, it is shown for the first time that the switching behavior of diastereomeric mesophase structures can be different, with one being ferroelectric and the other being antiferroelectric.

Compounds **F1, F2**, and **Fi2** were synthesized in an analogous manner as reported for the non-fluorinated oligo(dimethylsiloxane) derivatives **H*n***,[6] by hydrosilylation of the appropriate fluorinated olefinic precursor **F** (see Supporting Information). The properties of these new compounds were determined by polarizing microscopy, X-ray scattering, and electrooptical techniques. The observed mesophase types and transition temperatures are collated in Table 1 and compared with the olefinic precursor **F**. All compounds **F*n*** ($n = 1, 2$) show optically isotropic mesophases

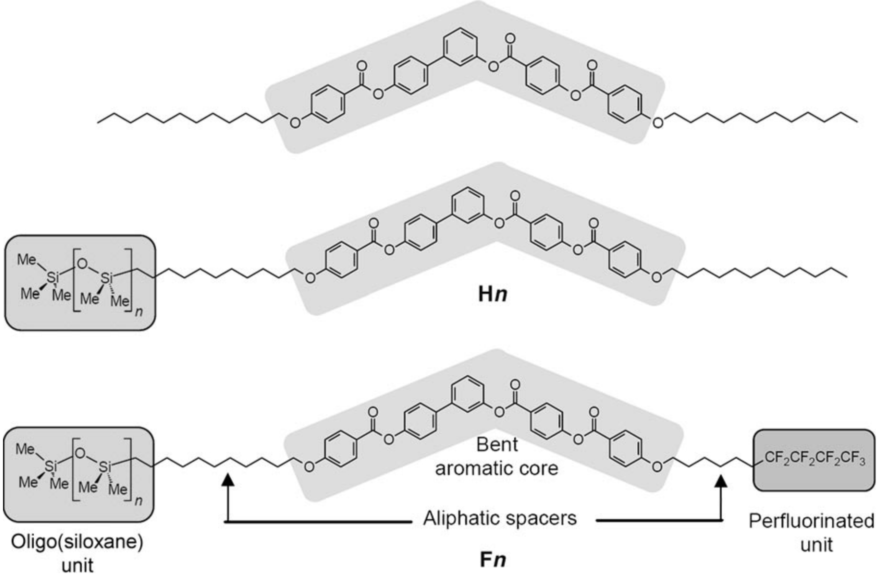
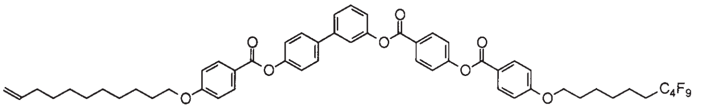
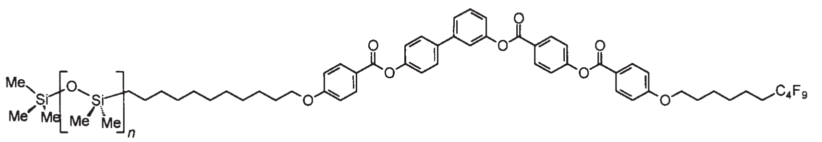


Figure 2. Structures of a classical bent-core molecule (top),[20] ternary bent-core molecules **H*n***,[6] and quaternary bent-core molecules **F*n***.

Table 1: Mesophases, transition temperatures, and transition enthalpy values (in brackets) of the fluorinated compounds **F*n*** in comparison with compound **F**, which lacks an oligo(dimethylsiloxane) group.[a]



F



F*n*

Compound	n	T [°C] (ΔH [kJ mol^{-1}])[b]
F	–	Cr 111 (29.3) SmCP$_A$ 123 (20.0) Iso
F1	1	Cr 94 (21.0) SmCP$_{A+F}$[*] ≈110 (–) SmCP$_F$[*] 130 (21.1) Iso
F2	2	Cr 104 (22.6) SmCP$_F$[*] 127 (19.2) Iso
Fi2[c]	2	Cr 105 (22.8) SmCP$_F$[*] 127 (20.1) Iso

[a] Abbreviations: Cr = crystalline solid state; SmCP$_A$ = AF switching polar smectic phase, with tilted arrangement of the molecules; SmCP$_F$[*] = FE switching polar smectic phase, with tilted arrangement of the molecules; superscript [*] indicates the formation of a chiral superstructure, as seen by domains of opposite chirality (see Supporting Information) although the molecules themselves are configurationally achiral; Iso = isotropic liquid state. [b] 10 K min^{-1}, first heating scan. [c] In this compound the branched $(Me_3SiO)_2Si(Me)$ group is used instead of the linear $Me_3Si(OSiMe_2)_2$ unit as used in compound **F2**.

composed of domains of opposite chirality sense (see Supporting Information) as also reported for the non-fluorinated analogues **H*n***.[6,7]

X-ray scattering of the mesophase of compound **F1** (see Figure 3 a) indicates a fluid layer structure without in-plane order, as characterized by a layer reflection together with the fourth order.[14] The layer thickness is 4.2 nm, which is much smaller than the calculated molecular length (l = 5.95 nm in the most-extended conformation with all-*trans* alkyl chains, according to CPK models) and is in line with a strongly tilted arrangement of the molecules in a smectic monolayer structure (Figure 4 a). This observation also indicates that there is no segregation of the fluorinated and the oligo(dimethylsiloxane) end chains into distinct sublayers which would otherwise lead to a bilayer structure with alternating oligo(siloxane) and perfluoroalkane sublayers (see Figure 4 b).[15] Nevertheless, the diffuse scattering in the wide-angle region has a very unsymmetrical profile in which two maxima can be distinguished (see inset in Figure 3 a). The maximum at 0.46 nm corresponds to the mean distance between the hydrocarbon parts of the molecules, while the shoulder corresponds to a mean distance of 0.62 nm and is assigned to the mean distance between the nanosegregated pentamethyldisiloxane units. Interestingly, this shoulder is absent in the diffraction pattern of the corresponding non-fluorinated pentamethyldisiloxane derivative **H1**[6] which indicates that although the fluorinated segments do not form their own sublayers they can facilitate the segregation of the oligo(dimethylsiloxane) parts. The mixed sublayers containing the fluorinated chains and aliphatic spacer segments (see Figure 4 a) are probably more incompatible with the pentamethyldisiloxane units than the alkyl chains themselves and favor a segregation of these units into separate sublayers.

Switching experiments with compound **F1** (10-μm thick noncoated ITO cell, Figure 3 b) indicate only one peak in the switching current curve down to a frequency of 0.1 Hz and point to a FE switching process. However, optical investigations indicated a more complex behavior. Although the shape of the polarization current curve does not change over the whole temperature range, a clear temperature-dependent change of the switching process is seen. Domains with an SmC$_a$P$_F$ structure[16] were grown under a triangular ac electric field at 100 Hz (see Figure 5 b). These domains are characterized by extinction crosses that coincide with the directions of the polarizer and analyzer, indicating an anticlinic organization of the molecules. Under the applied ac field, this SmC$_a$P$_F$ structure is stable at all temperatures. Upon switching off the field at T > 110 °C, there is no change in the orientation of the extinction crosses (see Figure 5 a) which means that the structure does not change and remains SmC$_a$P$_F$ also at zero voltage;

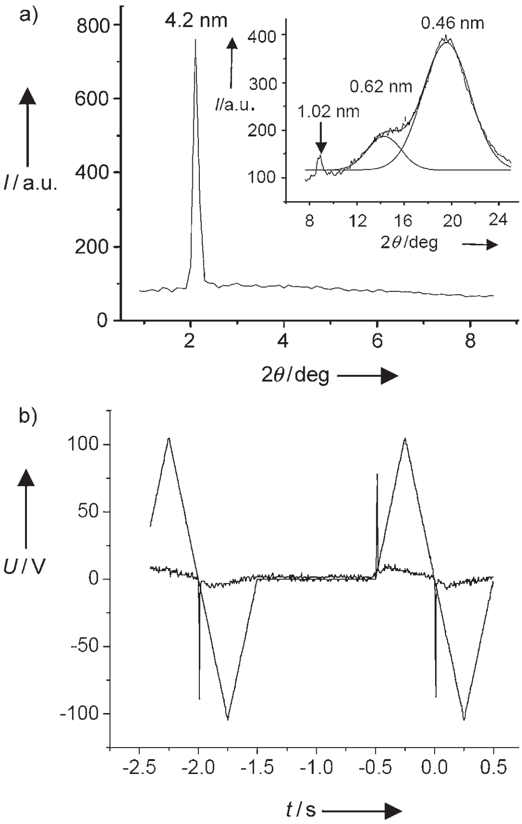


Figure 3. Investigation of compound **F1**: a) X-ray diffraction pattern at T = 110 °C; the inset shows the wide-angle region with two maxima, and the arrow within the inset shows the fourth-order smectic reflection. b) Switching current response at T = 115 °C in a 10-μm thick noncoated indium tin oxide (ITO) cell (EHC, Japan) on applying an alternating normal (1 Hz) and modified triangular-wave voltage.[11]

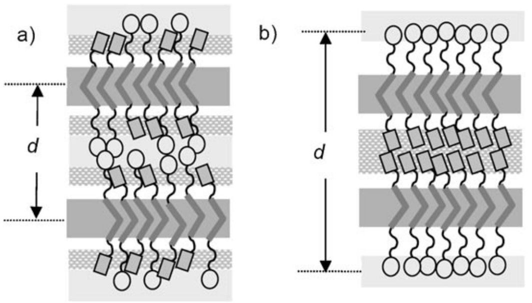


Figure 4. Models of the organization of compounds ***Fn*** in the smectic phases: a) Monolayer structure in which the fluorinated chains and the hydrocarbon chains are organized in common sublayers. b) Bilayer structure in which the fluorinated chains and hydrocarbon chains are organized in different sublayers (not observed for ***Fn***).

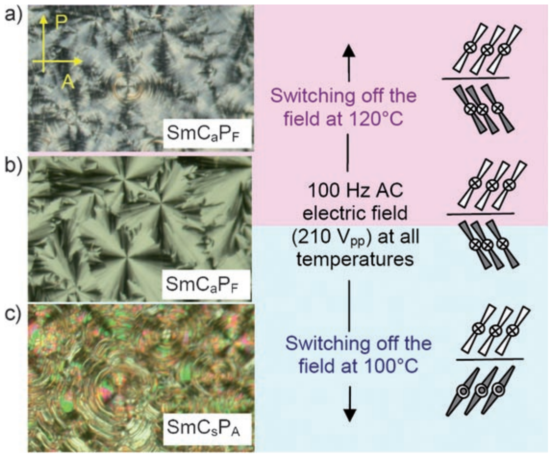


Figure 5. Textures and mesophase structures of compound **F1** in a 10-μm noncoated ITO cell obtained a) at $T > 110$ °C after switching off the ac field, b) under the applied ac field (V_{pp} = peak-to-peak voltage), and c) at $T < 110$ °C after switching off the field. Yellow arrows show the positions of the polarizer (P) and analyzer (A).

that is, the polar FE state seems to be stable (or long-living metastable) under the experimental conditions. These results indicate a bistable switching process, that is, a direct switching between two different polar FE states without a nonpolar AF state at zero voltage (FE switching).

Switching off the field at $T < 110$ °C leads to a different behavior. In this case, the extinction crosses slowly relax at zero voltage to a position that is inclined 45° with respect to polarizer and analyzer and the texture becomes more colored (i.e. the birefringence is increased, see Figure 5c). These observations indicate that the molecules now adopt a synclinic organization, with the molecules tilted by approximately 45° in the layers, achieved by a rotation of the molecules on a cone into the AF $\mathrm{SmC_sP_A}$ state. There are three stable states (the two polar FE states and the nonpolar AF state) which indicates an antiferroelectric type of switching. Hence, there is a transition from a FE switching process at high temperature to AF switching at lower temperatures. Such a change of the switching type has only rarely been observed for other bent-core molecules,[13] mostly in mixtures[12] or with a reverse sequence.[9]

Besides this temperature dependence, there is a remarkable frequency dependence of the switching process. At lower frequency (< 0.5 Hz) or under a dc field, the extinction crosses are only slightly inclined (ca. 15°) with the direction of the polarizer and analyzer (see Figure 6a). This can be explained with a structure in which an anticlinic organization ($\mathrm{SmC_aP_F}$, extinction crosses would be parallel to the polarizers) is mixed with a synclinic organization ($\mathrm{SmC_sP_F}$, extinction crosses would be inclined by 45°) on a mesoscopic scale (see models shown in Figure 6a).[17] In other words, two diastereomeric organizations, chiral ($\mathrm{SmC_sP_F}$) and racemic ($\mathrm{SmC_aP_F}$), coexist.

Again, a significant change of the switching process can be seen at around 110 °C. At $T > 110$ °C the extinction crosses do not change their position after switching off the field (compare Figure 6a and b), but upon application of an electric field with the opposite sign the crosses rotate by about 60°. In this way, the extinction crosses again become inclined with the direction of the polarizer and analyzer by 15° but in the opposite direction (compare Figure 6b and c). This indicates a bistable switching process, that is, a direct switching between two different FE states. Reorganization of the molecules takes place in each layer by a rotation on a cone which reverses the polar direction and the tilt direction in the synclinic as well as in the anticlinic domains (follow the black line in Figure 6 from a to c).

At $T < 110$ °C a different behavior is observed (see Figure 6a, c, d). At this temperature the extinction crosses

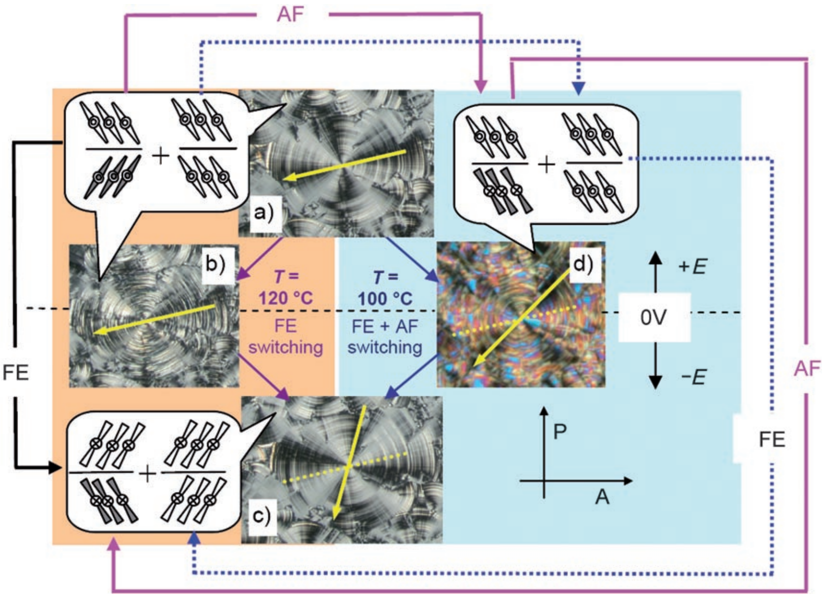


Figure 6. Temperature dependence of the switching process of compound **F1** (10-μm noncoated ITO cell) at low frequency (< 0.5 Hz) or under a dc field. Textures seen between crossed polarizers a) under an applied field (35 V_{dc}) at 100 °C or at 120 °C, b) after switching off the field at 120 °C, c) after reversal of the applied field at 120 °C or 100 °C, and d) after switching off the field at 100 °C.

relax at zero voltage to a position that is inclined by 45° with respect to the polarizer and analyzer, and the texture becomes more colored (i.e. the birefringence is increased, see Figure 6d). This behavior indicates that at zero voltage all molecules adopt a synclinic organization with the molecules tilted by about 45° in the layers. Hence, it seems that at $T<110\,^{\circ}\mathrm{C}$ only the anticlinic microdomains relax to the synclinic AF state (follow the pink line in Figure 6 from a to d), whereas the synclinic microdomains do not relax (follow the dotted blue line in Figure 6 from a to d). Upon field reversal, the extinction crosses continue rotation to the state shown in Figure 6c, inclined with the polarizers by approximately 15°, indicating that again synclinic and anticlinic microdomains coexist. This is achieved if in the homogeneously chiral microdomains all molecules switch around a cone from one synclinic FE structure to the other synclinic FE structure with an opposite tilt direction and polar direction (follow the dotted blue line in Figure 6 from d to c), whereas in the racemic domains the molecules in every second layer switch around a cone leading to a transition from the synclinic AF structure to the anticlinic FE structure (follow the pink line in Figure 6 from d to c). This means that the chiral synclinic FE microdomains ($\mathrm{SmC_sP_F}$) are more stable and retain their polar organization at zero voltage. Only after field reversal do these synclinic FE domains switch to the opposite FE state. The racemic anticlinic FE microdomains ($\mathrm{SmC_aP_F}$) are less stable and readily relax to the AF state at zero voltage. Hence at $T<110\,^{\circ}\mathrm{C}$ there is a coexistence of FE and AF switching microdomains and there is a temperature-dependent change of the switching mechanism from FE to AF only for the anticlinic (racemic) organization, whereas for the synclinic (chiral) organization the FE structure is stable also at zero voltage over the whole temperature range and FE switching is exclusively observed. This is the first time that the observation of such a distinct switching behavior is reported for diastereomeric configurations of a mesophase. However, the AF switching is slow and therefore at all the temperatures only one polarization reversal current peak is found under a triangular wave voltage.

In the case of compounds **F2** and **Fi2**, which have larger nonbranched or branched heptamethyltrisiloxane segments, optical investigations under a dc field indicate a bistable (FE) switching over the whole temperature range (see Supporting Information).[6]

Another remarkable feature of these compounds is seen during the growing process of the domains under an applied ac field (see Figure 7). Whereas for compound **F1** the racemic $\mathrm{SmC_aP_F}$ organization was exclusively obtained under these conditions (see Figure 5b), in the case of compound **F2** there is a temperature-dependent reorganization of the molecules. For **F2** a homogeneously chiral synclinic organization (extinction brushes inclined with the polarizers, $\mathrm{SmC_sP_F}$) is obtained upon cooling the isotropic liquid state, but on further cooling a slow transition to the (racemic) anticlinic organization (extinction brushes parallel to the polarizers, $\mathrm{SmC_aP_F}$) is observed. This means that there is a temperature-dependent change of the diastereomeric superstructures from synclinic FE at high temperature to anticlinic FE at lower temperatures.[19]

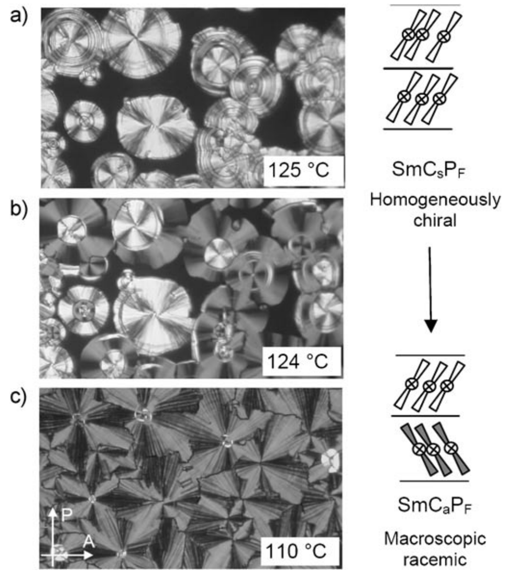


Figure 7. Changes in the molecular organization of compound **F2** as seen upon cooling under a triangular-wave electric ac field (150 $\mathrm{V_{pp}}$; 200 Hz; 5-μm noncoated ITO cell): a) Exclusively $\mathrm{SmC_sP_F}$ domains; b) Transition from $\mathrm{SmC_sP_F}$ to $\mathrm{SmC_aP_F}$; c) Nearly complete transition to $\mathrm{SmC_sP_F}$ domains (see also Supporting Information).

In summary, the first examples of quaternary four-block bent-core molecules are reported. Compounds **F2** and **Fi2** with large heptamethyltrisiloxane units show exclusively ferroelectric switching, whereas a clear antiferroelectric switching is observed for compound **F**, which lacks a siloxane unit (Table 1). It is thought that the segregation of the siloxane units favors the synpolar organization that leads to FE switching. For compounds **F2** and **Fi2**, the siloxane sublayers are robust and FE switching is observed at all temperatures. However, for compound **F1** with a short pentamethyldisiloxane unit there seems to be a competing influence of the fluorocarbon chains. At lower temperature, the fluorinated segments become more rigid and therefore the out-of-plane interlayer fluctuations between the layers become more important. These fluctuations are entropically favored and can take place more easily across synclinic and antipolar interfaces than across anticlinic and synpolar interfaces (see dotted arrows in Figure 1a,b).[6a,18] For this reason the $\mathrm{SmC_aP_F}$ domains, which have both types of unfavorable interfaces, are more strongly destabilized by a decrease in the temperature than the $\mathrm{SmC_sP_F}$ domains, which have only one type. This could explain why these domains relax to the $\mathrm{SmC_sP_A}$ state at zero voltage (AF switching), whereas the $\mathrm{SmC_sP_F}$ domains remain stable (FE switching). Hence, variations in the balance of fluorinated and siloxane end groups lead to interesting bulk properties and allow a fine-tuning of the mesophases of bent-core mesogens.

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[19] Usually, this phase sequence is the other way around; that is, the chiral organization (SmC_aP_A) is obtained by heating from a crystalline or B4[*] phase, whereas on cooling from the isotropic liquid the racemic structure (SmC_sP_A) is formed (see ref. [3]).

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