with response times of less than one minute. The average response ratio at 3 ppm NO_2 was 1.16.

Individual SnO_2 nanoribbons are small, fast and sensitive devices for detecting ppm-level NO_2 at room temperature under UV light. These nanodevices can be operated under laboratory conditions over many cycles without loss of sensitivity. The advantages of low-temperature, potentially drift-free operation make SnO_2 nanoribbons good candidates for miniaturized, ultrasensitive gas sensors in many applications. Further sensitivity increases should be achievable by using thinner nanoribbons, developing ohmic SnO_2–metal contacts and decorating these structures with catalysts. With such innovations, the chemical detection of single molecules on nanowires may soon be within reach.

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Chirality and Macroscopic Polar Order in a Ferroelectric Smectic Liquid-Crystalline Phase Formed by Achiral Polyphilic Bent-Core Molecules[**]

Gert Dantlgraber, Alexei Eremin, Siegmar Diele, Anton Hauser, Horst Kresse, Gerhard Pelzl, and Carsten Tschierske*

Materials with a macroscopic polar order have a variety of useful properties, such as piezo- and pyroelectricity and second-order nonlinear optical activity[1, 2] Especially ferroelectric (FE) and antiferroelectric (AF) liquid crystalline (LC) materials are of great interest, because they can be rapidly switched between different states by means of external electrical fields.[3, 4] These properties makes them useful for numerous applications, such as electrooptic devices, information storage, switchable NLO (nonlinear optic) devices and light modulators, which may be of interest for optical computing and other future technologies. At first, smectic LC phases with tilted arrangements of nonracemic chiral rodlike and disclike molecules have been used for this purpose and for a long time molecular chirality appeared to be essential for obtaining such materials.[3] However, the discovery by Niori et al. that bent-core mesogenic compounds (banana-shaped molecules) without molecular chirality, can also organize in fluid smectic phases with a polar order opened a new area in the field of LC research.[5, 6] The polar structure of the smectic layers of such molecules is provided by the dense directed packing of their bent aromatic cores. However, to escape from a macroscopic polar order 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.[7] In most cases of such mesophases the molecules are additionally tilted relative to the layer normal.[8] Therefore these phases (also known as "B2"-phases) can be described as tilted smectic phases (SmC) with a polar order of the molecules (P) within the layers, and an antiparallel polarization in adjacent layers (A), which leads to the notation $SmCP_A$. Because the molecules in adjacent layers can have either a synclinic (molecules in adjacent layers are tilted in the same direction, C_S) or an anticlinic (molecules in adjacent layers are tilted in opposite directions, C_A) interlayer correlation, the four different phase structures shown in Figure 1 may result for such mesophases.[7] Usually, the AF phases represent the ground states, whereas the FE states (SmC_SP_F and SmC_AP_F) can only be achieved after

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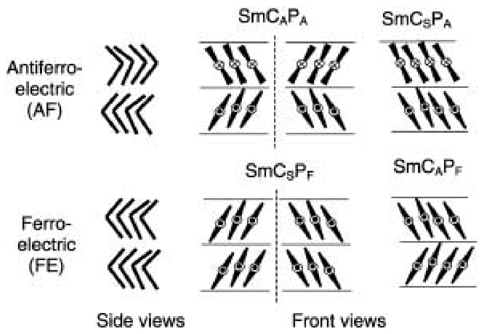
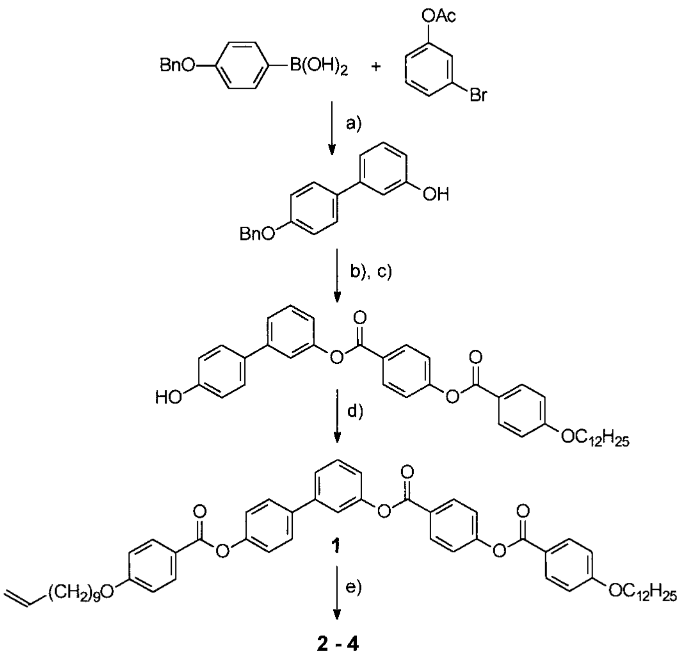
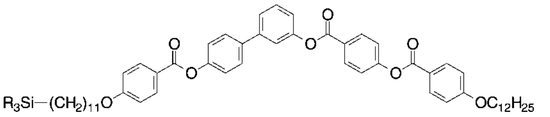


Figure 1. The four possible states of SmCP phases that are distinguished by the relative tilt sense and the polar order in adjacent layers. The notations C$_S$ and C$_A$ refer to synclinic and anticlinic tilt while P$_F$ and P$_A$ refer to ferroelectric (FE) and antiferroelectric (AF) polar order in adjacent layers.[7]



Scheme 1. Synthesis of compounds **1**–**4**. a) cat. [Pd(PPh$_3$)$_4$], NaHCO$_3$, H$_2$O, glyme, reflux, 8 h;[15] b) 4-(4-dodecyloxybenzoyloxy)benzoic acid,[13] CMC, DMAP, CH$_2$Cl$_2$, 20 °C, 24 h;[16] c) H$_2$, Pd/C, AcOEt, 20 °C, 24 h; d) 4-(10-undecene-1-yloxy)benzoic acid,[17] CMC, DMAP, CH$_2$Cl$_2$, 20 °C, 24 h;[16] e) R$_3$SiH (R is shown in Table 1), Karstedt's catalyst, toluene, 20 °C, 30 min;[14d] CMC = *N*-cyclohexyl-*N*′-(2-morpholinoethyl)carbodiimide methyl p-toluenesulfonate; DMAP = 4-dimethylaminopyridine

Table 1. Transition temperatures (T) and corresponding enthalpy values [in square brackets] of the compounds **2**–**4**.[a]



Compound	R$_3$Si-	T [°C] [ΔH/kJ mol^{-1}]				
2	Me$_3$SiOSiMe$_2$-	Cr	77 [17.0]	SmCP$_A$	118 [23.5]	Iso
3	Me$_3$Si(OSiMe$_2$)$_2$-	Cr	70 [29.3]	SmCP$_F$	115 [24.3]	Iso
4	(Me$_3$SiO)$_2$SiMe-	Cr	63 [8.9]	SmCP$_F$	116 [21.1]	Iso

[a] Abbreviations: Cr = crystalline solid state; SmCP$_A$ = antiferroelectrically switchable smectic mesophase in which the molecules are tilted with respect to the layer normal and have a polar order within the layers; SmCP$_F$ = ferroelectrically switchable smectic mesophase in which the molecules are tilted with respect to the layer normal and have a polar order within the layers; Iso = isotropic liquid phase. Transition temperatures and enthalpies were determined by DSC (Perkin-Elmer DSC-7, first heating scan, rate: 10 K min^{-1}) and confirmed by polarized-light optical microscopy.

applying a sufficiently strong external electric field. They are not stable and relax back to the AF state after the electric field is switched off. Only recently first examples of ferroelectric switchable mesophases were reported for a few special bent-core molecules. Remarkably, the materials showing this special switching behavior in fluid smectic phases (SmCP phases) are chiral molecules or their mixtures.[9] Ferroelectric switching was also observed for higher-ordered "banana phases", for a "B7" phase formed by a racemic mixture[10] of bent molecules and for a "B5" phase formed by achiral molecules.[11] Here we report first examples of nonchiral molecules forming a ferroelectrical switchable fluid smectic phase (SmCP$_F$ phase). They are a novel type of polyphilic liquid crystal[2, 12] composed of three incompatible units: A bent rigid aromatic core,[13] two flexible alkyl chains, and a bulky oligosiloxane unit[14] at one end.

The synthesis of these molecules is shown in Scheme 1 and the phase-transition temperatures obtained by polarized-light optical microscopy and differential scanning calorimetry (DSC) are summarized in Table 1.[18] The parent compound **1** of this series, composed only of the rigid bent-core unit and two terminal hydrocarbon chains shows a conventional SmCP$_A$-phase with a typical AF switching behavior, which is characterized by the occurrence of two polarization peaks in the switching current response. This phase is only monotropic [metastable, phase sequence: Cr 108 (SmCP$_A$ 98) Iso], but hydrosilylation[14d] leads to the ternary block molecules **2**–**4** which show significantly increased stabilities of their mesophases, despite that the oligosiloxane units are very bulky and therefore are expected to reduce the mesophase stability. Instead, the mesophase stability is nearly independent of the size of the siloxane units. Even for molecule **4**, with a branched trisiloxane unit, nearly the same transition temperature is found. All siloxane derivatives **2**–**4** form mesophases which are quite distinct from that of the parent compound **1** and all other known liquid-crystalline phases. Typically, they appear from the isotropic liquid state as fractal nuclei which coalesce to a grainy unspecific texture which is completely dark (optically isotropic) between crossed polarizers, showing only very small irregularly distributed bright spots. The most remarkable feature is that in these mesophases domains of opposite handedness can be distinguished. Rotating the analyzer by a small angle (5–10°) dark and more bright domains become visible. If the analyzer is rotated in the opposite direction the brightness of the domains is reversed (Figure 2). The light transmission does not change if the sample is rotated. This effect has already been reported for the "B4" phase,[19] which actually represents a soft crystal, and the "Sm1"-phase which also seems to have a three-dimensional superstructure though only a simple layer structure is found by X-ray diffraction.[20] However, in contrast to these

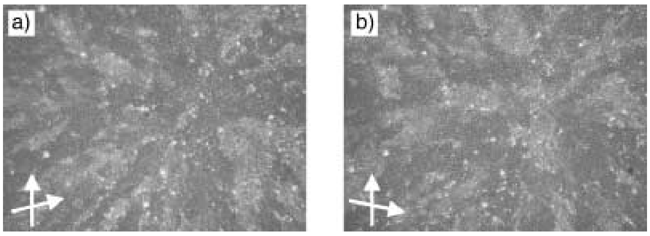


Figure 2. Texture of the mesophase of compound **4** ($T = 105\,^{\circ}C$) obtained by cooling the isotropic liquid without applied field. The photographs were taken with polarizer and analyzer slightly uncrossed to distinguish domains of opposite chirality. Changing the direction of the analyzer as indicated by the arrows [compare (a) and (b)] reverses the brightness of the domains. The brightness of the images is strongly enhanced to make the different regions visible.

phases, in the mesophases of **2**–**4** the transparent blue color which is typical for B4 and Sm1 phases cannot be observed, and these mesophases are highly fluid, like conventional SmA and SmC phases.

X-ray investigations (non-oriented samples, Guinier camera) confirm the presence of a well-defined layer structure by the appearance of a sharp layer reflection and its higher orders (up to the 4th order) with $d = 4.4$ nm for compound **4**. For this compound the diffuse scattering in the wide-angle range has a very asymmetric profile in which two maxima can be separated, one maximum at 0.45 nm corresponds to the mean distance between the fluid alkyl chains and the second one with a maximum at about 0.7 nm corresponding to the mean distance between the disordered siloxane units. This is an indication of a fluid nanosegregated organization. It can be assumed that because of the significantly larger space required by the siloxane units compared to the rest of the molecule the molecules should adapt an antiparallel end-to-end packing within the layers. In this way the siloxane units build up their own sublayers, which leads to the triple-layer structure shown in Figure 3. The effective molecular length L is around 5.5 nm, which is significantly larger than the layer spacing found in X-ray measurements. This result is in line with the proposed monolayer structure in which the molecules are additionally tilted by an angle of about 30–35 degrees with respect to the layer normal.

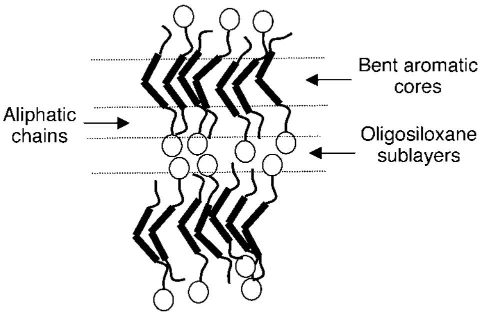


Figure 3. Proposed triple-layer organization of the molecules **3** and **4** in the $SmCP_F$ state.

In the next step electrooptical investigations were carried out in a transparent sandwich-type capacitor cell consisting of two indium-tin-oxide (ITO) coated glass plates. The repolarization current in response to an applied triangular-wave field[21] shows two peaks for the disiloxane derivative **2** (AF switching) and only one peak for compounds **3** and **4**, as typical for FE switching (Figure 4). Compound **4** was investigated in more detail. Even at very low frequency (0.02 Hz) we observed only one very sharp current response peak, corresponding to a high value of the spontaneous polarization of 700 nCcm^{-2}. This one-peak response is found in every case, independent of the sample preparation. It is a strong indication for an FE switching behavior which is additionally supported by optical observations of the switching process.

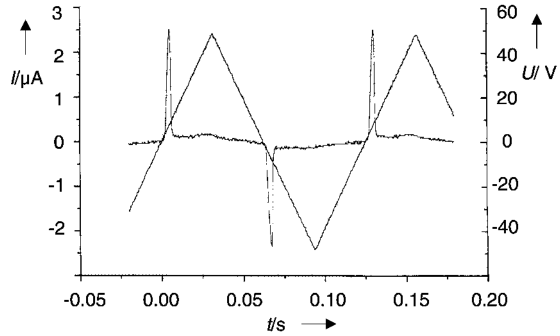


Figure 4. Switching current response in the mesophase of compound **4** on applying a triangular-wave voltage at 104 °C in a 10 μm non-coated ITO cell (EHC, Japan) at a frequency of 1 Hz.

If the isotropic liquid is slowly cooled under an applied dc electric field (10 V μm^{-1}) a texture with many circular domains appears (Figure 5a). In these domains the smectic layers are circularly arranged around the center of the domains. The characteristic feature of these domains are extinction crosses, whereby the direction of the extinction brushes corresponds to the direction of the optical axes of the smectic layers. In these bright birefringent field-induced circular domains the extinction crosses are rotated by 70–80° clockwise or anticlockwise depending on the sign of the applied field. This angle corresponds to twice the tilt angle. It should be emphasized that the extinction crosses remain unchanged if the field is switched off, that means, there is no relaxation of the switched state as observed in the AF phases. This bistable switching clearly points to an FE ground state, which confirms the results of the current-response measurements. In this FE ground state the correlation between adjacent smectic layers is synclinic (SmC_SP_F).

If however, an alternating field (ac, 10 V μm^{-1}, 200 Hz) is applied during cooling the isotropic liquid, the appearing mesophase shows in addition to a weakly birefringent fanlike texture also weakly birefringent circular domains (Figure 5b). In these domains the extinction crosses coincide with the direction of polarizer and analyzer. On applying an electric field the extinction crosses do not rotate, although a switching process is clearly visible. In this case the ferroelectric ground state can be explained by an anticlinic packing of the molecules in adjacent layers (SmC_AP_F).

In contrast to the states obtained under the influence of an external electric field, there is obviously no birefringence if the smectic phase is formed without such an applied field, that

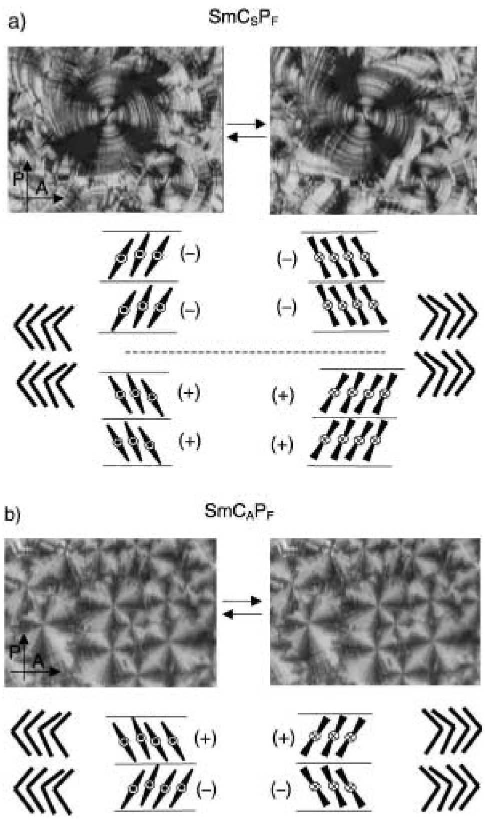


Figure 5. Switching behavior observed between crossed polarizers. a) Texture obtained by cooling the isotropic liquid under an electric dc field of $10\,\text{V}\,\mu\text{m}^{-1}$. The extinction cross of the circular domains does not coincide with the crossed polarizers. By switching the electric field between $+1.5\,\text{V}\,\mu\text{m}^{-1}$ (left-hand side) and $-1.5\,\text{V}\,\mu\text{m}^{-1}$ (right-hand side) the extinction cross rotates by an angle of 70–80° (sample thickness: 10 µm; $T=70\,^{\circ}\text{C}$)[22] b) Texture obtained by cooling the isotropic liquid under an electric ac field of $10\,\text{V}\,\mu\text{m}^{-1}$ (200 Hz). The extinction crosses coincide with the crossed polarizers and do not rotate on applying an electric field (sample thickness: 10 µm; $T=70\,^{\circ}\text{C}$).

is, this phase seems to be optically uniaxial. However, the polar order and the tilted organization of the molecules in the layers would require an optical biaxiality of this phase, that is, a birefringence is expected to occur. Another characteristic feature of this texture is the existence of domains with opposite chirality (see above). These findings point to the presence of a helical arrangement of the molecules with the helix axis perpendicular to the substrate surfaces, whereby the pitch of this helix is different from the wavelength of the visible light and the helix-sense is different in regions with opposite chirality. The helix axis can occur perpendicular to the layer planes (SmC*-like) or parallel to the layer planes (TGB-like). Both helical superstructures would lead to optical uniaxiality of the phases and would allow a compensation of the layer polarity on a macroscopic scale by retaining a nearly parallel alignment of the bent directions of the molecules in adjacent layers.

In summary, the mesophase presented here is the first FE switchable SmCP phase which is formed by achiral bent-core mesogens. Additionally, the materials have interesting properties which could be of use in applications; they are stable, have a low conductivity, and their mesophases occur at comparatively low temperatures. The appearance of siloxane sublayers seems to have an essential influence on the preference of a parallel alignment of the molecular bent directions in adjacent layers. Usually, the packing of the bent molecules in adjacent layers is antiparallel (AF), which provides synclinic interlayer interfaces (see side views in Figure 1). These easily allow interlayer fluctuations and are therefore entropically favorable. In the FE state the parallel molecular bent directions in adjacent layers lead to anticlinic interlayer interfaces between them, which are disfavored because they suppress the interlayer fluctuations. Decoupling the layer interfaces by the siloxane sublayers reduces or inhibits these interlayer penetrations and therefore their importance for the molecular organization is reduced, which allows a ferroelectric order more easily.[23] The importance of the decoupling of the layers is also shown in that reducing the number of siloxane units gives rise to AF properties (compounds **1** and **2**). This decoupling may also be responsible for the possibility to control the relative tilt direction of the molecules in adjacent layers (synclinic versus anticlinic) by changing the type of the applied electric field (dc versus ac). Additionally, it should be pointed out that the supramolecular organization of these molecules is strongly influenced not only by external fields, but also by the interactions with the substrate surfaces, which all together define the system as a whole.

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[22] Two distinct enantiomeric configurations, which differ in the tilt-direction and the direction of the polar axes of the molecules in the smectic layers (+/+ and −/−), are possible for the SmC_SP_F state.[7] They occur in different regions within the sample, in which the extinction crosses rotate either clockwise or anticlockwise.

[23] Quite similarly, decreasing the temperature reduces the out-of-layer fluctuations and could lead to a transition from an AF to FE order as recently shown for a B5-phase.[11]