

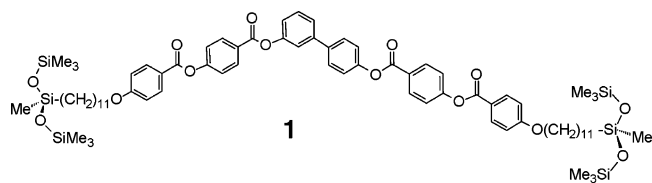
## Banana-Shaped Liquid Crystals with Two Oligosiloxane End-Groups: Field-Induced Switching of Supramolecular Chirality

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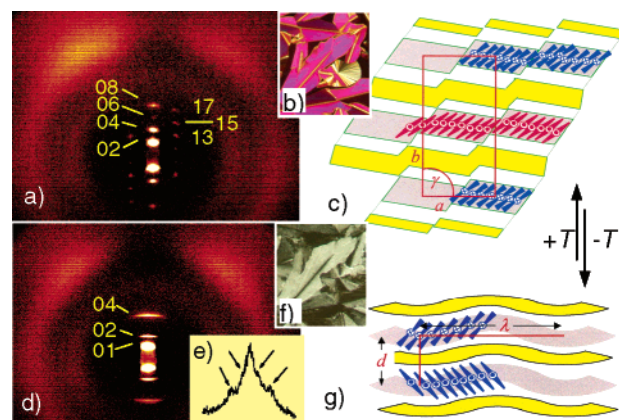
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The liquid crystalline (LC) state is a unique state of matter combining order and mobility. Apart from many practical applications, this combination is also of importance for biological self-assembly. LC molecules with a bent molecular shape, so-called banana-shaped liquid crystals, have attracted special attention, because such materials organize into fluid phases with polar order and supramolecular chirality,<sup>1</sup> properties which are of current interest in different areas of science. The polar order results from the directed organization of these molecules with the bend angles of adjacent molecules pointing into the same direction. Chirality arises due to the tilted organization of these *nonchiral* molecules in polar layers. Polar direction, tilt direction, and the layer normal define either a right-handed or a left-handed system (see Figure S1 in the Supporting Information).<sup>2</sup> Changing either polarization direction or tilt direction changes the chirality sense of the layer.<sup>2</sup> Such soft matter systems, capable of spontaneously generating polar and chiral superstructures, which can be switched by external fields could lead to novel functional materials. Bent core molecules, related to **1**, but without siloxane units form antiferroelectric (AF) switching layer structures.<sup>3a</sup> Attaching one oligosiloxane unit to such molecules leads to a transition from AF switching to ferroelectric switching liquid crystals.<sup>3b</sup> Now, the first bent core molecules containing oligosiloxane units at both ends have been prepared, and it was found that this gives rise to (i) the formation of modulated smectic phases in which the molecules adopt an AF polar order, (ii) extremely large tilt angles, and, most importantly, (iii) a field-induced switching of the molecules by collective rotation around the molecular long axes, a process which switches the chirality sense of the layers.



Compound **1** with branched siloxane units will be discussed as a representative example. It was synthesized by hydrosilylation<sup>3b</sup> of the diolefinic precursor with 1,1,1,3,5,5,5-heptamethyltrisiloxane using Karstedt's catalyst. Two different LC phases were identified between the melting point at 91 °C and the transition to the isotropic liquid state at 143 °C with a mesophase transition at 127 °C. The X-ray diffraction pattern of a surface-aligned sample of the high-temperature phase (Figure 1a) indicates a columnar mesophase with the monoclinic/oblique layer group  $p112/n$  ( $a = 4.5$  nm,  $b = 8.8$  nm,  $\gamma \approx 90^\circ$ ).<sup>4</sup> In the wide-angle region, two diffuse maxima could be observed; one at 0.74 nm forms a closed ring and corresponds to the mean distance between the microsegregated siloxane units.



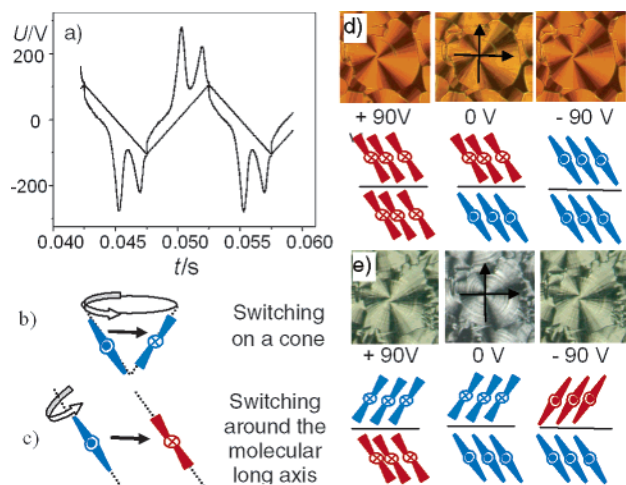
**Figure 1.** X-ray diffraction pattern of an aligned sample (a, d), textures as seen between crossed polarizers (b, f), and models of the mesophases (c, g) of compound **1**: (a–c) Col<sub>AF</sub> phase at 130 °C; (d–g) SmC<sub>APA</sub> phase at 110 °C; (e)  $\chi^2$ -scan of the 0.4 layer reflection (SmC<sub>APA</sub> phase), taken from the small-angle XRD pattern (see Figure S2 in the Supporting Information for details). The samples were surface aligned, and the X-ray beam was applied parallel to the surface (2D-detector, HI-Star, Siemens). Models: yellow = oligosiloxane units, white = alkyl chains, gray = aromatic cores; the view upon the bent aromatic cores is along the polar axis pointing out of the plane (points) or into the plane (crosses).

The diffuse scattering at 0.47 nm—assigned to the mean distance between the fluid aliphatic chains and the aromatic parts—has distinct maxima positioned out of the equator, indicating a tilted arrangement of the molecules with an average tilt angle of about 55°. The diffuse character of these reflections confirms the LC behavior of this mesophase. The presence of a preferred direction (higher intensity at the left, Figure 1a) indicates an organization with synclinal (uniform) tilt orientation of the molecules. On the basis of these experimental observations, the model shown in Figure 1c is proposed. Accordingly, this mesophase is a modulated smectic phase. The modulation should be due to the very different size of the branched oligosiloxane parts and the hydrocarbon parts of these hybrid molecules. Therefore, the organization in flat layers is not possible and the molecules are organized in ribbons which are shifted with respect to each other to overcome this steric frustration. This leads to the 2D-lattice. Because of this 2D-lattice and the AF switching behavior (see below), the phase is abbreviated as Col<sub>AF</sub>.

At the transition to the low-temperature phase, the cross reflections completely disappear, and in this phase only the reflections on the meridian are retained, which indicate a layer structure with  $d = 4.7$  nm (Figure 1d). The tilt angle decreases to 48°. Furthermore, satellites of weak intensity are arranged in lines beside the layer reflections (see Figure S2 in the Supporting Information). This indicates an undulated smectic structure (Figure 1g) with a temperature-dependent undulation wavelength ( $\lambda$ ) along the layers ( $\lambda = 12.5$  nm at 110 °C,  $\lambda = 10.5$  nm at 90 °C). The two distinct wide-angle reflections are retained, but the crescentlike diffuse outer scatterings ( $D = 0.47$  nm) become identical in

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**Figure 2.** (a) Switching current response curve obtained by applying a triangular-wave voltage at 116 °C ( $\pm 105$  V, 100 Hz, 5  $\mu$ m ITO coated cells, EHC, Japan); the two current peaks within one half-period of the applied voltage indicate an AF switching.<sup>2</sup> (b) Switching on a cone reverses only the layer polarity. (c) Switching around the molecular long axis reverses both polarity and layer chirality (chirality sense is indicated by red/blue). (d, e) Due to the switching around the long axes, the extinction crosses of the circular domains do not change their position by reversing the sign of the applied voltage; arrows give the positions of the polarizer and analyzer. (d) Col<sub>AF</sub> phase at 130 °C. (e) SmC<sub>APA</sub> phase at 115 °C.

intensity. This reveals that the tilt direction alternates in adjacent layers ( $C_A$ ); therefore, this phase is assigned as SmC<sub>APA</sub> ( $P_A$  = polar AF, see below). The change from synclinc to anticlinc tilt at the Col<sub>AF</sub> to SmC<sub>APA</sub> transition is in line with the significant decrease of the birefringence at this phase transition (Figure 1b, f). Because the tilt direction is coupled with layer chirality,<sup>2</sup> this corresponds to a transition from a macroscopic racemic to a homogeneously chiral phase structure (conglomerate).

Under a triangular-wave voltage, AF switching could be observed in the temperature region of both mesophases (Figure 2a). The spontaneous polarization values increase from 125 nC cm<sup>-2</sup> at 135 °C (Col<sub>AF</sub>) to 520 nC cm<sup>-2</sup> at 116 °C (SmC<sub>APA</sub>). This can be explained by a reduction of polar order at higher temperature, possibly due to the diminished barriers for rotation around the molecule long axis. Optical investigation of the switching behavior was done between crossed polarizers. On cooling the isotropic liquid, under a dc voltage of 65 V circular domains were obtained (Figure 2d). The characteristic feature is the appearance of extinction crosses which are inclined with respect to polarizer and analyzer. This indicates the presence of a synclinc tilt of the molecules. No change in the position of the extinction crosses could be seen either by reversing the sign of the applied voltage or on switching it off (Figure 2d). This means that the position of the molecules remains unchanged during the switching process, which can be explained by a polarization reversal that takes place by rotation around the molecular long axis (Figure 2c) and not on a cone (Figure 2b), as usually observed. This switching process reverses the chirality of every second modulated layer, leading to a field-induced transition from a racemic to a homogeneously chiral organization (Figure 2d). On decreasing temperature, at the transition into the SmC<sub>APA</sub> phase, the positions of the extinction crosses gradually change such that they align along the direction of the crossed polarizers (Figure 2e), indicating that the molecules now adopt an anticlinc organization. Again, the extinction crosses do not change their direction by reversing the sign of the applied electric field, which means that, in this mesophase also, the switching takes place around the molecular long axis.

It can be concluded that in both mesophases the two end-attached siloxane units segregate into distinct sublayers. The much larger cross-sectional areas of the branched siloxane units compared to the hydrocarbon parts lead to a significant steric frustration within the smectic layers. This gives rise to a modulation of the layers, to an unusually large tilt, and to a reduced packing density of the bent core units. However, the polar order is retained and increases with decreasing temperature. This allows a fast field-induced switching of the polar axes of the bent cores by rotation around the long axes. Such a switching process was only occasionally observed under special experimental conditions with other bent core materials.<sup>5,6b,d</sup> In compound **1**, however, this is the only switching mechanism observed under normal conditions. This process reverses the layer chirality, whereas the usually observed switching on a cone retains chirality. Additionally, there is a change from synclinc to anticlinc tilt organization with decreasing temperature. This has already been observed within some SmC<sup>7</sup> and SmCP phases,<sup>2,8</sup> but in the case of compound **1** this reorganization is associated with a transition between two different mesophases. Both mesophases can be regarded as modulated smectic phases. In the Col<sub>AF</sub> phase (synclinc tilt), the modulation is nonsymmetric and gives rise to an oblique-type lattice (Figure 1c). Such a ribbon structure is not possible if the tilt direction is anticlinc. Therefore, upon transition into the anticlinc organization, the molecules are forced to adopt a noninterrupted layer structure. To compensate the still existing steric stress, a sinusoidal undulation of the layers is induced (SmC<sub>APA</sub>, Figure 1g).

Hence, it was shown that the proper combination of microsegregation with the special packing properties of the bent cores enables the design of new complex soft matter systems with switchable polar order and field-induced switching of supramolecular chirality.

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**Supporting Information Available:** Synthesis, analytical data, and SAXD pattern of **1** and explanation of the origin of layer chirality. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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