# Influence of the core structure on the development of polar order and superstructural chirality in liquid crystalline phases formed by silylated bent-core molecules: naphthalene derivatives<sup>†</sup>‡

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Bent-core molecules based on a bent 2,7-disubstituted naphthalene unit and

heptamethyltrisiloxane units at one or both ends of the aliphatic side chains were synthesized and investigated by polarized light microscopy, differential scanning calorimetry, X-ray scattering and electrooptical investigations. The effect of fluorine substitution at the periphery of the rigid core and of the replacement of ether oxygens by carboxylate groups as linking units between the aromatic core and the flexible terminal chains was also investigated. All compounds form broad regions of liquid crystalline phases. Different types of non-polar and polar, *i.e.* antiferroelectric and ferroelectric switching smectic phases, and columnar phases were observed, depending on the molecular structure. Most interestingly, a temperature dependent transition from an antiferroelectric switching to a ferroelectric switching oblique columnar phase was observed. All double-silylated compounds show switching by a collective rotation around the molecular long axis, a process which switches the superstructural chirality in these LC systems.

#### 1. Introduction

Materials with macroscopic polar order are of significant interest for piezoelectric, pyroelectric and nonlinear optical applications. Fluid polar ordered materials with liquid crystalline properties are of special interest for fast switching electrooptical devices (displays) and liquid crystal over silicon (LCOS) devices, used for spatial light modulators (SLMs) and optical correlators.<sup>1</sup>

Meyer *et al.* first reported that ferroelectricity can occur in liquid crystalline phases with reduced symmetry.<sup>2</sup> This is achieved when enantiomerically enriched chiral molecules are arranged in layers and have an average tilt with respect to the layer normal (*e.g.* SmC\* phases).<sup>3,4</sup> In 1996 Niori *et al.* reported that (anti)ferroelectricity in smectic phases can also be achieved by achiral molecules with a chevron shape, also known as banana molecules or bent-core molecules.<sup>5</sup> The high values of the polarization ( $P_s = 600-1000 \text{ nC cm}^{-2}$ ), the occurrence of new LC phase types, unknown for other LC materials, the observation of chirality and spontaneous symmetry breaking in some cases, as well as the special

switching behavior of some mesophases attracted special interest in this field.  $^{6\mathrm{-8}}$ 

These unique properties are due to the restricted rotation of the bent molecules, giving rise to a polar direction parallel to the layers (see Fig. S1 in ESI<sup>†</sup>). In order to escape from the macroscopic polar order the bent direction usually alternates in adjacent layers, leading to antipolar (antiferroelectric = AF) ground state structures in most cases. These SmCPA phases show AF switching (see Fig. S1a<sup>†</sup>). Beside these smectic phases there are also columnar phases composed of ribbon-like segments of these layers which adopt a long range order in a 2D lattice. Rectangular (Col<sub>r</sub>) and oblique (Col<sub>ob</sub>) lattices can be distinguished in most cases.<sup>9</sup> Most of these ribbon phases are non-switchable  $(Col_r \text{ or } Col_{ob})$  or show AF switching  $(Col_r P_A \text{ or } Col_{ob} P_A)$ .<sup>10,11</sup> Several attempts have been made to design bent-core molecules with stable polar order in the absence of an electric field, leading to ferroelectric (FE) switching materials (see Fig. S1a<sup>†</sup>).<sup>12</sup> Some FE switching smectic phases and also FE switching columnar phases have been reported (Col<sub>r</sub>P<sub>FE</sub> or Col<sub>ob</sub>P<sub>FE</sub>) occasionally.<sup>13</sup> The possible modes of AF and FE organization are summarized in Fig. S1b.<sup>†</sup>

Beside the polar order, chirality in LC phases of *non-chiral* molecules and the observation of switching of the chirality sense by external fields gave rise to broad and general scientific interest in bent-core mesogens.<sup>7c-e,14</sup> Chirality in the mesophases of non-chiral bent-core molecules is due to the tilted organization of the molecules in the polar layers or ribbons. This combination of tilt and polar direction leads to the loss of mirror symmetry. Hence, layer normal, polar direction and tilt direction define either a right-handed or a left-handed system. Any change of polarization direction or tilt direction changes the chirality sense of the systems, whereas simultaneously

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changing both polar direction and tilt direction retains the chirality sense (see Fig. S2 $\dagger$ ).<sup>6</sup>

Oligo(siloxane) units at one or both ends of bent-core compounds have a large impact upon mesophase type, polar order and chirality.<sup>15–17</sup> Several of these materials exhibit surface stabilized FE switching (SmCP<sub>FE</sub> phases), and in addition show spontaneous achiral symmetry breaking, seen as a spontaneous formation of regions with opposite chirality sense in the so-called dark-conglomerate texture, designated with "[\*]" in the phase assignment.<sup>7c,8</sup> For this reason a large variety of bent-core molecules based on oligosiloxane and carbosilane segments have been synthesized in recent years.<sup>15–17</sup> As exemplified in the series of compounds in Scheme 1, the AF switching smectic phase (SmCPA) of the dialkyl-substituted molecule Bp-H<sup>18</sup> is replaced by a smectic phase showing ferroelectric switching (SmCP<sub>FE</sub><sup>[\*]</sup>) after introduction of the first heptamethyltrisiloxane unit.<sup>15a,c</sup> This smectic phase is replaced by a non-polar columnar phase (Colob), an AF switching columnar (ColobPA) and AF as well as FE switching smectic phases (SmCPA, SmCPFE) if a second silyl group is attached to the other end (compound **Bp-Si2**).<sup>17</sup> In addition the mechanism of the switching process is changed by the introduction of silvl units. The switching in the mesophases of Bp-H and Bp-Si1 takes place by a collective rotation of the bent-core molecules on a cone. This process, which is usually observed for bent-core molecules, reverses the polar direction as well as the tilt direction and hence retains the chirality of the layers as well as the macroscopic chirality (Fig. S2a<sup>†</sup>). In contrast, the switching in all mesophases of compounds Bp-Si2, silvlated at both ends, takes place by a collective rotation around the long axis which changes only the polar

direction, whereas the tilt direction is not changed. In this switching process the chirality of the layers and hence the mesophase chirality is changed (Fig. S2b†).<sup>14,17</sup> These effects of the silyl groups are mainly due to the nano-segregation of the oligo(siloxane) units into distinct sublayers located at the inter-layer interfaces, and due to the size of these units which influences the packing density between the aromatic cores and in addition can lead to a distortion of an organization in flat layers.

In nearly all silylated materials the 3,4'-disubstituted biphenyl unit<sup>18</sup> was used as the central bent unit (BU) within the bent aromatic core.<sup>15,16*a*-*c*,*f*,*g*,<sup>17</sup> In order to improve our understanding of the general structure–property relations of bent-core mesogens, to further modify the mesomorphic properties and to find new LC phases with interesting application properties we have modified the bent aromatic core. Herein we report the effects of replacing the 3,4'-biphenyl core used in compounds **Bp-Si2** and **Bp-Si1** by a 2,7-disubstituted naphthyl unit,<sup>19</sup> leading to compounds **1-Si** and **4-Si**, respectively. In addition, the effect of lateral substituents at the outer phenyl rings (Y = F, **2-Si**) and the type of linking unit X connecting the terminal chains to the bent rigid cores (ether unit in **1-Si** *vs.* ester unit in **3-Si**) was investigated for the double silylated bent-core molecule **1-Si**.</sup>

#### 2. Results and discussion

#### 2.1. Synthesis

The general synthetic pathway used to obtain compounds **1-Si** to **3-Si** is outlined in Scheme 2. As shown, the 4-(benzoyloxy) benzoic acids **B** were obtained by the esterification reaction of



Bp-Si2: Cr 89 °C SmCP<sub>FE</sub> 126 °C SmCP<sub>A</sub> 143 °C Col<sub>ob</sub>P<sub>A</sub> 147 °C Col<sub>ob</sub> 155 °C Iso

Scheme 1 Comparison of the mesomorphic properties of a compound consisting of conventional bent-core molecules (compound **Bp-H**<sup>18</sup>) with a related one having one heptamethyltrisiloxane-1-yl unit at one end (compound **Bp-Si1**<sup>15a,c</sup>) and compound **Bp-Si2** having heptamethyltrisiloxane units at both ends.<sup>17</sup> In this compound there is an additional *p*-substituted benzene ring in the bent aromatic core which gives rise to significantly enhanced mesophase stabilities in comparison to compounds **Bp-H** and **Bp-Si1**; abbreviations: Cr = crystalline state; Iso = isotropic liquid state; SmCP<sub>A</sub> = antiferroelectric switching birefringent SmC phase; SmCP<sub>FE</sub><sup>[\*]</sup> = ferroelectric switching SmC phase which is optically isotropic and composed of a conglomerate of optically active domains of opposite handedness (dark conglomerate phase); SmCP<sub>FE</sub> = ferroelectric switching birefringent SmC phase; Col<sub>ob</sub>P<sub>A</sub> = antiferroelectric switching oblique columnar phase; Col<sub>ob</sub> = non-switchable oblique columnar phase.



4-(10-undecen-1-yloxy)benzoic acid, of 3-fluoro-4-(10-undecen-1-yloxy)benzoic acid or 4-(9-decen-1-yloxycarbonyl)benzoic acid with 4-hydroxybenzaldehyde to give **A**, followed by the oxidation of the aldehyde to the corresponding benzoic acid **B**.<sup>20</sup> These substituted benzoic acids were further esterified with naphthalene-2,7-diol to yield the olefinic precursors **1-En** to **3-En**.<sup>19d</sup> The hydrosilylation of these olefinic compounds using 1,1,1,3,3,5,5-heptamethyltrisiloxane resulted in the corresponding siloxane substituted compounds **1-Si** to **3-Si**.<sup>17</sup>

The unsymmetrical olefin **4-En** with a double bond at only one end was synthesized from the precursor **C**, similar to earlier reports,<sup>19d</sup> by esterification with 4-(10-undecen-1yloxy)benzoic acid. Hydrosilylation with 1,1,1,3,3,5,5-heptamethyltrisiloxane yielded compound **4-Si** with only one silyl unit (see Scheme 3). All target compounds were purified using centrifugal thin layer chromatography followed by several crystallizations. The purity was checked by thin-layer chromatography. The chemical structure of all these compounds was confirmed by <sup>1</sup>H-, <sup>13</sup>C-, <sup>19</sup>F-, <sup>29</sup>Si-NMR and elemental analysis (see ESI<sup>+</sup> for details). The mesophase behaviour was



investigated by polarized light microscopy, differential scanning calorimetry, electro-optical investigations and X-ray scattering using powder investigations (Guinier film camera) and 2D patterns of aligned samples.

#### 2.2. Mesomorphic properties of the olefinic precursors

Transition temperatures and associated enthalpies for the intermediate compounds *n*-En with olefinic double bonds on both the terminals are collated in Table 1. Compound 1-En exhibits an enantiotropic AF switching smectic phase, which is optically isotropic and shows chiral domains of opposite handedness, as seen by slightly uncrossing the polarizers.<sup>19d</sup> Hence, it belongs to the dark conglomerate phases and this phase is assigned as SmCPA<sup>[\*]</sup>. Though the earlier reports indicate that this mesophase is a non-polar  $B_X$  phase,<sup>19d</sup> our observations clearly demonstrate two polarization current peaks indicating an AF switching which is shown in Fig. S3.<sup>†</sup> Compound 2-En with fluorine substituents at the two outer phenyl rings, in *ortho* positions to the terminal alkoxy chains, also shows a smectic phase with chiral domains. However for this compound no electro-optical response can be observed up to a voltage of about 400  $V_{\rm pp}$  (peak-to-peak voltage) for a 5  $\mu m$ thick cell, the maximum voltage attainable from our experimental set-up. Though no switching is found experimentally, the appearance of a dark conglomerate texture suggests the presence of polar order, but the voltage required for switching is obviously not reached. Therefore this mesophase is assigned as a SmCP<sup>[\*]</sup> phase.



Scheme 2 Synthesis of compounds 1-Si to 3-Si (X = CH<sub>2</sub>O, OOC; Y = H, F; R<sub>3</sub>SiH = Me<sub>3</sub>Si(OMe<sub>2</sub>Si)<sub>2</sub>H,). *Reagents and conditions: i*: 4-hydroxybenzaldehyde, DCC, DMAP, dry CH<sub>2</sub>Cl<sub>2</sub>, *ii*: NaClO<sub>2</sub>, NaH<sub>2</sub>PO<sub>4</sub>, resorcinol, *t*-BuOH, iii: DCC, DMAP, dry CH<sub>2</sub>Cl<sub>2</sub>, *iv*: Karstedt's cat., dry toluene, 25 °C, 48 h.

Scheme 3 Synthesis of monofunctionalized compounds 4-En and 4-Si ( $R_3SiH = Me_3Si(OMe_2Si)_2H$ ). *Reagents and conditions: i:* DCC, DMAP, CH<sub>2</sub>Cl<sub>2</sub>, *ii:* Karstedt's cat., toluene, 25 °C, 48 h.





SmCP<sup>(A)</sup> = smectic C phase with dark congromerate texture which does not show electrooptical switching under the used experimental conditions (see text),  $Col_{ob}P_{FE}$  = ferroelectric switching oblique columnar phase, for the other abbreviations, see Scheme 1; transition temperatures were determined from DSC heating scans (10 K min<sup>-1</sup>).

The most interesting LC phase was observed for compound 3-En, with ester groups linking the terminal chains to the rigid core. The optical texture shown in Fig. 1a indicates the columnar nature of the mesophase. The X-ray diffraction pattern of a partially aligned sample (Fig. 1b,c) can be indexed to an oblique cell. In this way the lattice parameters a = 56.4 Å; b = 46 Å and  $\gamma = 114^{\circ}$  were obtained (see Table 1 and Table S1<sup>†</sup>). Most columnar phases of bent-core mesogens represent modulated smectic phases built up by ribbon-like fragments of smectic layers organized in a 2D lattice. The parameter aprovides information about the cross section of the ribbons. It was estimated that the total number of molecules per unit cell  $(n_{cell})$  amounts to 8–9, which means that on average 8–9 molecules are located in the cross section of each ribbon (see Table S2<sup>†</sup>).<sup>21</sup> The parameter b is smaller than the molecular length  $(L = 55 \text{ Å})^{22}$  which indicates that the molecules are tilted with respect to direction b. The scattering in the wideangle region with a maximum at d = 4.7 Å is diffuse and indicates the liquid crystalline character of the mesophase. The position of the maxima of the wide angle scattering between meridian and equator and the unequal distribution of the intensity with respect to the meridian reveals a synclinic tilt (tilt angle  $\approx 27^{\circ}$ ) of the molecules in this mesophase (see Fig. 1b and S4<sup>†</sup>).

The transition enthalpy ( $\Delta H = 24 \text{ kJ mol}^{-1}$ ) for the Col<sub>ob</sub> to Iso transition is rather large (Table 1). As no sharp reflections in the wide angle region of the X-ray diffraction pattern can be found (see Fig. 1b) a highly ordered (semi-crystalline) mesophase can be excluded. In this case the high transition enthalpy is a hint of a polar organization in this mesophase. A single polarization current peak was detected in electrooptical experiments only at a very high voltage of more than 300  $V_{pp}$ in a 5 µm cell (see Fig. 1d). It disappears at the transition to the isotropic liquid state and the appearance of this peak is associated with a change of the texture. Hence, it could be possible that either a FE switching smectic phase is induced at high voltage or FE switching of the columnar phase itself is observed under these conditions. Upon slow cooling under an AC field partially aligned circular domains were obtained which do not change their position upon reversal of the applied electric field.<sup>23</sup> In these domains the extinction crosses are inclined with the polarizers, which confirms the synclinic

organization of the molecules in this mesophase. Due to the relatively dense packing of the molecules the switching process requires very high voltages. In the case of compound 3-En the dense packing might be due to the presence of the electron deficient terephthalate units which increase the attractive  $\pi$ - $\pi$ interactions between adjacent aromatic rings. The best packing of the molecules in a ribbon phase with a tilted organization of the molecules is provided in an AF structure where the polar direction changes within the modulated smectic layers along direction a and with a synpolar order along direction b (see Fig. 1e). In such an arrangement all molecules are aligned parallel at the inter-ribbon interfaces. The synpolar order between adjacent ribbons along direction b requires a splay of the polar direction, as shown in Fig. 1e, to reduce the polarization within the layer stacks and to improve the packing of the molecules at the inter-ribbon interfaces.<sup>24</sup> Due to the rather large number of molecules organized in the cross section of the ribbons the occurrence of some splay of polarization is likely.<sup>25</sup> The fact that related bent-core mesogens with ester bonds interconnecting the rigid core with the alkyl chains show B7 type mesophases with FE switching additionally supports this model.<sup>13a,b,26</sup>

#### 2.3. Mesomorphic properties of Si-containing compounds

2.3.1 Influence of the bent unit on the mesomorphic properties. Table 2 shows the influence of the central bent unit (BU) on the mesomorphic properties of the terminally silvlated bentcore molecules. It can be seen that the highest transition temperatures were found for the 2,7-disubstituted naphthalene derivative 1-Si, whereas the broadest mesomorphic range was obtained for the 3,4'-disubstituted biphenyl derivative Bp-Si2.17b The resorcinol derivative Ph-Si shows only one oblique columnar phase (ColobPA) over the whole mesomorphic temperature range.<sup>27</sup> In contrast, compounds Bp-Si2 and 1-Si with larger bent rigid cores show a series of quite different smectic and columnar mesophases. It is interesting to note that for the biphenyl derivative **Bp-Si2** the smectic phases occur below the columnar phases, whereas for the naphthalene derivative 1-Si a smectic phase is observed at temperatures above the columnar phases. However, not only the position of these smectic phases in the phase sequence, but also their structure and switching behaviour, are different.



Fig. 1 The mesophase of compound 3-En: (a) optical photomicrograph (crossed polarizers) at 168 °C during growing from the liquid state (dark region); (b) XRD pattern obtained for a partially aligned sample at 162 °C, intensity of the isotropic liquid is subtracted to enhance the visibility of the anisotropic distribution of the diffuse scattering (the slightly higher intensity at the top right suggests a synclinic tilt of the molecules); (c) small angle pattern at 162 °C; (d) switching current response attained under a triangular wave field (360 V<sub>pp</sub>, 5 Hz, 5  $\mu$ m, 155 °C); (e) model of the organization in the ribbon phase (only 5 of the 8–9 molecules located in the cross section of the ribbons are shown).

**2.3.2 Compound 1-Si**—transition from AF to FE switching columnar phases. Phase transition temperatures and associated enthalpies for the Si-containing bent-core molecules **1-Si** to **3-Si** are summarized in Table 3. Silylation of the precursors *n*-En (Table 1) gives rise to a stabilization of the mesophases and in most cases the melting points are depressed. Hence, all compounds *n*-Si form enantiotropic liquid crystalline phases with enlarged mesophase regions and these mesophases are distinct from those of the related precursors *n*-En.

Compound **1-Si** in which the 3,4'-disubstituted biphenyl unit is replaced by a 2,7-disubstituted naphthalene central unit shows three different mesophases. The high temperature phase shows a typical SmC schlieren texture, but also a broken fan texture can be observed (Fig. 2a,b). The phase transitions to the other mesophases can be observed optically by slight textural changes (see Fig. 2c,d). The high temperature phase is a tilted smectic phase (d = 44.7 Å, L = 69.5 Å<sup>22</sup>). The other two mesophases are columnar phases as indicated by XRD of aligned samples (Fig. 2f,g, Fig. 3, Table 4 and Table S1†).

In all diffraction patterns the diffuse scattering in the wide angle region indicates a synclinic tilted organization of the molecules in all three LC phases (tilt angle about 50° in the two phases at higher temperatures, about 45° in the lowtemperature phase) with microsegregated oligosiloxane sublayers (diffuse ring at d = 6.9 Å). Electrooptical investigations (see below for a more detailed discussion) indicate a non-polar SmC phase at high temperature, the columnar phase below this smectic phase shows AF switching (Col<sub>ob</sub>P<sub>A</sub>) which changes to FE at the transition to the low temperature columnar phase (Col<sub>ob</sub>P<sub>FE</sub>).

The XRD pattern of the high temperature columnar phase (Fig. 2f, 3a) can be indexed to a rectangular cell with the lattice parameters a = 23.8 Å and b = 87 Å. However, the proven synclinic tilted organization of the molecules in this columnar phase (see wide angle region in Fig. 2f which shows a clear maximum of the intensity at the right top) excludes a true rectangular lattice. In fact this mesophase has an oblique lattice with the parameters a = 23.8 Å, b = 45.1 Å and  $\gamma = 105^{\circ}$ (Fig. 3b), which accidentally coincides with a larger pseudorectangular cell, and therefore this mesophase is assigned as Col<sub>ob</sub>P<sub>A</sub>. In Fig. 4a the pseudo-rectangular lattice is shown in dotted black lines together with an oblique lattice (shown in solid lines) in a possible model of the ColobPA phase. It should be pointed out that this phase assignment, based on nonresonant X-ray scattering, cannot distinguish the polar direction of the columns. The assignment to an overall AF structure is based on electrooptical investigations which indicate an AF switching in this mesophase. There are several different possible modes for such an AF organization. In the most probable model, shown in Fig. 4a, there is an overlapping of the rod-like wings of the bent cores at the interfaces between adjacent ribbons in the modulated layers, as also proposed for the Colob phase of 3-En. However the actual organization is slightly different, as there is no interaction of the aromatic cores across adjacent layers. This avoids any unfavourable interruption of the oligosiloxane sublayers. A change of the polar direction between each ribbon within these modulated layers (along direction a) provides a parallel organization of the rod-like wings at the interfaces between the ribbons (see



**Table 2** Influence of the bent unit (BU) upon the liquid crystalline phases  $(T/^{\circ}C)$  of silvlated bent-core mesogens<sup>a</sup>

**Table 3** Phase transition temperatures  $(T/^{\circ}C)$ , and enthalpy values  $(\Delta H/kJ \text{ mol}^{-1}, \text{ values in square brackets})$  obtained for the silul-terminated bent-core compounds 1-Si to 3-Si





**Fig. 2** (a)–(d) Optical textures and (e)–(g) XRD patterns of aligned samples of the mesophases of compound **1-Si**: (a) SmC phase at 171 °C; (b) Iso–SmC transition at 173 °C; (c) paramorphotic texture of the  $Col_{ob}P_A$  phase at 160 °C; (d) paramorphotic texture of the  $Col_{ob}P_{FE}$  phase at 140 °C; (e) SmC phase at 171 °C; (f)  $Col_{ob}P_A$  phase at 160 °C; (g)  $Col_{ob}P_{FE}$  phase at 140 °C.



comp.	II C	Phase type	Lattice parameters/Å; °	$n_{\text{cell}}$
3-En 1-Si	162 160 140	Col <sub>ob</sub> P <sub>FE</sub> Col <sub>ob</sub> P <sub>A</sub> Col <sub>ob</sub> P <sub>FE</sub>	$a = 56.4; b = 46; \gamma = 114^{\circ}$ $a = 23.8, b = 45.1; \gamma = 105^{\circ}$ $a = 51.2, b = 47.5; \gamma = 110.4^{\circ}$	8–9 2–3 5–6
2-Si 3-Si	151 170	Col <sub>ob</sub> Col <sub>ob</sub>	$a = 84.5; b = 53.2; \gamma = 113.4^{\circ}$ $a = 87.9, b = 55.5; \gamma = 114.5^{\circ}$	10–11 11

<sup>*a*</sup> For details see Table S1 (ESI); abbreviations:  $n_{cell} =$  molecules per unit cell, for the calculations see Table S2 (ESI).



**Fig. 4** Proposed models for (a) the  $\text{Col}_{ob}P_A$  phase of **1-Si** (the dotted rectangle indicates the pseudo-rectangular lattice, the solid lines indicate the oblique lattice and the black arrows indicate the settings of the layer group, the light gray areas indicate the position of the oligosiloxane subspaces); (b) FE order within the modulated layers leads to unfavourable inter-ribbon interfaces; the insets in (a) and (b) show the organization of the aromatic cores at the inter-ribbon interfaces in a side view along direction *a*; (c) model of the AF ground state structure assumed for the Col<sub>ob</sub>P<sub>FE</sub> phases of **1-Si**.

of the silylated bent-core molecules.<sup>15d,16g,17b</sup> This organization would correspond to the monoclinic/oblique layer group p112/a,<sup>10b,28</sup> indicated by arrows in Fig. 4a. A splay of polarization is unlikely in this case as the ribbons have only a few molecules in the cross section.

On decreasing temperature, a complete change of the XRD small angle pattern could be observed at the transition to the lowest temperature phase (see Fig. 3d,e) and these reflections can be indexed to an oblique cell with the lattice parameters a = 51.2 Å, b = 47.5 Å and  $\gamma = 110.4^{\circ}$  (Tables 4 and S1†). Hence, the lattice parameter *a* is more than doubled whereas the parameters *b* and  $\gamma$  are only slightly increased. This means that the number of molecules in the cross section of the ribbons is nearly doubled from 2–3 to 5–6 (see Tables 4 and S2†) at the phase transition. As no significant change of the wide angle scattering is observed at the transition between the two columnar phases (see Fig. 2f,g), the tilt direction of the molecules should not be fundamentally changed at this transition. As seen in Fig. 2f and g there is a maximum



b)

a)

**Fig. 3** Indexing of the 2D X-ray patterns for a surface-aligned sample of compound **1-Si** in the  $\text{Col}_{ob}P_A$  (160 °C, (a)–(c)) and in the  $\text{Col}_{ob}P_{FE}$  phase (140 °C, (d)–(f)); (a),(d) original patterns and (b),(e) reciprocal lattices with *hk* values for the observed reflections in the small-angle region; (c),(f) full scattering range with reciprocal lattice (gray lines), real lattice (black lines), direction of the maximum of the outer diffuse scattering (dashed line), and the most probable orientation of the molecules (wedge shapes) with respect to the axes of the 2D unit cell.

Fig. 4a, inset). In addition, it is assumed that the correlation between adjacent ribbons is synclinic and synpolar, as typically observed for the preferred organization in the smectic phases intensity of the outer scattering at the right side in both mesophases. Such an asymmetric distribution arises from a packing of molecules with synclinic tilt in a sample consisting of polydomains that are not perfectly fibre-like disordered around an axis perpendicular to the alignment surface, but with a preferred orientation. In this case the orientation of the molecules with respect to the axes of the 2D lattice can be deduced from the position of this maximum. The actual tilt angle of the molecules with respect to the b axis (see Fig. 3c,f) may be estimated from the direction of the maximum of the outer scattering with respect to the  $b^*$  axis on the meridian of the 2D X-ray patterns (=  $90^{\circ}$  – tilt angle) and the lattice parameter  $\gamma$  as  $\gamma$  – (90° – tilt angle). This tilt is almost the same in both phases and amounts to about 65°. But the tilt of the molecules with respect to direction  $a (90^{\circ} - \text{tilt angle})$ changes from about  $40^{\circ}$  in the high temperature phase to about  $45^{\circ}$  in the lower temperature phase, *i.e.* the molecules become less inclined against the normal to the broken layers, and simultaneously the ribbons become broader at the phase transition.

A model of the  $Col_{ob}P_{FE}$  phase is shown in Fig. 4c. As will be explained later, the ground state structure of this mesophase is assumed to be AF, though a FE switching is observed experimentally. The organization of the molecules is very similar to that proposed for the  $Col_{ob}P_A$  phase observed for **1-Si** at higher temperature with the difference that the ribbons have a larger size.

As already mentioned, the high-temperature columnar phase shows AF switching  $(Col_{ob}P_A)$  which changes to FE in the temperature range of the low temperature  $Col_{ob}$  phase



The behaviour of the  $\text{Col}_{ob}P_A$  phase is in line with the observations made with other  $\text{Col}_{ob}P_A$  phases of bent-core molecules with silyl groups.<sup>15,17</sup> For these mesophases it is assumed that the unfavourable inter-ribbon interfaces occurring in the FE organization along the modulated layers (see Fig. 4b) are responsible for the stabilization of the AF ground state structure, leading to high threshold voltages and relatively low polarization values.<sup>15c,17b</sup>

The FE switching at lower temperature is more difficult to explain. In principle it is possible that the layer distortion is removed under the alignment field and a smectic phase is induced. In this induced smectic phase the unfavourable interribbon interfaces (stabilizing an AF organization) are largely



**Fig. 5** Switching current response traces obtained under a triangular wave (300  $V_{pp}$ , 100 Hz, 5  $\mu$ m) for the mesophases of compound **1-Si**: (a) Col<sub>ob</sub>P<sub>A</sub> phase at 155 °C, (b) Col<sub>ob</sub>P<sub>FE</sub> phase at 135 °C.



**Fig. 6** Circular domains with extinction crosses as grown under a triangular wave voltage (300 V<sub>pp</sub>, 100 Hz, 5 µm) for compound **1-Si**, their position under the applied field (left) is compared with that after switching off the applied field (right): (a) SmC phase at 172 °C; (b)  $Col_{ob}P_A$  phase at 160 °C; (c)  $Col_{ob}P_{FE}$  phase at 140 °C; the positions of the extinctions are inclined with the polarizers (indicated by arrows) which indicates a synclinic organization in all mesophases; in (a) and (c) the circular domains are smooth indicating a smectic phase, a segmented structure can clearly be seen in (b), there is a slightly lower birefringence in the 0 V states for (b) and (c) which is typically seen for a polar switching by rotation around the long axis.

removed, and hence, surface stabilized FE switching can take place, as typical for the smectic phases ( $SmCP_{FF}$ ) of other silvlated bent-core molecules.<sup>15,16g</sup> This is in line with the behaviour of other silvlated bent core molecules where a transition from ColobPA phases at higher temperature to smectic and undulated smectic phases at lower temperature is often observed.<sup>15c,17</sup> This transition is due to the larger thermal expansion coefficient of the oligosiloxane units in comparison to the other parts of the molecules, giving rise to a stronger steric frustration caused by these units at higher temperature. This is in line with the observation that the size of the ribbons is nearly doubled at the phase transition  $Col_{ob}P_A$  to  $Col_{ob}P_{FE}$ . Also the smooth appearance of the texture seen under an electric field (Fig. 6c), which is similar to that of the SmC phase (Fig 6a) but different from the ColobPA phase (Fig. 6b) is in line with the assumption of a field induced SmCP<sub>FE</sub> phase. However, in these  $SmCP_{FE}$  phases the switching between the FE states usually occurs at very low voltage, closely after zerovoltage crossing and high values of the spontaneous polarization (600–1000 nC cm<sup>-2</sup>) were measured.<sup>15,16a-c,f,g,17b</sup> This is clearly not the case for the switching of the  $Col_{ob}P_{FE}$  phase which is characterized by relatively low polarization values and a rather high threshold voltage. One possible reason could be that in the field induced smectic phase there is still some layer undulation or layer modulation which provides an energetic barrier for the switching between the two field induced FE states.

2.3.3 Influence of F-substitution at the periphery of the rigid core (compound 2-Si). Remarkably, fluorine substitution at the outer phenyl rings (compound 2-Si) eliminates the non-polar SmC phase, as well as the AF switching columnar phase and only an oblique columnar phase (Fig. 7, a = 84.5Å, b = 53.2 Å and  $\gamma = 113.4^{\circ}$ ) is found throughout the whole mesomorphic temperature range. About 10-11 molecules are organized in the cross section of these ribbons, which means that the size of the ribbons is nearly doubled in comparison to the FE switching Col<sub>ob</sub>P<sub>FE</sub> phase of 1-Si. However, this Col<sub>ob</sub> phase shows no polarization peak under a triangular wave electric field. It is also important to mention that the transition enthalpy of the Iso-Colob transition is only nearly half of the value observed for the Iso-SmC-ColobPA transition of 1-Si. Hence it is likely that there is no polar order within the ribbons of this Colob phase and that the formation of the ribbon structure is in this case only due to the steric effect of the silyl end-groups.

**2.3.4 Influence of the linking group (compound 3-Si).** In compound **3-Si** the flexible chains are connected to the aromatic core by carboxylate linking groups (X, X') instead of the ether groups in **1-Si**. This compound shows two mesophases with textures shown in Fig. 8a,b. The growth of the high temperature phase suggests a columnar or undulated smectic phase (Fig. 8a). This is confirmed by shearing experiments, where the birefringence is retained, but no schlieren texture or oily streaks texture as typical for smectic phases can be observed. However, in the XRD pattern only layer reflections can be found (Fig. 8c). In order to resolve this contradiction it is assumed that the cross reflections of a

modulated smectic phase (ribbon phase) are too weak or that this mesophase is a smectic phase with a very long or only weakly correlated layer undulation (wavy deformed layers). The wide-angle pattern of a partly aligned sample (Fig. S5a†) evidences a tilted smectic mesophase. In electrooptical investigations no polar switching could be observed, and therefore, the mesophase is tentatively assigned as a USmC phase. On further cooling a transition to an oblique columnar phase takes place which is associated with a textural change (Fig. 8b) and a change of the XRD pattern (a = 87.9 Å, b =55.5 Å and  $\gamma = 114.5^{\circ}$ , synclinic tilt, see Fig. 8d,e, Fig. S5b†



**Fig. 7** Investigation of compound **2-Si**: (a) optical texture (crossed polarizers) obtained at the Iso–Col<sub>ob</sub> transition at 178 °C, (b) natural texture of the Col<sub>ob</sub> phase at 170 °C; (c)–(e) 2D X-ray patterns for a surface-aligned sample of compound **2-Si** in the Col<sub>ob</sub> phase (151 °C): (c) small angle region; (d) indexing of the reflections in the small-angle region; reciprocal lattices of the two mainly scattering domains of the fibre-like disordered sample (black and gray lines, respectively) with *hk* values for the observed reflections and axes given for the black lattice; (e) complete diffraction pattern.



**Fig. 8** Optical textures (crossed polarizers) and XRD pattern obtained for compound **3-Si**: (a) texture of the USmC phase at 178 °C; (b) texture of the Col<sub>ob</sub> phase at 170 °C; (c) small angle XRD patterns of an aligned sample in the USmC phase at 178 °C; (d) in the Col<sub>ob</sub> phase at 150 °C; (e) indexation of the Col<sub>ob</sub> phase showing the reciprocal lattices of the two mainly scattering domains of the fibre-like disordered sample (black and gray lines, respectively) with *hk* values for the observed reflections and axes given for the black lattice.

and Table 4). The diffraction pattern and the lattice parameters are very similar to those of the  $Col_{ob}$  phase of **2-Si**. There are about 11 molecules in the cross section of the ribbons and as for **2-Si** no electro-optical current response could be detected in this mesophase, indicating a non-polar structure of this columnar phase ( $Col_{ob}$ ). The presence of a non-polar USmC phase above the  $Col_{ob}$  phase and also the small phase transition enthalpies (see Table 3) are in line with this observation.

### 2.4. Functionalization of only one end—compounds 4-En and 4-Si

For comparison we have also synthesized the naphthalene derived compound **4-Si** with an oligosiloxane unit at only one terminus. This compound shows a completely different mesophase than the double silylated compound **1-Si**. The

texture is optically isotropic and exhibits chiral domains of opposite handedness under slightly uncrossed polarizers as shown in Fig. 9a–c (dark conglomerate texture). XRD indicates a smectic phase with a layer spacing of d = 45.5 Å at 130 °C which is again smaller than the calculated molecular length (L = 66 Å)<sup>22</sup> suggesting a tilted organization. Moreover, this mesophase shows FE switching (see Fig. 9d) with a polarization of about 440 nC cm<sup>-2</sup>. Hence the mesophase is similar to that observed for the monosilylated biphenyl derivative **Bp-Si1** (SmCP<sub>FE</sub><sup>[\*]</sup> phase, see Table 2).<sup>15c</sup> However, the value of the spontaneous polarization is smaller. This is because the aromatic bent core is smaller than that of **Bp-Si1**. In this case the steric effect of the silyl groups becomes more important. As a consequence, the aromatic cores become more separated and polar order is reduced.

It is also interesting to note that the two very different compounds, the non-silvlated compound 4-En and the silvlated compound 4-Si, both show the same dark conglomerate textures, though they have a different switching behaviour. Compounds related to 4-En (with decyl and dodecyl chains) were reported to show no switching,<sup>19d</sup> but in our experiments with a higher voltage (>75  $V_{pp} \mu m^{-1}$ ) we can indicate an AF switching for 4-En (SmCP<sub>A</sub><sup>[\*]</sup> phase). Introduction of a heptametyltrisiloxane segment at one end changes the interlayer interfaces in such a way that only one polarization current peak is observed for the mesophase of 4-Si. This peak does not split under a modified triangular wave voltage (see Fig. 9d) and indicates FE switching. This behaviour is very similar to that observed for the related biphenyl derivatives and suggests that this mesophase is composed of  $[SmC_sP_F]_aP_A$  layer stacks (see Fig. 10b) as explained earlier.<sup>15c,16g,17b</sup> For **4-Si** the size of these  $SmC_sP_F$ layer stacks is sufficiently large to efficiently stabilize the FE states by polar interaction with the substrate surfaces and hence FE switching is experimentally observed.<sup>17b</sup> In addition the steric layer distorting effect of only a single silyl group is not sufficient to induce a ribbon structure and therefore FE switching is retained.

Interestingly, the birefringent textures induced under an applied electric field are stable only under the field, on terminating the applied field the birefringence disappears rather quickly and the field of view becomes dark as shown in Fig. 9f. It seems that upon field removal the layers relax to a randomly deformed layer structure, similar to the dark conglomerate phase in the ground state. Such a relaxation was also found for the SmCP<sub>FE</sub><sup>[\*]</sup> phases of some disilylated bent-core molecules with 3,4'-disubstituted biphenyl based bent-core units<sup>17b</sup> and it was attributed to a relaxation of the field induced racemic  $[SmC_sP_F]_aP_S$  structure into a (+)/(-)- $[SmC_{s}P_{F}]_{s}P_{A}$  structure (see Fig. 10) which immediately forms the optically isotropic texture, as explained in ref. 17b. As there is an equal probability for the relaxation either into a (+)- $[SmC_sP_F]_sP_A$  or into a (-)- $[SmC_sP_F]_sP_A$  structure (follow either *i* or *ii* in Fig. 10) the chiral domains are microscopically mixed and the optically isotropic state obtained after field removal does not exhibit macroscopic chiral domains. This kind of relaxation requires a rotation of the molecules around the long axis (see Fig. 10). It seems that in the series of monosilylated compounds this relaxation process is more easy



**4-En**: Cr 120 °C [12 kJmol<sup>-1</sup>] SmCP<sub>A</sub><sup>[\*]</sup> 165 °C [19 kJ mol<sup>-1</sup>] Iso



4-Si: Cr 118 °C [5.3 kJmol<sup>-1</sup>] SmCP<sub>FE</sub><sup>l+J</sup> 181 °C [23 kJ mol<sup>-1</sup>] Iso



Fig. 9 Characterization of the mesophase of compound 4-Si: (a)–(c) textures at 150 °C; (a), (c) were obtained with slightly uncrossed polarizers showing macroscopic chiral domains; (b) dark texture as seen between crossed polarizers; (d) switching current response trace obtained under a modified triangular wave field (300  $V_{pp}$ , 0.5 Hz, 5  $\mu$ m) at 130 °C, indicating a surface stabilized FE switching; (e) birefringent textures obtained under these conditions; (f) relaxation to the dark texture within a few seconds after removal of the applied field.

for the 2,7-disubstituted naphthalene derivatives which have a shorter rigid core than for the analogous 3,4'-disubstituted biphenyl derivatives, with a larger rigid core, where it is not observed or significantly slower.<sup>15c</sup>

This indicates that an oligosiloxane unit at only one of the wings is sufficient to induce FE switching, while retaining the layer structure and polar order. The second siloxane unit in compound **1-Si** further increases the steric packing frustration, giving rise to a transition to columnar ribbon phases where the inter-ribbon interfaces destabilize the FE states and change the switching process to AF. A complete loss of polar order is observed in this case at higher temperature.

#### 3. Summary and conclusions

Novel bent-core molecules based on a rigid core incorporating a bent 2,7-disubstituted naphthalene unit with oligosiloxane terminated alkyl chains at one or both ends have been synthesized and their mesophase behaviour has been investigated.

Despite the smaller size of the 2,7-naphthyl unit in comparison to the 3,4'-biphenyl unit these compounds exhibit enhanced mesophase stabilities. This is rather unexpected and indicates that probably stronger  $\pi$ -stacking interactions in the aromatic sublayers (flat  $\pi$ -system of the naphthalene core in comparison to the twisted biphenyl unit) are of significant importance for the mesophase stability. This and also the enhanced symmetry of the naphthalene unit leads to increased melting temperatures and this is the major reason for the smaller mesophase ranges observed for the naphthalene derived compounds in most cases (see Table 2). It is also interesting to note that all non-silvlated naphthalene derivatives *n*-En require very high voltages for electrooptical switching. This might also be caused by the relatively strong  $\pi$ -stacking interactions which provide a more dense packing of the bent cores. The bulky silyl groups can reduce the packing density in the aromatic sublayers and this contributes to the reduction of the threshold voltages. However, this reduced packing density also reduces the polarization values and influences the switching mechanism. These effects are



Fig. 10 Models showing the modes of organization of compound 4-Si. The assignment of the phases is given at the bottom, where the structure within the layer-stacks  $(SmC_sP_F)$  is given in square brackets and the following subscripts define the correlation of the interfaces between the layer stacks (a = anticlinic, s = synclinic, A = antipolar, S = synpolar): (a) apparently anticlinic and synpolar rac-[SmC<sub>s</sub>P<sub>F</sub>]<sub>s</sub>P<sub>S</sub> structure as obtained by cooling under an applied AC voltage; (b) the two enantiomeric  $[SmC_sP_F]_aP_A$  structures as obtained either by cooling from the isotropic liquid state without applied field or in the relaxation process after switching off an applied AC voltage, it seems that the formation of this structure is associated with a layer deformation into a dark texture for which a sponge-like deformation of the layers is proposed, the chiral domains are microscopic in size (no chiral domains can be detected) if the phase is formed by relaxation from structure (a) and macroscopic upon cooling from the isotropic liquid (dark conglomerate texture).<sup>17b</sup>

stronger for the naphthalene derivatives, because the packing of these shorter bent cores can more easily be distorted.

Bent-core compounds having only one heptamethyltrisiloxane unit are characterized by smectic phases showing surface stabilized FE switching as well as dark conglomerate textures (SmCP<sub>FE</sub><sup>[\*]</sup> phases), irrespective of whether a 3,4'-biphenyl or a 2,7-naphthalene structure is incorporated into the bent aromatic core. However, the polarization values are reduced for the naphthalene derivative due to the reduced size of the bent aromatic core.

Introduction of a second heptamethyltrisiloxane unit at the other end completely removes the  $SmCP_{FE}^{[*]}$  phases and the polar smectic phases are replaced by a non-polar smectic phase and by columnar phases. This is due to the steric frustration arising from the packing of the bulky silyl groups in a layer structure. It leads to a fragmentation of these layers into ribbon-like segments which adopt a regular organization in a 2D lattice, giving rise to columnar ribbon phases. Only at high temperature can a non-polar smectic phase arise, in which the molecules can freely rotate, as in smectic phases of calamitic molecules. It seems that in this case the increased rotational

disorder of the rigid cores at higher temperature (no polar order) increases the effective space required by the aromatic cores and this can partly compensate the steric frustration provided by the silvl units. With decreasing temperature the space occupied by the silvl groups is reduced. As a consequence polar order can set in and due to the more dense packing of the aromatic cores the layer distorting effect of the silvl groups is increased. This leads to the formation of ribbons and in the resulting columnar phase the FE state is destabilized, giving rise to an AF switching oblique columnar phases (Col<sub>ob</sub>P<sub>A</sub>). With further decreasing temperature the layer frustration is further reduced and this gives rise to an increase of the size of the ribbons, which in turns allows a relatively easy (complete or partial) removal of the layer frustration under an electric field and in this field induced mesophase FE switching takes place  $(Col_{ob}P_{FE})$ . The introduction of fluorine on the outer phenyl rings (2-Si) as well as introduction of carboxylate groups as linking units (3-Si) removes polar order. This is surprising, as in related nonsilvlated molecules (e.g. 3-En) these units favour a polar packing and FE switching.

As another consequence of the steric frustration and the less dense packing of the aromatic cores the switching process within the polar smectic and columnar phases takes place by a collective rotation around the long axis for all disilylated compounds. This switching process is of special interest as it switches the superstructural chirality in these LC systems.

In summary, these investigations have contributed to a better understanding of the structure–property relationships in bent-core LCs, especially concerning the effects of micro-segregation and packing density upon the mesophase structure and the mode of switching.

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