

Supporting Information

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

R. Amaranatha Reddy^a, U. Baumeister^b, C. Keith^a and C. Tschierske^{a,*}

^[a]Institute of Organic Chemistry, Martin-Luther-University Halle-Wittenberg, Kurt-Mothes-Str. 2, D-06120 Halle, Germany; Fax: +49 345 552 7346; Tel: +49 345 552 5664; *E-mail: carsten.tschierske@chemie.uni-halle.de

^[b]Institute of Physical Chemistry, Martin-Luther-University Halle-Wittenberg, Mühlpforte, D-06108 Halle, Germany.

1. Additional Figures

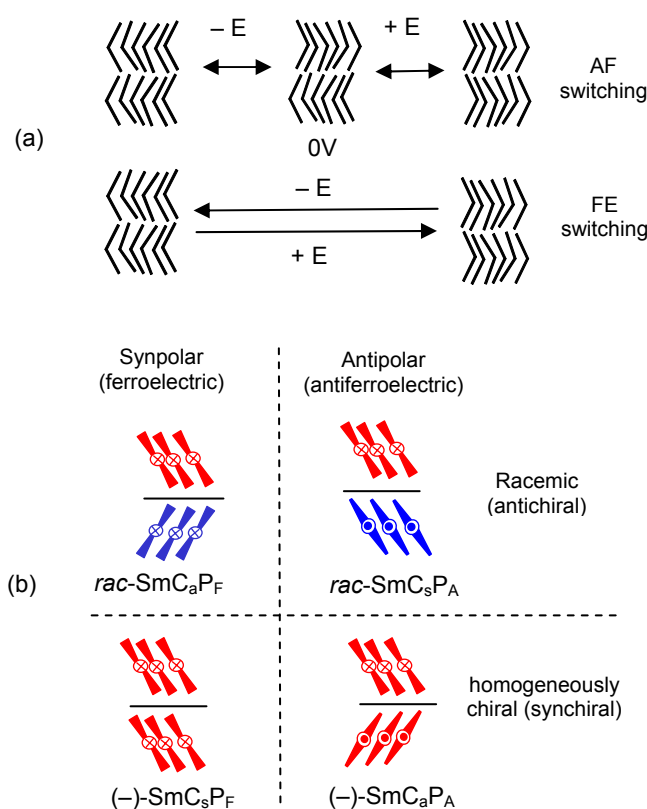


Fig. S1. Fundamental issues of the organization of bent-core molecules; (a) FE and AF switching of bent-core molecules (side views); (b) the four possible arrangements in tilted polar smectic phases; the subscripts 's' and 'a' indicate the correlation of the tilt direction in adjacent layers: s = synclinic means an identical tilt direction; a = anticlinic indicates an opposite tilt direction; subscripts 'A' and 'F' indicate the correlation of the polar direction in adjacent layers; P_A is indicative for an antipolar structure (polar direction alternates); this structure is macroscopically non-polar and usually assigned as 'antiferroelectric'; P_F stands

for a synpolar structure (polar direction is identical); this structure is macroscopically polar and usually assigned as ‘ferroelectric’; the color indicates the chirality of the layers, red (–), blue (+); the SmC_aP_A and SmC_sP_F structures are homogeneously chiral (identical chirality sense in the layers, synchiral), the SmC_sP_A and SmC_aP_F structures are macroscopically racemic (alternating chirality sense in the layers, antichiral).

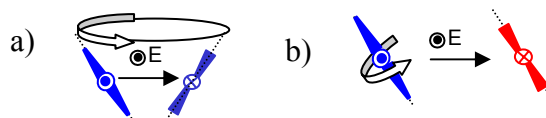


Fig. S2. (a) Switching by collective rotation on a cone simultaneously changes polar direction and tilt direction and therefore retains the layer chirality; (b) switching by collective rotation around the molecular long axes only changes the polar direction and therefore reverses the layer chirality.

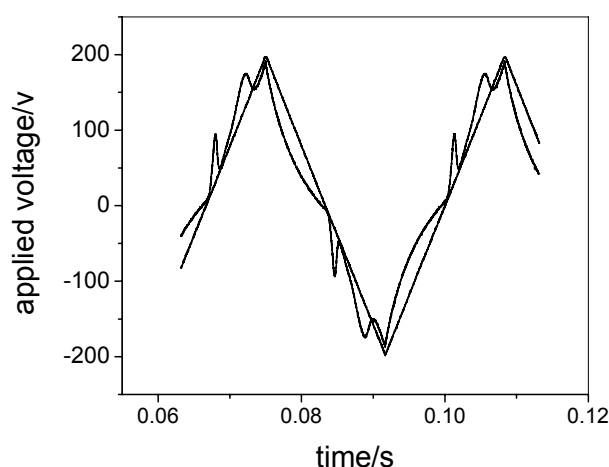


Fig. S3: Antiferroelectric switching current response obtained for the mesophase of compound **1-En** after application of a triangular-wave voltage (400 Vpp, 30 Hz, 5 μm , 130°C, polarization: 550 nC cm⁻²).

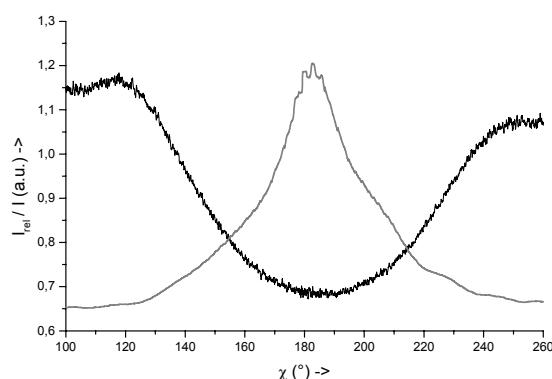


Fig. S4: χ -scan for the outer diffuse scattering in the 2D X-ray pattern of a partially surface-aligned sample of the $\text{Col}_{\text{ob}}\text{P}_{\text{FE}}$ phase of **3-En** at 162 °C (black line, $I_{\text{rel}} = I(162\text{ °C}) / I(172\text{ °C, iso})$, for comparison the position of the 01 reflection is added (gray line, I in a.u.).

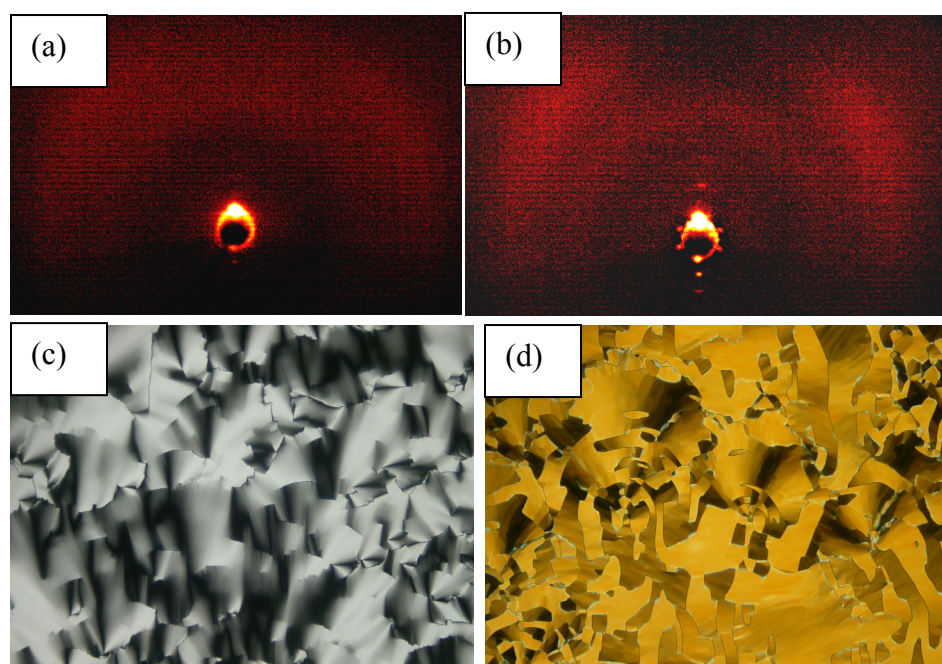


Fig. S5. (a,b) 2D XRD patterns for surface-aligned samples attained for compound **3-Si**; (a) USmC phase at 180 °C, (b) Col_{ob} phase at 170 °C; (c,d) textures obtained under a triangular wave field (400 Vpp, 50 Hz, 5 μm), (c) USmC phase at 178 °C, (d) Col_{ob} phase at 170 °C; position of the extinction crosses is independent of the applied field..

2. Additional Tables

Table S1. X-ray data of compounds **3-En** and **1-Si** to **4-Si**.^a

Compd.	$d / \text{\AA}$	$T / ^\circ\text{C}$	Phase type/Lattice parameters/ $\text{\AA}$	n_{cell}
3-En	51.5 (10); 42.0 (01 and -11); 27.5 (11); 23.8 (-12); 21.2 (02)	162	Col _{ob} P _{FE} $a = 56.4$; $b = 46$; $\gamma = 114^\circ$	8-9
1-Si	44 (1), 22 (2)	170	SmC	
	43.5 (01), 23.1 (10 and 1-1), 21.8 (02), 18.4 (1-2), 13.9 (1-3), 14.4 (03), 11.0 (1-4), 10.8 (04)	160	Col _{ob} P _A $a = 23.8$, $b = 45.1$ $\gamma = 105^\circ$	2-3
	48.0 (10), 44.5 (01), 40.4 (1-1), 22.3 (02), 17.9 (12), 12.9 (13), 11.1 (04), 10.1 (14)	140	Col _{ob} P _{FE} $a = 51.2$, $b = 47.5$, $\gamma = 110.4^\circ$	5-6

Table S1 continued

Compd.	$d / \text{\AA}$	$T / ^\circ\text{C}$	Phase type/Lattice parameters/ $\text{\AA}$	n_{cell}
2-Si	77.6 (10), 51.2 (1-1), 48.8 (01), 38.8 (20 and 2-1), 24.2 (02), 16.1 (03)	151	Col _{ob} $a = 84.5$; $b = 53.2$, $\gamma = 113.4^\circ$	10-11
3-Si	51.6 (1)	180	USmC	
	79.8 (10), 54.0 (1-1), 50.5 (01), 40.0 (20 and 2-1), 25.3 (02), 16.8 (03)	170	Col _{ob} $a = 87.9$, $b = 55.5$, $\gamma = 114.5^\circ$	11
4-Si	45.5 (1), 22.7 (2)	130	SmCP _{FE}	

^a abbreviations: n_{cell} = molecules per unit cell,

Tab. S2 An estimate of the number of molecules in the cross section of the ribbons within the Col_{ob} phases of compounds **3-En**, **1-Si**, **2-Si**, and **3-Si**; $V_{\text{mol,cr}}$ = molecular volume ($\text{\AA}^3$) in the crystal calculated using crystal volume increments [1], average packing coefficient in the crystal $k = 0.7$ according to $V_{\text{mol,is}}$ = molecular volume ($\text{\AA}^3$) in the isotropic liquid, average packing coefficient [2] $k = 0.55$; V_{cell} = unit cell volume ($\text{\AA}^3$) obtained from the lattice parameters and assuming a height of $h = 5.2 \text{ \AA}$ (assuming a stacking in bend direction of molecules with a bend angle of 120°); n_{cell} = number of molecules in a unit cell with crystal-like density (cr) according to $n_{\text{cell,cr}} = V_{\text{cell}}/V_{\text{mol,cr}}$, with liquid-like density (is) according to $n_{\text{cell,is}} = n_{\text{cell,cr}} \cdot 0.55/0.7$, and in the LC phase (LC) estimated as the intermediate between that in the crystalline and the liquid phase.

Comp.	$V_{\text{mol,cr}}$	$V_{\text{mol,is}}$	V_{cell}	$n_{\text{cell,cr}}$	$n_{\text{cell,is}}$	$n_{\text{cell,LC}}$
1-Si (Col _{ob} P _{FE})	1891.2	2407.0	11853.2	6.3	4.9	5-6
1-Si (Col _{ob} P _A)	1891.2	2407.0	5391.4	2.9	2.2	2-3
2-Si (Col _{ob})	1903.0	2422.0	21453.5	11.3	8.9	10-11
3-Si (Col _{ob})	1897.0	2414.4	23083.8	12.2	9.6	11
3-En (Col _{ob} P _{FE})	1320.6	1680.8	12324.5	9.3	7.3	8-9

3. Experimental Methods

The mesophase behaviour of all the compounds was examined under a polarized light optical microscope (Optiphot-2, Nikon) attached with a hot stage (FP-82 HT, Mettler) by sandwiching the sample between a glass slide and a cover-slip. The transition temperatures and the associated enthalpies were obtained from thermograms recorded on a Perkin-Elmer DSC-7, differential scanning calorimeter. The cooling and heating rates were $10 ^\circ\text{C min}^{-1}$.

The electro-optical switching characteristics were examined using a triangular-wave method or under a DC field using polyimide coated ITO cells, EHC Japan.

Powder X-ray diffraction measurements were carried out with a Guinier film camera (Huber) with samples in glass capillaries (1 mm) in a temperature-controlled heating stage using quartz-monochromatized CuK α radiation (1.54 Å; 30 to 60 min exposure time), calibration with the powder pattern of Pb(NO₃)₂. 2D patterns for aligned samples on a glass plate on a temperature controlled heating stage (alignment at the sample – glass or at the sample – air interface) were recorded with a 2D detector (HI-STAR, Siemens).

4. Analytical data

1-En: Yield: 70%; Cr 126 SmCP_A^[*] 158 Iso (Ref [3].: Cr 123 B_X 152 Iso); ¹H-NMR (400 MHz, CDCl₃): δ 8.32-8.30 (m, 4H, Ar-H), 8.16-8.13 (m, 2H, Ar-H), 7.94-7.92 (d, ³J=8.8Hz, 2H, Ar-H), 7.689-7.684 (d, ⁴J=2.0Hz, 2H, Ar-H), 7.39-7.35 (m, 6H, Ar-H), 6.99-6.96 (m, 4H, Ar-H), 5.85-5.75 (m, 2H, 2 $\times$ -CH=C), 5.01-4.90 (m, 4H, 2 $\times$ -C=CH₂), 4.06-4.02 (t, ³J=6.4Hz, 4H, 2 $\times$ Ar-OCH₂), 2.06-2.01 (q, ³J=6.8Hz, 4H, 2 $\times$ -CH₂), 1.85-1.78 (q, ³J=6.8Hz, 4H, 2 $\times$ -CH₂), 1.50-1.30 (m, 24H, 12 $\times$ -CH₂). Elemental analysis calcd (%) for C₆₀H₆₄O₁₀: C 76.25, H 6.82; found: C 75.98, H 6.84.

2-En Yield: 70%; ¹H-NMR (400 MHz, CDCl₃): δ 8.33-8.30 (d, ³J=8.8Hz, 4H, Ar-H), 7.97-7.88 (m, 6H, Ar-H), 7.69-7.68 (d, ⁴J=2.4Hz, 2H, Ar-H), 7.38-7.35 (m, 6H, Ar-H), 7.05-7.01 (t, ³J=8.4Hz, 2H, Ar-H), 5.85-5.75 (m, 2H, 2 $\times$ -CH=C), 5.01-4.91 (m, 4H, 2 $\times$ -C=CH₂), 4.13-4.09 (t, ³J=6.4Hz, 4H, 2 $\times$ Ar-OCH₂), 2.06-2.01 (q, ³J=6.8Hz, 4H, 2 $\times$ -CH₂), 1.89-1.82 (q, ³J=6.8Hz, 4H, 2 $\times$ -CH₂), 1.52-1.29 (m, 24H, 12 $\times$ -CH₂). Elemental analysis calcd (%) for C₆₀H₆₂F₂O₁₀: C 73.45, H 6.37; found: C 73.30, H 6.53.

3-En Yield: 72%; ¹H-NMR (400 MHz, CDCl₃): δ 8.36-8.16 (m, 12H, Ar-H), 7.95-7.92 (d, ³J=8.8Hz, 2H, Ar-H), 7.69 (d, ⁴J=2.0Hz, 2H, Ar-H), 7.43-7.36 (m, 6H, Ar-H), 5.85-5.74 (m, 2H, 2 $\times$ -CH=C), 5.01-4.90 (m, 4H, 2 $\times$ -C=CH₂), 4.37-4.34 (t, ³J=6.4Hz, 4H, 2 $\times$ Ar-COOCH₂), 2.06-2.01 (q, ³J=6.8Hz, 4H, 2 $\times$ -CH₂), 1.82-1.75 (q, ³J=6.8Hz, 4H, 2 $\times$ -CH₂), 1.53-1.32 (m, 20H, 10 $\times$ -CH₂). Elemental analysis calcd (%) for C₆₀H₆₀O₁₂: C 74.06, H 6.21; found: C 74.07, H 6.41.

4-En: Yield: 70%; ¹H-NMR (400 MHz, CDCl₃): δ 8.32-8.30 (dd, ³J=7.0Hz, ⁴J=2.0Hz, 4H, Ar-H), 8.16-8.13 (m, 4H, Ar-H), 7.94-7.92 (d, ³J=8.8Hz, 2H, Ar-H), 7.689-7.684 (d, ⁴J=2.0Hz, 2H, Ar-H), 7.39-7.35 (m, 6H, Ar-H), 6.99-6.96 (m, 4H, Ar-H), 5.84-5.77 (m, 1H, -CH=C), 5.01-4.91 (m, 2H, -C=CH₂), 4.06-4.02 (t, ³J=6.4Hz, 4H, 2 $\times$ Ar-OCH₂), 2.06-2.01 (q, ³J=6.8Hz, 2H, 1 $\times$ -CH₂), 1.85-1.78 (q, ³J=6.8Hz, 4H, 2 $\times$ -CH₂), 1.54-1.02 (m, 34H, 17 $\times$ -CH₂), 0.88-0.85 (m, 3H, 1 $\times$ -CH₃). Elemental analysis calcd (%) for C₆₃H₇₂O₁₀: C 76.49, H 7.34; found: C 76.44, H 7.44.

1-Si: Yield: 62%; ¹H-NMR (500 MHz, CDCl₃): δ 8.33-8.30 (dd, ³J=9.0Hz, ⁴J=2.0Hz, 4H, Ar-H), 8.16-8.13 (dd, ³J=9.0Hz, ⁴J=2.0Hz, 4H, Ar-H), 7.94-7.92 (d, ³J=9.0Hz, 2H, Ar-H), 7.691-7.686 (d, ⁴J=2.5Hz, 2H, Ar-H), 7.39-7.35 (m, 6H, Ar-H), 6.99-6.96 (dd, ³J=9.0Hz, ⁴J=2.0Hz, 4H, Ar-H), 4.05-4.03 (t, ³J=6.5Hz, 4H, 2 $\times$ Ar-OCH₂), 1.84-1.78 (q, ³J=7.0Hz, 4H, 2 $\times$ OCH₂CH₂), 1.50-1.44 (q, ³J=7.0Hz, 4H, 2 $\times$ OCH₂CH₂CH₂), 1.36-1.27 (m, 28H, 14 $\times$ CH₂), 0.53-0.5 (m, 4H, 2 $\times$ SiCH₂), 0.074-0.067 [s, 18H, 2 $\times$ Si-(CH₃)₃], 0.053-0.035 [s, 12H, 2 $\times$ Si-(CH₃)₂], 0.014-0.007 [s, 12H, 2 $\times$ Si-(CH₃)₂]. ¹³C-NMR (125 MHz, CDCl₃): δ 164.53, 164.32, 163.84, 155.48, 149.30, 134.42, 132.42, 131.88, 129.62, 129.42, 126.82, 122.14, 121.22, 120.97, 118.60, 114.43, 68.40, 33.44, 29.62, 29.57, 29.56, 29.38, 29.37, 29.09, 25.98, 23.22, 18.29, 1.81, 1.27, 0.20. ²⁹Si-NMR (99.3 MHz, CDCl₃): δ 7.47, 7.03, -

21.06. Elemental analysis calcd (%) for $C_{74}H_{108}O_{14}Si_6$: C 63.94, H 7.83; found: C 64.28, H 7.87.

2-Si: Yield: 55%; 1H -NMR (500 MHz, $CDCl_3$): δ 8.33-8.31 (d, $^3J=9.0$ Hz, 4H, Ar-H), 7.97-7.89 (m, 6H, Ar-H), 7.69-7.68 (d, $^4J=2.0$ Hz, 2H, Ar-H), 7.38-7.35 (m, 6H, Ar-H), 7.05-7.01 (t, $^3J=8.5$ Hz, 2H, Ar-H), 4.13-4.10 (t, $^3J=6.5$ Hz, 4H, $2 \times$ Ar-OCH₂), 1.88-1.83 (q, $^3J=7.0$ Hz, 4H, $2 \times$ OCH₂CH₂), 1.51-1.45 (q, $^3J=7.5$ Hz, 4H, $2 \times$ OCH₂CH₂CH₂), 1.37-1.27 (m, 28H, $14 \times$ CH₂), 0.53-0.5 (m, 4H, $2 \times$ SiCH₂), 0.075-0.067 [s, 18H, $2 \times$ Si-(CH₃)₃], 0.053-0.035 [s, 12H, $2 \times$ Si-(CH₃)₂], 0.014-0.008 [s, 12H, $2 \times$ Si-(CH₃)₂]. ^{13}C -NMR (125 MHz, $CDCl_3$): δ 164.46, 163.49, 155.21, 152.93, 152.33, 152.25, 150.96, 149.29, 134.42, 131.93, 129.64, 129.46, 127.57, 127.04, 122.04, 121.28, 121.22, 118.60, 117.96, 117.8, 113.52, 69.52, 33.44, 29.62, 29.58, 29.53, 29.39, 29.34, 29.0, 25.88, 23.23, 18.3, 1.81, 1.27, 0.21. ^{29}Si -NMR (99.3 MHz, $CDCl_3$): δ 7.48, 7.03, -21.06. ^{19}F -NMR (188.1 MHz, $CDCl_3$): δ -133.65, -133.69, -133.75. Elemental analysis calcd (%) for $C_{74}H_{106}F_2O_{14}Si_6$: C 62.32, H 7.49; found: C 61.98, H 7.71.

3-Si: Yield: 51%; 1H -NMR (500 MHz, $CDCl_3$): δ 8.35-8.18 (m, 12H, Ar-H), 7.95-7.93 (d, $^3J=9.0$ Hz, 2H, Ar-H), 7.70 (d, $^4J=2.0$ Hz, 2H, Ar-H), 7.43-7.24 (m, 6H, Ar-H), 4.37-4.35 (t, $^3J=7.0$ Hz, 4H, $2 \times$ Ar-COOCH₂), 1.82-1.76 (q, $^3J=6.5$ Hz, 4H, $2 \times$ COOCH₂CH₂), 1.48-1.42 (q, $^3J=7.5$ Hz, 4H, $2 \times$ COOCH₂CH₂CH₂), 1.37-1.24 (m, 24H, $12 \times$ CH₂), 0.53-0.50 (t, $^3J=7.5$ Hz, 4H, $2 \times$ SiCH₂), 0.087-0.060 [s, 18H, $2 \times$ Si-(CH₃)₃], 0.048-0.014 [s, 12H, $2 \times$ Si-(CH₃)₂], 0.008-0.001 [s, 12H, $2 \times$ Si-(CH₃)₂]. ^{13}C -NMR (125 MHz, $CDCl_3$): δ 165.64, 164.39, 163.84, 155.0, 149.27, 135.25, 134.40, 132.65, 131.99, 130.21, 129.77, 129.66, 129.47, 127.3, 121.98, 121.2, 118.6, 65.79, 33.41, 29.56, 29.51, 29.36, 29.28, 28.67, 26.02, 23.22, 18.28, 1.80, 1.26, 0.19. ^{29}Si -NMR (99.3 MHz, $CDCl_3$): δ 7.46, 7.03, -21.06. Elemental analysis calcd (%) for $C_{74}H_{104}O_{16}Si_6$: C 62.67, H 7.39; found: C 62.79, H 7.38.

4-Si: Yield: 58%; 1H -NMR (500 MHz, $CDCl_3$): δ 8.33-8.30 (dd, $^3J=8.5$ Hz, $^4J=1.5$ Hz, 4H, Ar-H), 8.15-8.14 (d, $^3J=8.5$ Hz, 4H, Ar-H), 7.94-7.92 (d, $^3J=9.0$ Hz, 2H, Ar-H), 7.689-7.684 (d, $^4J=2.0$ Hz, 2H, Ar-H), 7.39-7.37 (m, 6H, Ar-H), 6.98-6.97 (d, $^3J=9.0$ Hz, 4H, Ar-H), 4.05-4.03 (t, $^3J=6.5$ Hz, 4H, $2 \times$ Ar-OCH₂), 1.82-1.78 (q, $^3J=7.0$ Hz, 4H, $2 \times$ OCH₂CH₂), 1.48-1.43 (q, $^3J=7.5$ Hz, 4H, $2 \times$ OCH₂CH₂CH₂), 1.36-1.25 (m, 34H, $17 \times$ CH₂), 0.88-0.85 (t, $^3J=7.0$ Hz, 3H, $1 \times$ CH₃), 0.53-0.5 (m, 2H, $1 \times$ SiCH₂), 0.079-0.066 [s, 9H, $1 \times$ Si-(CH₃)₃], 0.052-0.039 [s, 6H, $1 \times$ Si-(CH₃)₂], 0.013-(-0.002) [s, 6H, $1 \times$ Si-(CH₃)₂]. ^{13}C -NMR (125 MHz, $CDCl_3$): δ 164.53, 164.32, 163.84, 155.48, 149.3, 134.42, 132.42, 131.88, 129.62, 129.43, 126.82, 122.14, 122.14, 121.22, 120.96, 118.6, 114.43, 68.40, 33.44, 31.92, 29.68, 29.66, 29.65, 29.62, 29.58, 29.55, 29.37, 29.35, 29.08, 25.97, 23.22, 22.68, 18.29, 14.10, 1.81, 1.27, 0.20. ^{29}Si -NMR (99.3 MHz, $CDCl_3$): δ 7.47, 7.03, -21.06. Elemental analysis calcd (%) for $C_{70}H_{94}O_{12}Si_3$: C 69.38, H 7.82; found: C 69.59, H 7.91.

5. References

- [1] A. Immirzi, B. Perini, *Acta Cryst. Sect. A* 1977, **33**, 216.
- [2] A. I. Kitaigorodski, "Molekulkristalle", Akademieverlag Berlin, 1979,
- [3] V. Kozmik, A. Kovarova, M. Kuchar, J. Svoboda, V. Novotna, M. Glogarova and J. Kroupa, *Liq. Cryst.*, 2006, **33**, 41; J. Svoboda, V. Novotna, V. Kozmik, M. Glogarova, W. Weissflog, S. Diele, G. Pelzl, *J Mater. Chem.* 2003, **13**, 2104.