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: Lateral Substituents

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1. Estimation of the number of molecules in the unit cell

Estimation of the number of molecules in the cross section of the ribbons within the Col_{ob} phases of compounds **1-Si, 2-Si**, **3-Si,** and **3-CSi** was done in the following way: $V_{mol,cr}$ = molecular volume (Å^3) in the crystal calculated using crystal volume increments [1], average packing coefficient in the crystal k = 0.7 [2], $V_{mol,is}$ = molecular volume in the isotropic liquid (Å^3), average packing coefficient k = 0.55 [2]; V_{cell} = unit cell volume (Å^3) obtained from the lattice parameters and assuming a height of h = 0.52 nm (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 $n_{cell,cr} = V_{cell}/V_{mol,cr}$, with liquid-like density (is) according to $n_{cell,is} = n_{cell,cr}\cdot 0.55/0.7$, and in the LC phase (LC) estimated as the intermediate between that in the crystalline and the liquid phase

Table S1. Calculation of the number of molecules organized in the unit cells of the Col_{ob} phases of **n-Si**

Comp.	$V_{mol,cr}$	$V_{mol,is}$	V_{cell}	$n_{cell,cr}$	$n_{cell,is}$	$n_{cell,LC}$
1-Si	1802	2294	4550	2.5	2.0	2
2-Si	1827	2325	4600	2.5	2.0	2
3-Si	1821	2317.5	51377	28.2	22.2	25
3-CSi	2389	3041	60744	25.4	20.0	23

2. Experimental

2.1 Methods

The mesophase behaviour of all the compounds was examined under a polarized light optical microscope attached with a heating stage by sandwiching the sample between a glass slide and a coverslip. 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 °C min^{-1}. The electro-optical switching characteristics were examined using a triangular-wave method or under a DC field and optical observations were made under a polarizing microscope using a polyimide coated ITO cells, EHC Japan.
X-ray investigations on powder-like samples 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 CuKα radiation (1.54 Å; 30 to 60 min exposure time, calibration with the powder pattern of $Pb(NO_3)_2$). 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).

2.2 Syntheses

The syntheses were carried out in an analogous manner as reported previously.[3,4]

2.2.1 Synthesis of compounds *n*-En:

3-En: A solution of 2-nitroresorcinol (0.38 g, 2.4 mmol), 4-[4-(undec-10-enyloxy)benzoyloxy]benzoic acid (2.1 g, 5.1 mmol) and a catalytic amount of DMAP in dry dichloromethane (40 ml) was stirred at room temperature for 10 minutes. To this mixture, DCC (1.1 g, 5.3 mmol) was added and the stirring continued overnight. The precipitated *N,N*-dicyclohexylurea was filtered off and washed with excess of dichloromethane. The solvent was removed and the solid material was purified by column chromatography on silica gel using chloroform/2% methanol as an eluent. Removal of solvent afforded a solid, which was repeatedly crystallized from butan-2-one or a mixture of chloroform and acetonitrile.
Yield: 1.6g (70%); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.22-8.20 (dd, ^3J=8.8Hz, ^4J=2.0Hz, 4H, Ar-H), 8.14-8.12 (m, 4H, Ar-H), 7.67-7.63 (t, ^3J=8.4Hz, 1H, Ar-H),7.41-7.24 (m, 6H, Ar-H), 6.98-6.96 (dd, ^3J=6.8Hz, ^4J=2.4Hz, 4H, Ar-H), 5.85-5.75 (m, 2H, 2 × -CH=C), 5.01-4.90 (m, 4H, 2 × C=CH_2), 4.05-4.02 (t, ^3J=6.8Hz, 4H, 2 × Ar-OCH_2), 2.06-2.01 (q, ^3J=6.8Hz, 4H, 2 × -CH_2), 1.85-1.77 (q, ^3J=6.8Hz, 4H, 2 × CH_2), 1.50-1.19 (m, 24H, 12 × -CH_2). Elemental analysis calcd (%) for $C_{56}H_{61}NO_{12}$: C 71.55, H 6.54, N 1.49; found: C 71.28, H 6.50, N 1.43.

5-En: Yield: 62%; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.32-8.12 (m, 8H, Ar-H), 7.79-7.77 (d, ^3J=8.4Hz, 1H, Ar-H), 7.53-7.52 (d, ^4J=2.0Hz, 1H, Ar-H), 7.40-7.30 (m, 5H, Ar-H), 6.98-6.96 (d, ^3J=8.8Hz, 4H, Ar-H), 5.85-5.75 (m, 2H, 2 × -CH=C), 5.01-4.90 (m, 4H, 2 × -C=CH_2), 4.06-4.02 (t, ^3J=6.8Hz, 4H, 2 × Ar-OCH_2), 2.06-2.01 (q, ^3J=6.4Hz, 4H, 2 × CH_2), 1.85-1.81 (q, ^3J=6.8Hz, 4H, 2 × CH_2), 1.54-1.30 (m, 24H, 12 × -CH_2). Elemental analysis calcd (%) for $C_{57}H_{61}NO_{10}$: C 74.4, H 6.68, N 1.52; found: C 74.1, H 6.77, N 1.39.

The analytical data of the compounds **1-En**, **2-En** and **4-En** correspond to those reported earlier.[5,6]

2.2.2 Synthesis of compounds *n*-Si

1-Si: Compound **1-En** (0.3g, 0.34 mmol) was dissolved in anhydrous toluene (5 ml) under an argon atmosphere. To this solution, was added 1,1,3,3,5,5,5-heptamethyltrisiloxane (0.16 g, 0.74 mmol) and a drop of Karstedt's catalyst (platinum-divinyltetramethyl-siloxane complex in xylene). The resultant reaction mixture was stirred continuously at room temperature under argon till completion of the reaction (approx.. 48 hours), which was determined by TLC. The solvent was evaporated and the crude product was repeatedly purified by flash chromatography on silica gel using $CHCl_3$ as an eluent.
Yield: 0.27g (61%); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.27-8.25 (dd, ^3J=8.5Hz, ^4J=2.0Hz, 4H, Ar-H), 8.15-8.12 (dd, ^3J=9.0Hz, ^4J=2.0Hz, 4H, Ar-H), 7.5-7.46 (t, ^3J=8.0Hz, 1H, Ar-H), 7.37-7.35 (dd, ^3J=9.0Hz, ^4J=2.0Hz, 4H, Ar-H), 7.20-7.16 (m, 3H, Ar-H), 6.98-6.96 (dd, ^3J=9.0Hz, ^4J=2.0Hz, 4H, Ar-H), 4.05-4.02 (t, ^3J=6.5Hz, 4H, 2 × Ar-OCH_2), 1.84-1.78 (q, ^3J=7.5Hz, 4H, 2 × OCH_2CH_2), 1.51-1.43 (q, ^3J=7.5Hz, 4H, 2 × $OCH_2CH_2CH_2$), 1.35-1.27 (m, 28H, 14×CH_2), 0.53-0.5 (m, 4H, 2 × $SiCH_2$), 0.073-0.066 [s, 18H, 2 × Si-$(CH_3)_3$], 0.046-0.040 [s, 12H, 2 × Si-$(CH_3)_2$], 0.013-0.006 [s, 12H, 2 × Si-$(CH_3)_2$]. ^{13}C-NMR (125 MHz, $CDCl_3$): δ 164.29, 164.091, 163.84, 155.50, 151.43, 132.42, 131.85, 129.87, 126.62, 122.13, 120.95, 119.28, 114.42, 68.40, 33.43, 29.62, 29.57, 29.55, 29.38, 29.37, 29.09, 25.98, 23.22, 18.29, 1.81, 1.27, 0.20. ^{29}Si-NMR (99.3 MHz, $CDCl_3$): δ 7.47, 7.03, -21.07. Elemental analysis calcd (%) for $C_{70}H_{106}O_{14}Si_6$: C 62.74, H 7.97; found: C 62.62, H 8.30.

2-Si: Yield: 55%; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.30-8.28 (dd, ^3J=8.25Hz, ^4J=2.0Hz, 4H, Ar-H), 8.15-8.13 (dd, ^3J=8.5Hz, ^4J=2.5Hz, 4H, Ar-H), 7.38-7.24 (m, 5H, Ar-H), 7.13-7.11 (d, ^3J=10.5Hz, 2H, Ar-H), 6.98-6.96 (dd, ^3J=8.75Hz, ^4J=3.0Hz, 4H, Ar-H), 4.05-4.02 (t, ^3J=8.5Hz, 4H, 2 × Ar-OCH_2), 2.11(s, 3H, Ar-CH_3), 1.83-1.80 (q, ^3J=9.0Hz, 4H, 2 × OCH_2CH_2), 1.50-1.45 (q, ^3J=9.0Hz, 4H, 2 × $OCH_2CH_2CH_2$), 1.29-1.27 (m, 28H, 14×CH_2), 0.54-0.50 (m, 4H, 2 × $SiCH_2$), 0.083-0.055 [s, 18H, 2 × Si-$(CH_3)_3$], 0.047-0.035 [s, 12H, 2 × Si-$(CH_3)_2$], 0.016-0.001 [s, 12H, 2 × Si-$(CH_3)_2$]. ^{13}C-NMR (125 MHz, $CDCl_3$): δ 164.18, 163.78, 163.71, 155.39, 150.17, 132.34, 131.78, 126.56, 126.49, 123.91, 122.12, 120.89, 119.9, 114.38, 68.44, 33.51, 29.71, 29.66, 29.64, 29.47, 29.19, 26.08, 23.33, 18.41, 10.23, 1.94, 1.4, 0.34. ^{29}Si-NMR (99.3 MHz, $CDCl_3$): δ 7.47, 7.03, -21.06. Elemental analysis calcd (%) for $C_{71}H_{108}O_{14}Si_6$: C 62.98, H 8.04; found: C 63.15, H 8.17.

3-Si: Yield: 50%; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.22-8.20 (dd, ^3J=11Hz, ^4J=2.5Hz, 4H, Ar-H), 8.14-8.12 (m, 4H, Ar-H), 7.65-7.63 (t, ^3J=10.5Hz, 1H, Ar-H), 7.41-7.24 (m, 6H, Ar-H), 6.98-6.96 (m, 4H, Ar-H), 4.05-4.02 (t, ^3J=8.5Hz, 4H, 2 × Ar-OCH_2), 1.83-1.79 (q, ^3J=9.0Hz, 4H, 2 × OCH_2CH_2), 1.50-1.45 (q, ^3J=9.5Hz, 4H, 2 × $OCH_2CH_2CH_2$), 1.29-1.27 (m, 28H, 14×CH_2), 0.54-0.50 (m, 4H, 2 × $SiCH_2$), 0.082-0.055 [s, 18H, 2 × Si-$(CH_3)_3$], 0.047-0.035 [s, 12H, 2 × Si-$(CH_3)_2$], 0.016-0.007 [s, 12H, 2 × Si-$(CH_3)_2$]. ^{13}C-NMR (125 MHz, $CDCl_3$): δ 164.12, 163.83, 162.92, 155.96, 143.73, 132.41, 132.21, 125.19, 122.30, 121.71, 120.85, 114.42, 68.43, 33.46, 29.65, 29.61, 29.59, 29.42, 29.13, 26.02, 23.26, 18.34, 1.86, 1.32, 0.26. ^{29}Si-NMR (99.3 MHz, $CDCl_3$): δ 7.47, 7.03, -21.06. Elemental analysis calcd (%) for $C_{70}H_{105}NO_{16}Si_6$: C 60.70, H 7.64 N 1.01; found: C 60.97, H 7.87, N 0.78.

3-CSi: Yield: 52%; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.29-8.27 (dd, ^3J=10Hz, ^4J=2.5Hz, 4H, Ar-H), 8.22-8.19 (dd, ^3J=6.5Hz, ^4J=3.0Hz, 4H, Ar-H), 7.73-7.70 (t, ^3J=8.5Hz, 1H, Ar-H), 7.45-7.31 (m, 6H, Ar-H), 7.05-7.02 (m, 4H, Ar-H), 4.1-4.09 (t, ^3J=6.5Hz, 4H, 2 × Ar-OCH_2), 1.89-1.85 (q, ^3J=7.0Hz, 4H, 2 × OCH_2CH_2), 1.55-1.5 (q, ^3J=7.5Hz, 4H, 2 × $OCH_2CH_2CH_2$), 1.42-1.30 (m, 40H, 20×CH_2), 0.62-0.53 (m, 28H, 14 × $SiCH_2$), 0.032-0.015 [s, 18H, 2 × Si-$(CH_3)_3$], 0.000 to -0.006 [s, 36H, 6 × Si-$(CH_3)_2$]. ^{13}C-NMR (125 MHz, $CDCl_3$): δ 164.17, 163.87, 162.98, 155.99, 143.76, 132.45, 132.25, 131.66, 131.57, 125.19, 124.61, 122.33,

122.27, 122.24, 121.76, 120.85, 114.43, 68.40, 33.71, 32.56, 32.5, 29.64, 29.6, 29.56, 29.38, 29.29, 29.09, 25.98, 25.95, 23.92, 21.37, 20.12, 20.03, 20.01, 18.41, 17.91, 15.39, -1.53, -2.99, -3.181, -3.26. ^{29}Si-NMR (99.3 MHz, $CDCl_3$): δ 1.59, 0.98, 0.57, 0.009. Elemental analysis calcd (%) for $C_{91}H_{150}NO_{12}Si_8$: C 65.26, H 9.03, N 0.84; found: C 65.32, H 9.05, N 0.62.

4-Si: Yield: 48%; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.31-8.28 (d, ^3J=8.5Hz, 2H, Ar-H), 8.25-8.23 (d, ^3J=8.5Hz, 2H, Ar-H), 8.15-8.12 (dd, ^3J=9.0Hz, ^4J=3.0Hz, 4H, Ar-H), 7.54-7.52 (d, ^3J=9.0Hz, 1H, Ar-H), 7.39-7.35 (m, 4H, Ar-H), 7.29-7.28 (d, ^4J=2.5Hz, 1H, Ar-H), 7.17-7.15 (dd, ^3J=9.0Hz, ^4J=2.5Hz, 1H, Ar-H), 6.98-6.96 (dd, ^3J=8.5Hz, ^4J=1.0Hz, 4H, Ar-H), 4.05-4.02 (t, ^3J=6.5Hz, 4H, 2 × Ar-OCH_2), 1.84-1.78 (q, ^3J=7.0Hz, 4H, 2 × OCH_2CH_2), 1.50-1.43 (q, ^3J=8.0Hz, 4H, 2 × $OCH_2CH_2CH_2$), 1.35-1.27 (m, 28H, 14 × CH_2), 0.53-0.5 (m, 4H, 2 × $SiCH_2$), 0.079-0.066 [s, 18H, 2 × Si-$(CH_3)_3$], 0.052-0.039 [s, 12H, 2 × Si-$(CH_3)_2$], 0.013-(-0.001) [s, 12H, 2 × Si-$(CH_3)_2$]. ^{13}C-NMR (125 MHz, $CDCl_3$): δ 164.26, 163.86, 163.2, 155.71, 155.63, 149.75, 147.47, 132.43, 132.09, 131.88, 130.47, 126.27, 125.95, 124.28, 122.22, 122.2, 120.91, 120.9, 120.49, 117.86, 114.43, 68.40, 33.43, 29.61, 29.57, 29.57, 29.55, 29.38, 29.36, 29.08, 25.98, 23.22, 18.28, 1.80, 1.26, 0.20. ^{29}Si-NMR (99.3 MHz, $CDCl_3$): δ 7.47, 7.03, -21.07. Elemental analysis calcd (%) for $C_{70}H_{105}ClO_{14}Si_6$: C 61.17, H 7.70; found: C 61.15, H 7.88.

5-Si: Yield: 55%; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.33-8.30 (d, ^3J=7.0Hz, 2H, Ar-H), 8.26-8.24 (d, ^3J=7.0Hz, 2H, Ar-H), 8.15-8.12 (d, ^3J=6.5Hz, 4H, Ar-H), 7.79-7.77 (d, ^3J=8.5Hz, 1H, Ar-H), 7.53-7.52 (d, ^4J=2.5Hz, 1H, Ar-H), 7.40-7.37 (m, 4H, Ar-H), 7.32-7.30 (d, ^3J=8.5Hz, 1H, Ar-H), 6.98-6.96 (dd, ^3J=9.0Hz, ^3J=2.0Hz, 4H, Ar-H), 4.05-4.02 (t, ^3J=6.5Hz, 4H, 2 × Ar-OCH_2), 1.82-1.78 (q, ^3J=7.0Hz, 4H, 2 × OCH_2CH_2), 1.48-1.45 (q, ^3J=7.0Hz, 4H, 2 × $OCH_2CH_2CH_2$), 1.36-1.27 (m, 28H, 14 × CH_2), 0.53-0.5 (m, 4H, 2 × $SiCH_2$), 0.077-0.063 [s, 18H, 2 × Si-$(CH_3)_3$], 0.050-0.037 [s, 12H, 2 × Si-$(CH_3)_2$], 0.010-(-0.004) [s, 12H, 2 × Si-$(CH_3)_2$]. ^{13}C-NMR (125 MHz, $CDCl_3$): δ 164.22, 164.17, 163.91, 163.87, 163.29, 162.91, 156.01, 155.92, 154.79, 153.48, 133.96, 132.46, 132.26, 132.01, 125.71, 125.32, 122.39, 122.34, 120.86, 120.8, 120.02, 117.41, 114.45, 114.44, 104.26, 68.42, 33.43, 29.62, 29.57, 29.55, 29.08, 25.98, 23.22, 18.29, 1.80, 1.26, 0.20. ^{29}Si-NMR (99.3 MHz, $CDCl_3$): δ 7.47, 7.03, -21.06. Elemental analysis calcd (%) for $C_{71}H_{105}NO_{14}Si_6$: C 62.47, H 7.75, N 1.03; found: C 62.62, H 7.83, N 0.74.

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