Supplementary material (ESI) for Journal of Materials Chemistry

Supporting Information

The influence of shape and size of silyl units on the properties of bent-core liquid crystals – from dimers via oligomers and dendrimers to polymers

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1. Additional figures and tables

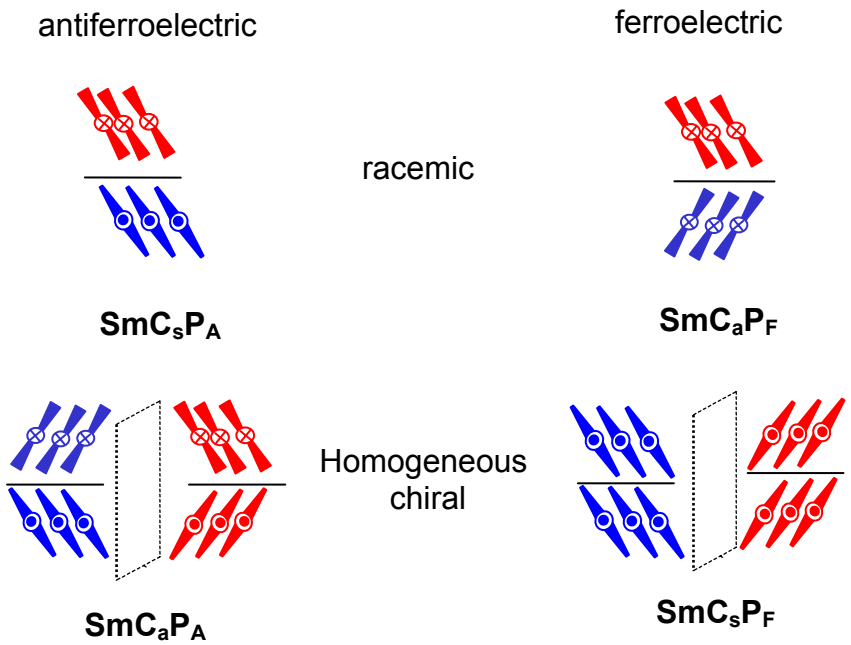


Fig. S1 Phase structures of polar smectic phases (SmCP) of bent-core mesogens and their classification according to polar direction, tilt-correlation and phase chirality: ferroelectric (F) = polar direction in adjacent layers is parallel; antiferroelectric (A) = polar direction in adjacent layers is antiparallel; synclinic tilt (s) = identical tilt direction in adjacent layers; anticlinic (a) = opposite tilt direction in adjacent layers; racemic (SmC_sP_A, SmC_aP_F) = layer chirality in adjacent layers is identical; homogeneous chiral (SmC_aP_A, SmC_sP_F) = layer chirality in adjacent layers is opposite.

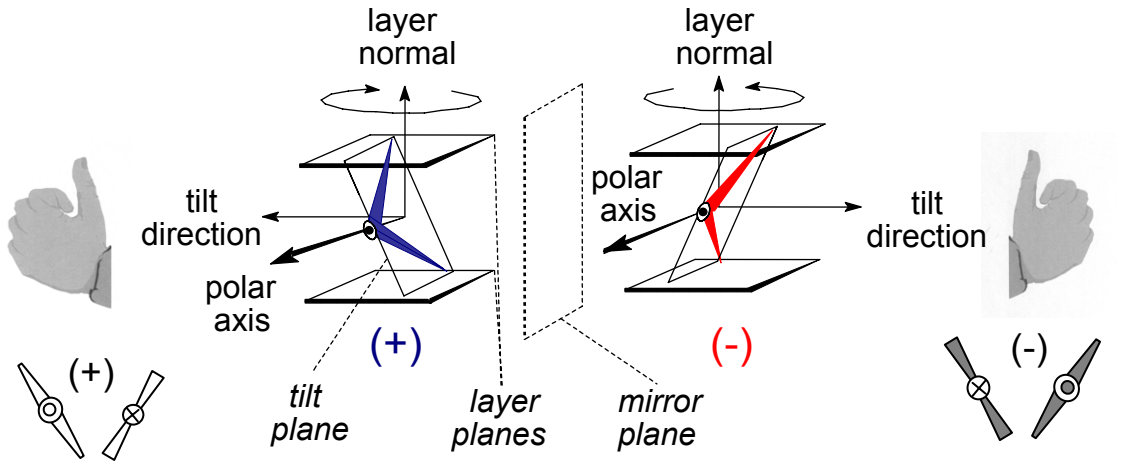


Fig. S2 (a) Origin of the chirality within the smectic phases of bent-core molecules.[4] Owing to the bend shape each molecule possesses a dipole moment in the molecular plane and perpendicular to the long axis of the molecules. Layer normal, tilt direction and the polar axis define either a right handed coordinate system (+), whereas in the mirror image these vectors define a left handed system (-). Changing either polarisation direction or tilt direction changes the chirality sense of the layer (indicated by blue/red colour). Changing both, polarisation direction and tilt direction retains the chirality sense.

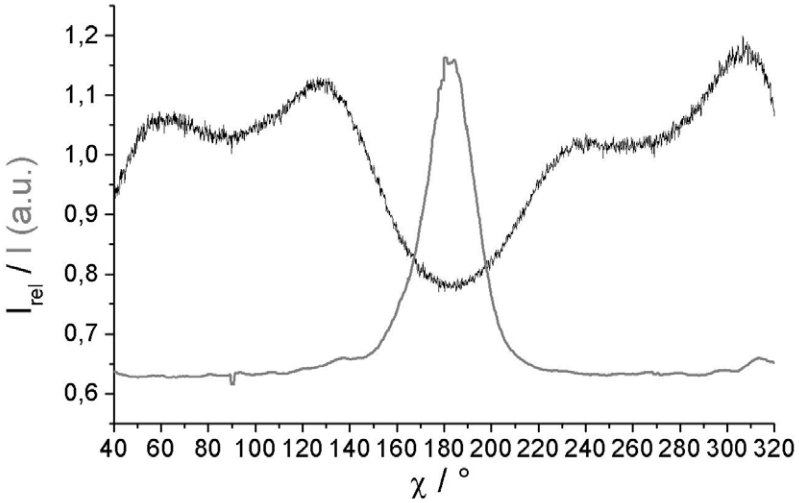
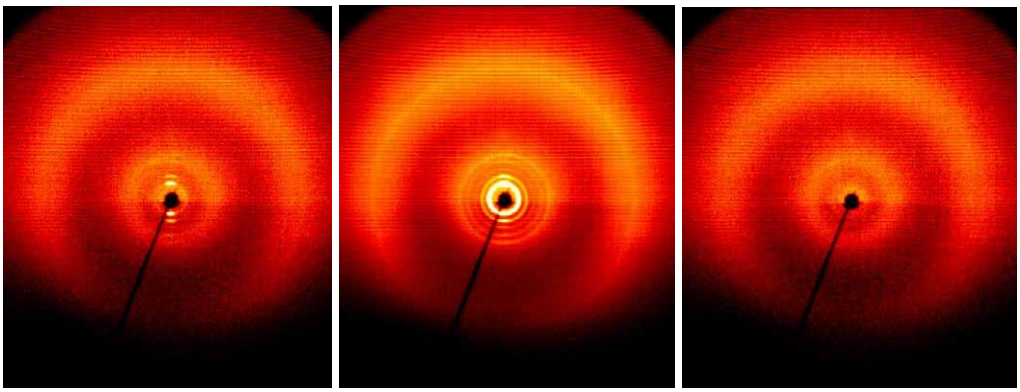


Fig. S3 XRD pattern from a partially surface-aligned sample of **3b** at 135 °C: distribution of the wide-angle scattering along χ (black line) with maxima at χ = 58, 130, 243, and 314° in comparison with the χ position of the layer reflections (gray line) at χ = 182° giving an average tilt angle of the molecules with respect to the layer normal of 36° [I_{rel} = I(135 °C) / I(143 °C, iso)]. The higher intensity of the maxima at 130 and 314° compared with the other two is a hint to a synclinic tilt of the molecules in different layers.



(a) (b) (c)

Fig. S4 2D XRD pattern from a partially surface-aligned sample of **4b:** a) $SmCP_A$ phase at 144 °C on heating, b) partially crystallized sample at 138 °C, c) scattering of the isotropic liquid at 150 °C for comparison.

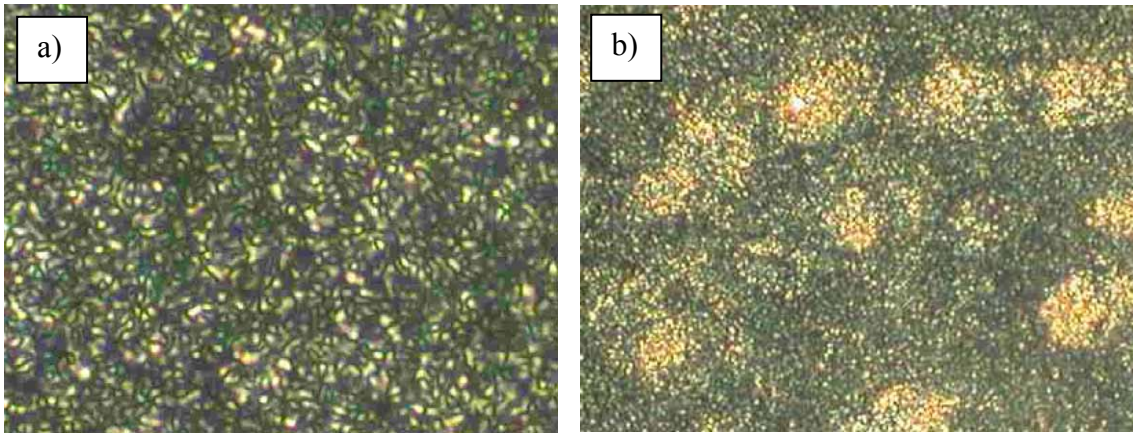


Fig. S5 Low birefringent textures as seen between crossed polarizers for: a) the smectic phase of compound **4b** at T = 130 °C; b) compound **1/3a** after cooling with a rate of 10 K min^{-1} at 100 °C.

Table S1. X-ray diffraction data: d_{exp} ... according to the Bragg equation, d_{calc} ...calculated from the parameter given in column 5.

Compound	T/°C	d_{exp}/Å	Order of the layer reflection	Layer distance/ Å	d_{calc}/ Å	d_{exp}-d_{calc}/ Å
1/3a	81	39.1	1	39.5	39.5	-0.4
		13.2	3		13.2	0.0
2b	100	44,3	1	44,4	44,4	-0,1
		22,3	2		22,2	0,1
		14,8	3		14,8	0,0
3b	135	74.2	1	77.8	77.8	-3.6
		39.1	2		38.9	0.2
		25.9	3		25.9	0.0
		15.5	5		15.6	-0.1
		13.0	6		13.0	0.0
4b	135	40.2	2	80.3	40.2	0.0
		26.8	3		26.8	0.0
5b	120	45.6	1	45.6	45.6	0.0
		22.8	2		22.8	0.0

2. Experimental 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 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 °C min^{-1}
For the investigation of the switching behaviour a home built setup for electrooptical investigations was used. The sample as an isotropic liquid was filled into commercial ITO coated glass cells (E.H.C., Japan) with a sample thickness of 5 µm or 6 µm. These cells are also available with an additional polyimide coating for better alignment. The cells were placed into the temperature controlled oven (Mettler FP 90) of the polarizing microscope (Nikon Optiphot 2).Triangular wave field experiments were carried out with an electric field in the range of 20-400 V_{pp} with a frequency of 0.1-100 Hz. DC field experiments were carried out under a DC electric field of 10-40 V_{DC}.
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).

3. Synthesis and analytical data

3.1. General procedure for the hydrosilylation reaction

Under an argon atmosphere the olefine (1equ.) was dissolved in anhydrous toluene (3 mL/ mmol). The H-terminated carbosilane or siloxane (1.05 equ. per Si-H equ.) and one drop of Karstedt's catalyst (platinum-divinyltetramethylsiloxane complex in xylene, Gelest Inc.) were added to this solution. The mixture was stirred at room temperature. After reaction was completed (detection by TLC, ca. 72 hours) the solvent was evaporated and the crude product was purified by repeated column chromatography with silica gel (Silica gel 60, 0.040-0.063 µm, Merck) using $CHCl_3$ as eluent.

3.2. Analytical data

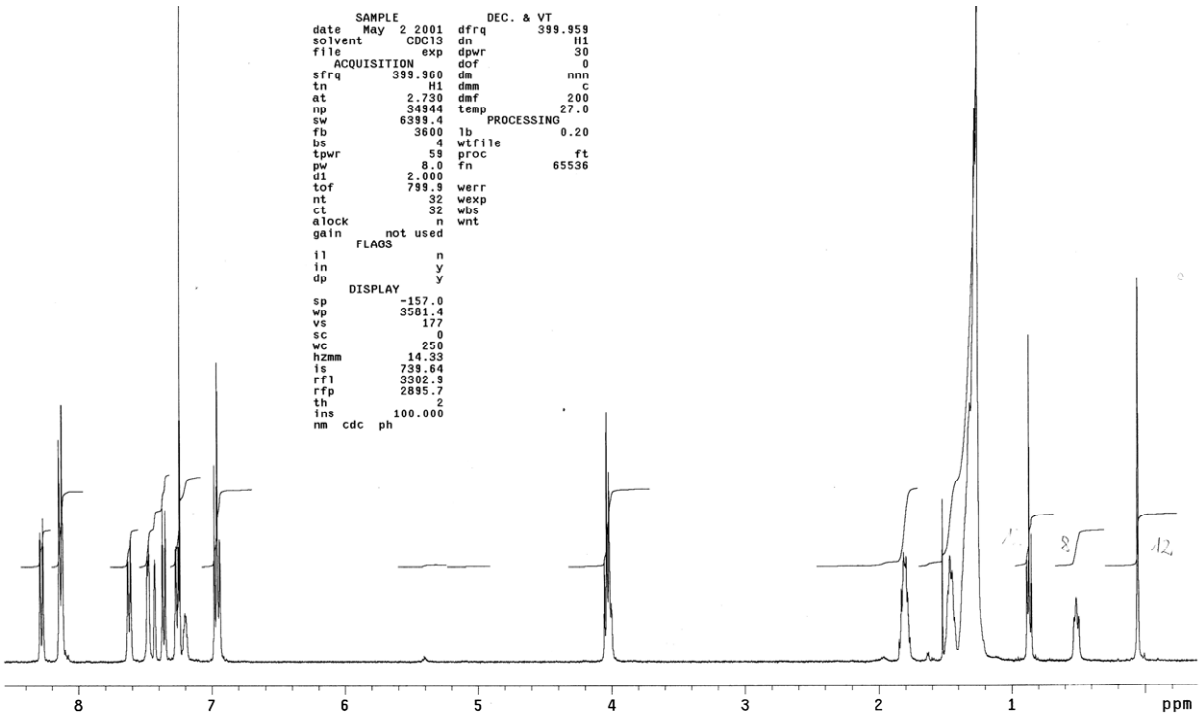
1/3a: Yield: 120 mg (29 %); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.28 (d, *J* 8.7 Hz, 6H, Ar-H), 8.13 (d, *J* 8.1 Hz, 12H, Ar-H), 7.62 (d, *J* 8.5 Hz, 6H, Ar-H), 7.48 (d, *J* 4.8 Hz, 6H, Ar-H), 7.43 (s, 3H, Ar-H), 7.36 (d, *J* 8.7 Hz, 6H, Ar-H), 7.26 (d, *J* 8.5 Hz, 6H, Ar-H), 7.21 (m, 3H, Ar-H), 6.97 (d, *J* 8.9 Hz, 6H, Ar-H), 6.96 (d, *J* 8.7 Hz, 6H, Ar-H), 4.03 (m, 12H, OCH_2), 3.41 (t, *J* 6.6 Hz, 6H, CH_2), 3.35 (t, *J* 7.0 Hz, 6H, CH_2), 1.82 (m, 12H, CH_2), 1.65-1.23 (m, 78H, CH_2), 0.87 (t, *J* 6.8 Hz, 9H, CH_3), 0.54 (m, 12H, $SiCH_2$), 0.44 (m, 6H, $SiCH_2$), -0.05 [s, 18H, Si-$(CH_3)_2$], -0.09 (s, 3H, Si-CH_3); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 164.82, 164.40, 164.25, 163.79, 163.50, 155.39, 151.30, 150.83, 142.12, 137.71, 132.37, 132.27, 131.78, 129.79, 128.19, 126.85, 124.63, 122.14, 122.07, 121.50, 120.96, 120.51, 120.38, 114.41, 114.29, 74.01, 70.72, 68.40, 68.23, 31.92, 29.78, 29.66, 29.64, 29.59, 29.56, 29.36, 29.35, 29.10, 26.05, 25.99, 25.93, 24.20, 22.69, 20.08, 18.86, 18.48, 14.12, 11.36, -3.30, -4.90; ^{29}Si-NMR (99.3 MHz, $CDCl_3$): δ 2.19, 0.97; EA: calc. for $C_{178}H_{228}O_{27}Si_4$,: C, 73.42 %, H, 7.89 %, found: C, 73.27 %, H, 7.92 %.

1/6a: Yield: 95 mg (28 %); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.27 (d, *J* 8.9 Hz, 12H, Ar-H), 8.14 (m, 24H, Ar-H), 7.61 (d, *J* 8.7 Hz, 12H, Ar-H), 7.47 (d, ^{3}J = 4.9 Hz, 12H, Ar-H), 7.42 (s, 6H, Ar-H), 7.36 (d, *J* 8.7 Hz, 12H, Ar-H), 7.26-7.19 (m, 12H, Ar-H), 7.17 (m, 6H, Ar-H), 6.96 (m, 24H, Ar-H), 4.01 (m, 24H, OCH_2), 3.40 (t, *J* 6.6 Hz, 12H, OCH_2), 3.34 (t, ^{3}J = 7.0 Hz, 12H, OCH_2), 1.79 (m, 26H, CH_2), 1.64-1.25 (m, 174H, CH_2), 0.87 (t, *J* = 6.6 Hz, 18H, CH_3), 0.54 (m, 36H, $SiCH_2$), 0.44 (m, 12H, $SiCH_2$), -0.04 [s, 36H, Si-$(CH_3)_2$], -0.09 (s, 12H, Si-CH_3); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 164.87, 164.31, 163.82, 163.53, 155.42, 151.32, 150.84, 142.13, 137.73, 132.41, 132.30, 131.82, 129.83, 128.22, 126.86, 124.66, 122.16, 122.11, 121.49, 120.96, 120.39, 114.42, 114.29, 74.04, 70.77, 68.39, 68.22, 31.90, 29.77, 29.64, 29.62, 29.57, 29.54, 29.33, 29.07, 26.05, 25.97, 24.17, 22.68, 20.08, 18.84, 18.47, 14.10, 11.33, -3.30, -4.92; ^{29}Si-NMR (99.3 MHz, $CDCl_3$): δ 2.24, 1.02; EA: calc. for $C_{367}H_{480}O_{54}Si_{10}$: C, 73.02 %, H, 8.01 %, found: C, 73.14 %, H, 8.80 %.

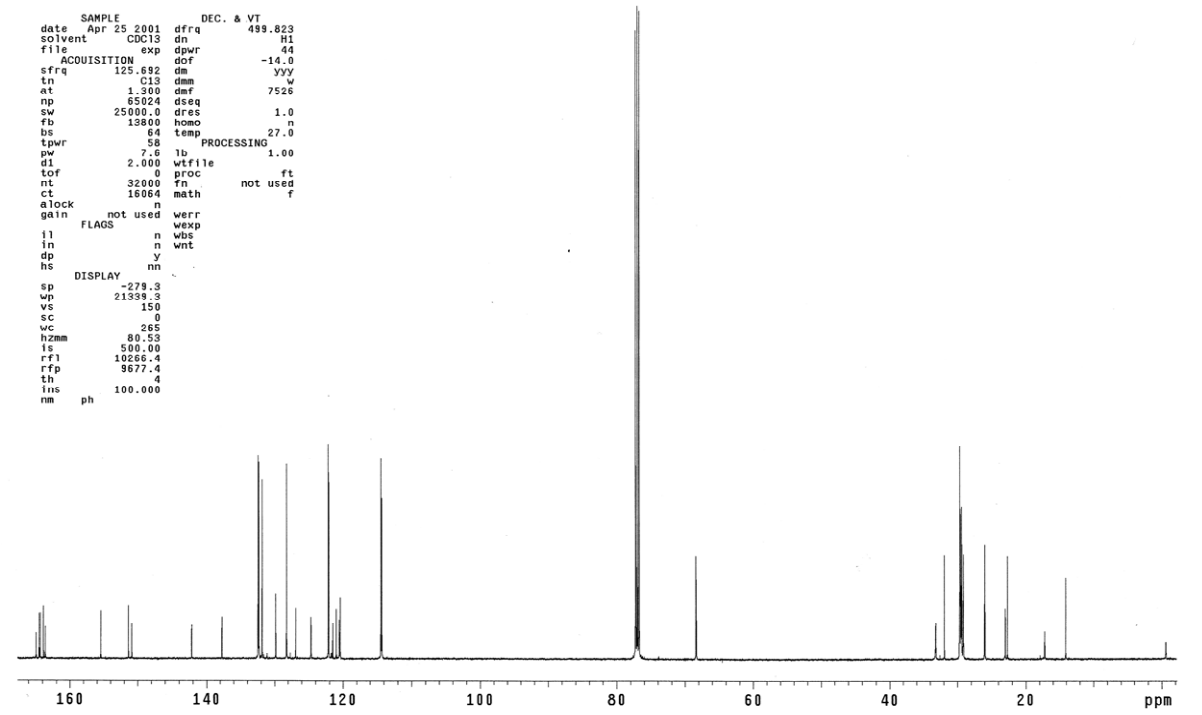
2b: Yield: 55 mg (10 %); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.29 (d, *J* 8.7, 6H, Ar-H), 8.14 (d, *J* 8.7, 12H, Ar-H), 7.63 (d, *J* 8.7, 6H, Ar-H), 7.49 (d, *J* 5.0, 6H, Ar-H), 7.44 (m, 3H, Ar-H), 7.37 (d, *J* 8.9, 6H, Ar-H), 7.27 (d, J 8.5, 6H, Ar-H), 7.22-7.19 (m, 3H, Ar-H), 6.97 (d, *J* 8.9, 6H, Ar-H), 6.96 (d, *J* 8.9, 6H, Ar-H), 4.05-3.98 (m, 15H, OCH_2, SiOCH), 1.85-1.80 (m, 12H, CH_2), 1.49-1.43 (m, 12H, CH_2), 1.37-1.27 (m, 90H, CH_2), 1.17 (d, J 6.2, 9H, $CHCH_3$), 0.88 (t, J 6.6, 9H, CH_3), 0.50-0.46 (m, 12H, Si- CH_2), 0.10 (s, 3H, Si- CH_3), -0.06 (s, 18H, Si-$(CH_3)_2$); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 164.80, 164.37, 164.21, 163.76, 163.52, 155.37, 151.28, 150.81, 142.09, 137.68, 132.35, 132.24, 131.76, 129.76, 128.17, 126.83, 124.61, 122.11, 122.05, 121.45, 120.94, 120.49, 120.35, 114.39, 114.28, 68.57, 68.38, 68.34, 39.24, 33.76, 31.92, 29.66, 29.64, 29.59, 29.56, 29.42, 29.35, 29.14, 29.10, 26.02, 25.99, 24.06, 23.95, 23.51, 22.69, 15.44, 15.35, 12.12, -3.30, -4.86; EA calc. for $C_{193}H_{258}O_{27}Si_4$: C, 74.24 %, H, 8.33 %, found: C, 73.74 %, H, 8.26 %.

3b: Yield: 48 mg (19 %); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.28 (d, *J* 8.0, 8H, Ar-H), 8.14 (d, *J* 8.8, 8H, Ar-H), 8.13 (d, *J* 8.8, 8H, Ar-H), 7.62 (d, *J* 8.6, 4H, Ar-H), 7.61 (d, *J* 8.6, 4H, Ar-H), 7.48-7.47 (m, 8H, Ar-H), 7.43-7.42 (m, 4H, Ar-H), 7.36 (d, *J* 8.4, 8H, Ar-H), 7.26 (d, *J* 8.8, 8H, Ar-H), 7.23-7.19 (m, 4H, Ar-H), 6.97 (d, *J* 8.7, 8H, Ar-H), 6.95 (d, *J* 8.6, 8H, Ar-H), 4.05-4.00 (m, 16H, OCH_2), 1.83-1.78 (m, 16H, CH_2), 1.53-1.45 (m, 16H, CH_2), 1.31-1.26 (m, 120H, CH_2), 0.87 (t, J 6.6, 12H, CH_3), 0.51 (t, *J* 6.6, 8H, Si- CH_2), 0.06 (s, 12H, Si- CH_3); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 164.86, 164.45, 164.29, 163.82, 163.57, 155.42, 151.33, 150.84, 142.13, 137.73, 132.40, 132.29, 131.81, 129.82, 128.21, 126.87, 124.65, 122.15, 122.09, 121.49, 120.97, 120.53, 120.39, 114.42, 114.29, 68.39, 68.33, 33.20, 33.16, 31.90, 29.69, 29.64, 29.62, 29.57, 29.54, 29.44, 29.42, 29.34, 29.33, 29.13, 29.08, 26.03, 26.02, 25.97, 22.98, 22.67, 17.20, 17.18, 14.09.

^{1}H-NMR:



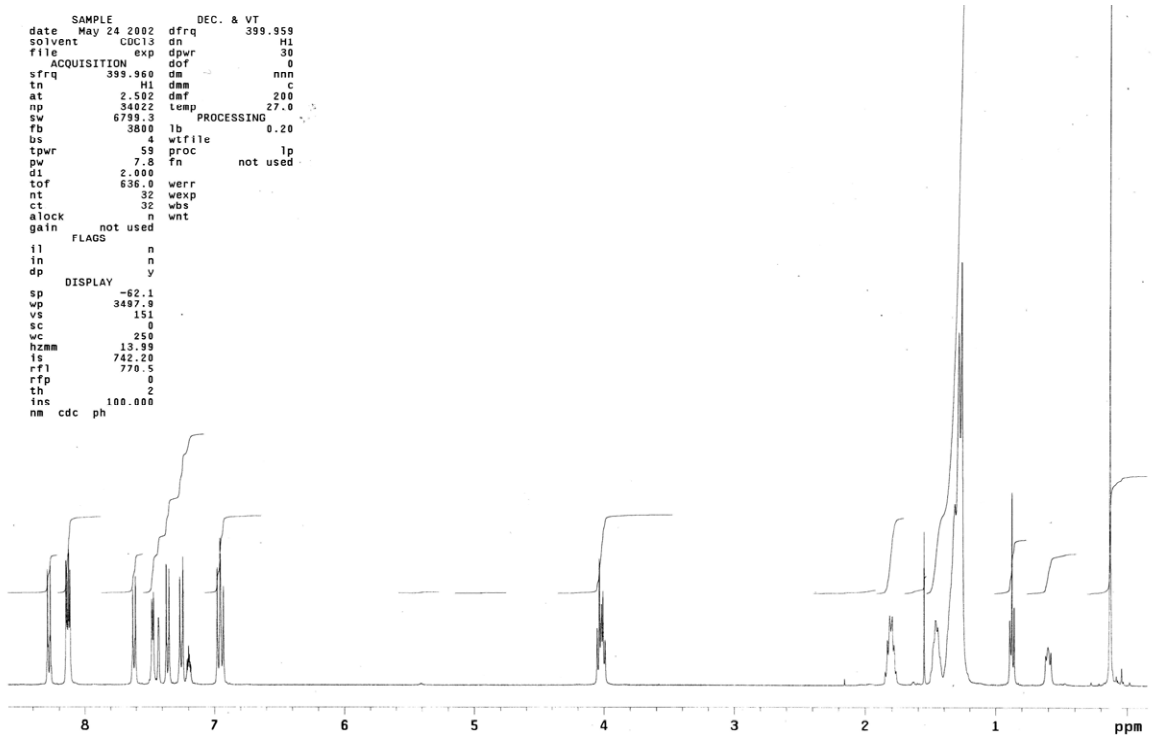
^{13}C-NMR:



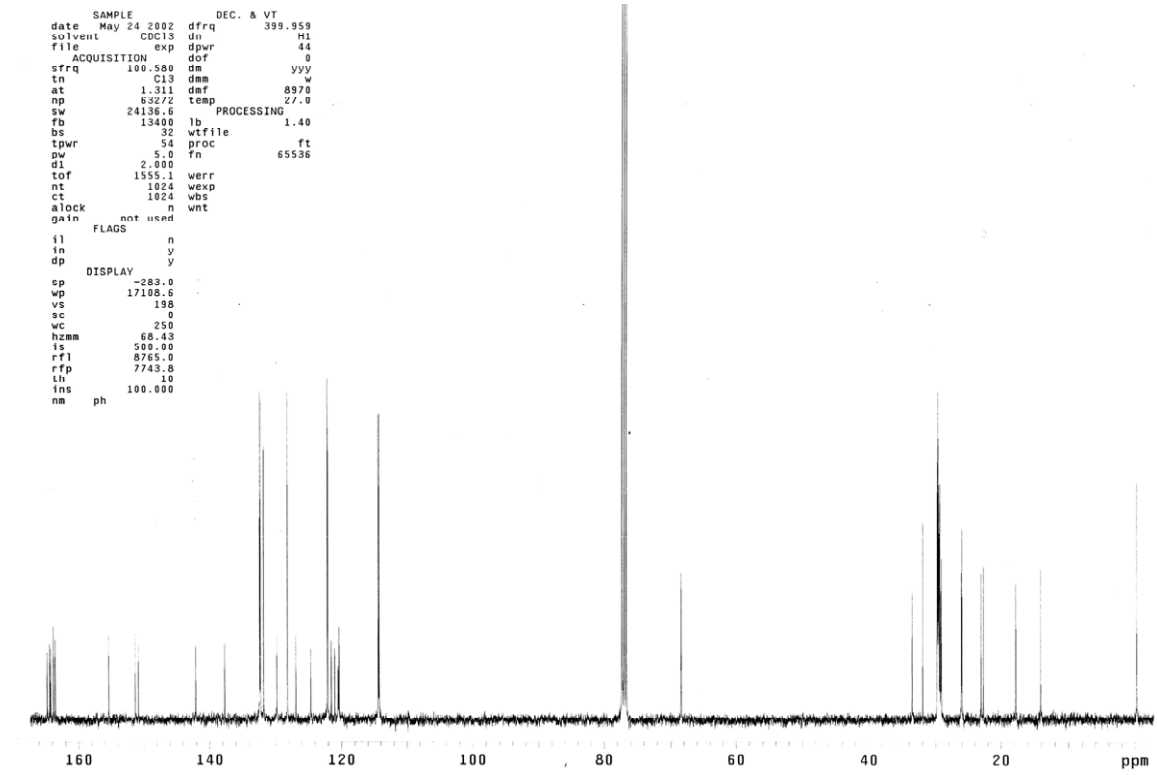
4b: Yield: 35 mg (13 %); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.27 (d, *J* 8.8, 16H, Ar-H), 8.13 (d, *J* 9.0, 16H, Ar-H), 8.12 (d, *J* 8.8, 16H, Ar-H), 7.61 (d, *J* 8.6, 16H, Ar-H), 7.46 (d, *J* 4.9, 16H, Ar-H), 7.42-7.41 (m, 8H, Ar-H), 7.35 (d, *J* 8.8, 16H, Ar-H), 7.25 (d, *J* 8.6, 16H, Ar-H), 7.23-7.19 (m, 8H, Ar-H), 6.96 (d, *J* 9.0, 16H, Ar-H), 6.93 (d, *J* 9.0, 16H, Ar-H), 4.05-3.98 (m, 32H, OCH_2), 1.84-1.77 (m, 32H, CH_2), 1.52-1.44 (m, 32H, CH_2), 1.31-1.26 (m, 240H, CH_2), 0.89 (m, 24H, CH_3), 0.61-0.57 (m, 16H, Si- CH_2), 0.12 (s, 48H, Si- CH_3); ^{13}C-NMR (125

MHz, $CDCl_3$): δ 164.74, 164.35, 164.19, 163.79, 163.51, 155.38, 151.31, 150.82, 142.08, 137.68, 132.35, 132.23, 131.74, 129.76, 128.15, 126.85, 124.59, 122.10, 122.04, 121.52, 121.00, 120.34, 114.41, 114.28, 68.42, 68.36, 33.52, 31.93, 29.75, 29.67, 29.64, 29.60, 29.56, 29.51, 29.48, 29.37, 29.35, 29.21, 29.12, 26.09, 26.00, 23.05, 22.69, 17.79, 14.11, -0.24.

^{1}H-NMR:



^{13}C-NMR



5b: Yield: 70 mg (18 %); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.29 (d, *J* 8.8, 4H, Ar-H), 8.14 (d, *J* 9.0, 8H, Ar-H), 7.64 (d, *J* 8.6, 4H, Ar-H), 7.49 (d, *J* 5.1, 4H, Ar-H), 7.44 (m, 2H, Ar-H), 7.37 (d, *J* 8.8, 4H, Ar-H), 7.27 (d, *J* 8.6, 4H, Ar-H), 7.22-7.19 (m, 2H, Ar-H), 6.97 (d, *J* 9.0, 4H, Ar-H), 6.96 (d, *J* 9.0, 4H, Ar-H), 4.06-4.01 (m, 8H, OCH_2), 1.85-1.78 (m, 8H, CH_2), 1.46 (q, *J* 7.0, 8H, CH_2), 1.35-1.26 (m, 60H, CH_2), 0.88 (t, *J* 6.6, 6H, CH_3), 0.53 (t, *J* 7.4, 4H, Si-CH_2), 0.07 (s, 24H, Si-CH_3), 0.06 (s, 12H, Si-CH_3), 0.06 (s, 12H, Si-CH_3); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 164.81, 164.38, 164.23, 163.76, 163.53, 155.38, 151.29, 150.82, 142.11, 137.69, 132.36, 132.25, 131.77, 129.78, 128.18, 126.84, 124.62, 122.12, 122.06, 121.45, 120.95, 120.49, 120.37, 114.40, 114.28, 68.40, 68.35, 33.47, 31.93, 29.67, 29.65, 29.62, 29.60, 29.56, 29.42, 29.37, 29.36, 29.15, 29.11, 26.02, 26.00, 23.26, 22.07, 18.31, 14.13, 1.22, 1.10, 0.24.
EA: calc. for: $C_{128}H_{182}O_{23}Si_8$: C, 66.45 %, H, 7.93 %, found: C, 66.23 %, H, 7.91 %.

Sia: Yield 105 mg (42 %); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.28 (d, ^{3}J = 8.7 Hz, 2H, Ar-H), 8.14 (d, ^{3}J = 8.7 Hz, 4H, Ar-H), 7.63 (d, ^{3}J = 8.5 Hz, 2H, Ar-H), 7.49 (d, ^{3}J = 4.8 Hz, 2H, Ar-H), 7.44 (s, 1H, Ar-H), 7.36 (d, ^{3}J = 8.7 Hz, 2H, Ar-H), 7.27 (d, ^{3}J = 8.5 Hz, 2H, Ar-H), 7.19 (m, 1H, Ar-H), 6.97 (d, ^{3}J = 8.7 Hz, 2H, Ar-H), 6.96 (d, ^{3}J = 8.9 Hz, 2H, Ar-H), 4.04 (t, ^{3}J = 6.5 Hz, 4H, OCH_2), 3.41 (t, ^{3}J = 6.5 Hz, 2H, OCH_2), 3.36 (t, ^{3}J = 7.0 Hz, 2H, OCH_2), 1.81 (m, 4H, $OCH_2C\mathit{H}_2$), 1.45 (m, 4H, CH_2), 1.26 (m, 18H, CH_2), 0.87 (t, ^{3}J = 6.9 Hz, 3H, CH_3), 0.54 (m, 2H, $SiCH_2$), 0.07 [s, 9H, Si-$(CH_3)_3$], 0.066 [s, 6H, Si-$(CH_3)_2$], 0.007 [s, 6H, Si-$(CH_3)_2$]; ^{13}C-NMR (125 MHz, $CDCl_3$): δ 164.74, 164.32, 164.16, 163.69, 163.42, 155.31, 151.22, 150.75, 142.06, 137.66, 132.32, 131.73, 129.74, 128.15, 126.81, 124.59, 122.09, 121.45, 120.92, 120.47, 120.35, 114.38, 114.36, 73.75, 68.43, 68.26, 31.99, 29.84, 29.74, 29.71, 29.687, 29.63, 29.43, 29.17, 26.12, 26.07, 26.00, 25.88, 23.60, 22.78, 14.36, 14.21, 1.94, 1.40, 0.27; ^{29}Si-NMR (99.3 MHz, $CDCl_3$): δ 7.59, 7.13, -20.85; EA calc. for $C_{61}H_{84}O_{11}Si_3$: C, 67.99; H, 7.86, found: C, 67.94; H, 8.01.