Supplementary material (ESI) for Journal of Materials Chemistry

Supporting Information

Continuous transition from antiferroelectric to ferroelectric switching liquid crystalline phases in two homologous series of bent core mesogenic dimers based on carbosilane spacer units

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1. Additional figures and tables

Table S1 Transition temperatures and corresponding enthalpy values (values in square brackets) of compounds **2/*n*** and **3/*n***.

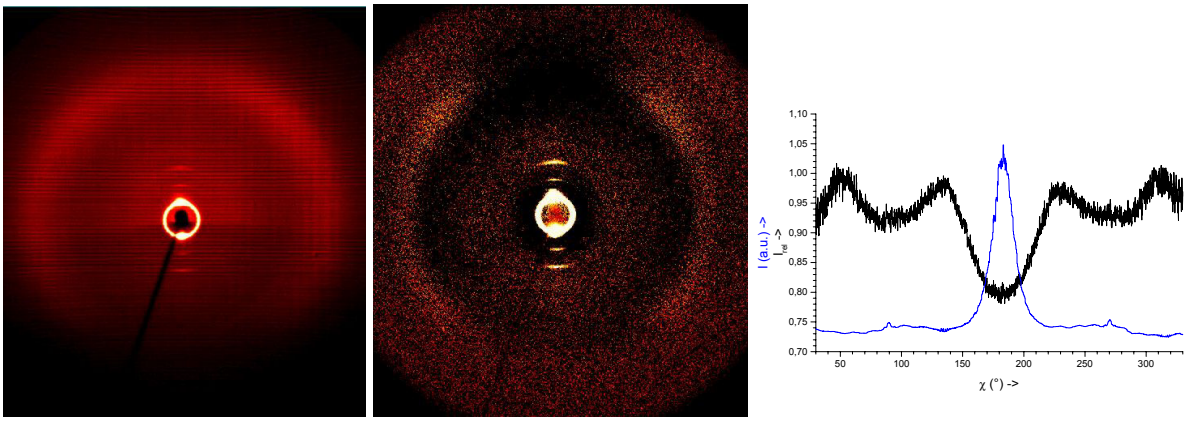
Comp.	T/°C [ΔH/kJ mol^{-1}]				
2/2	Cr	81 [51.2]	$SmCP_A$	108 [37.2]	Iso
2/4	Cr	68 [16.8]	$SmCP_F$[*]	103 [32.7]	Iso
2/6	Cr	67 [18.3]	$SmCP_F$[*]	100 [33.0]	Iso
2/8	Cr	98 [84.0]	($SmCP_F$[*]	95 [33.9])[a]	Iso
3/3	Cr	64 [35.0]	$SmCP_A$	105 [33.3]	Iso
3/5	Cr	68 [29.5]	$SmCP_F$[*]	97 [34.0]	Iso
3/7	Cr	57 [16.3]	$SmCP_F$[*]	98 [33.4]	Iso

[a] Monotropic (metastable) LC phase.

Table S2 Layer spacings as determined by different X-ray diffraction methods (see 2. Conditions for X-ray diffraction)

Comp.	*T* (°C)	*d* (nm)			
		Guinier film	Guinier goniometer	SAX-PSD	2D detector
2/2	90 - 50	3.80	3.74		3.74
2/4	80	4.07			
	70	4.08			
	60	4.09			
	50	4.10			
2/6	90 - 60	4.53			
2/8	98/95	4.77[a,c], 2.37[b,c]	4.84	4.75	
3/3	90	3.97			
	70	3.95			
	50	3.94			
3/5	80 - 40	4.31			
3/7	80 - 60	4.84[a], 2.42[b]	4.85[a], 2.39[b]	4.87	4.90[a], 2.43[b]

[a] first order, [b] second order layer reflection, [c] beginning phase transition, photo shows additional reflections from the phase below $SmCP_F$[*]



(a) (b) (c)

Fig. S1 2D X-ray pattern from a partially surface-aligned sample of **2/2** at 90 °C on cooling: a) original pattern, b) scattering of the isotropic liquid substracted to enhance the effect of the anisotropic distribution of the wide-angle scattering in the $SmCP_A$ phase, c) distribution of the wide-angle scattering along χ (black line) with maxima at χ = 49, 134, 227, and 316° in comparison with the χ position of the layer reflections (blue line) at χ = 180° giving an average tilt angle of the molecules with respect to the layer normal of 43.5° [$I_{rel} = I$(90 °C) / I(111 °C, iso)]

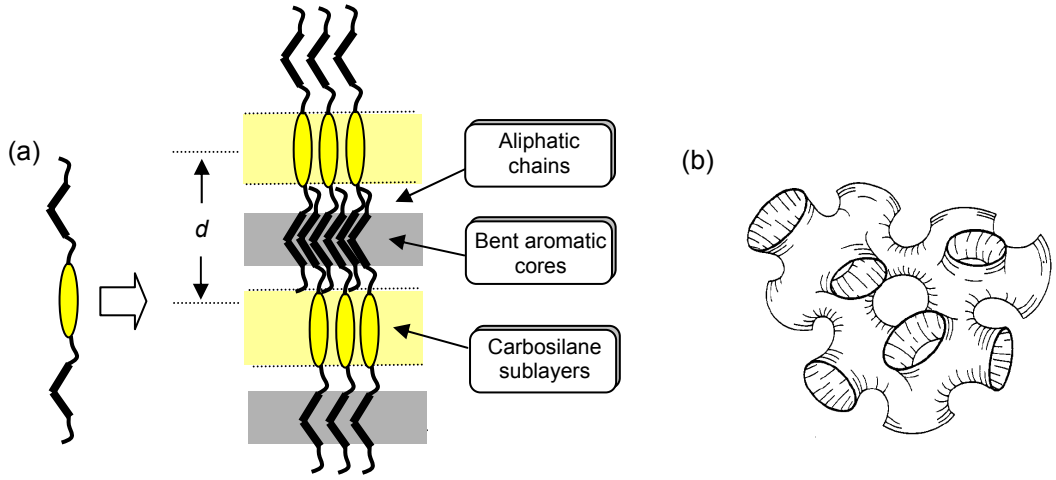


Fig. S2 (a) Model of the organization of the molecules **2/*n*** and **3/*n*** in the triply segregated smectic phases (the molecules are additionally tilted with respect to the projection plane); (b) shows a model of a sponge phase where a random web of the aromatic layers divides the fluid regions (segregated carbosilane sublayers are not shown).

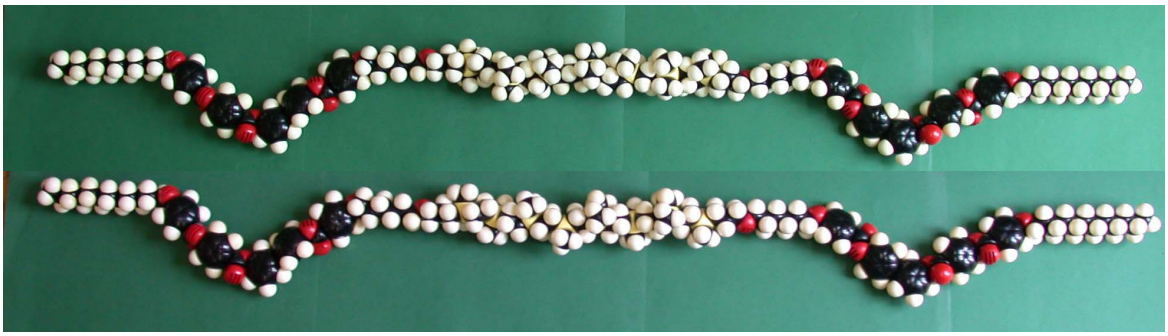


Fig. S3 Conformation used for the determination of the molecular length; CPK-Models of compounds **3/7** (top, L = 13.4) and **2/8** (bottom, L = 13.5) are shown as examples. Though the aromatic cores and the carbosilane spacer units appear to have only a slightly different cross-section in the shown views, it must be considered that the aromatic rings do not have a circular cross section, as seen from a top-view, whereas they are much flatter if seen from the side; in contrast, the carbosilane units have an overall circular average cross section, i.e. the space required by these units is much larger than that of the aromatic parts, as also indicated in Fig. S2a.

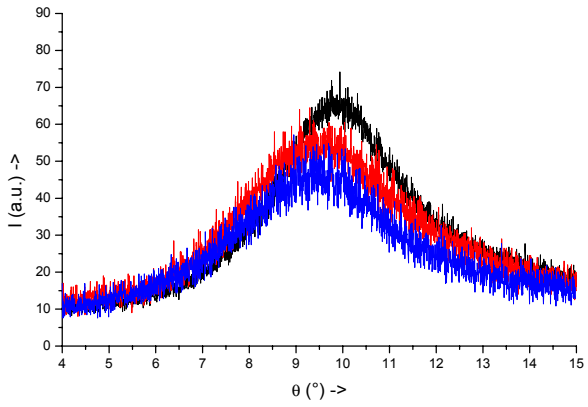


Fig. S4 Comparison of the wide-angle X-ray scattering from compounds **2/2** (black line, 90 °C, maximum at θ = 9.85°), **2/8** (blue line, 95 °C, maximum at θ = 9.45°), and **3/7** (red line, 70 °C, maximum at θ = 9.62°) measured on cooling with the Guinier goniometer using CuK_α radiation.

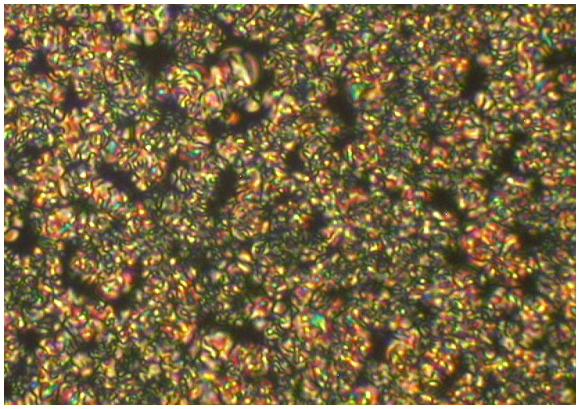


Fig. S5 Texture of the $SmCP_A$ phase of compound **3/3** as seen between crossed polarizers at T = 104 °C (dark areas are residues of the isotropic liquid).

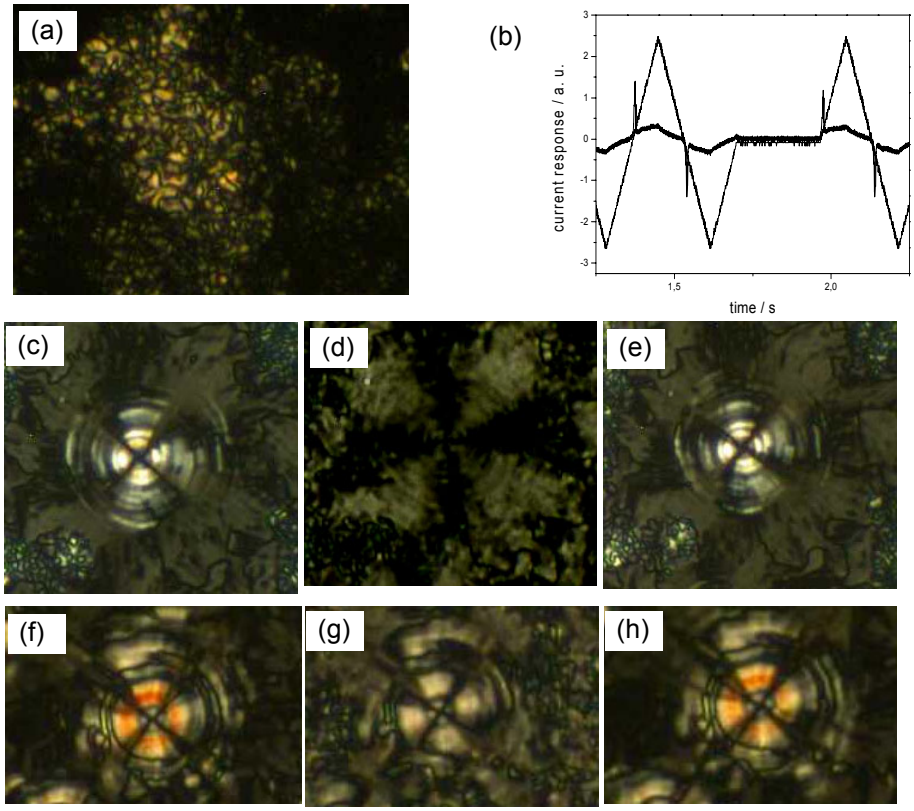


Fig. S6 Mesophase of compound **2/4**: (a) Texture between crossed polarizers at T = 90 °C shows the coexistence of dark and birefringent textures; (b) switching current response obtained under a modified triangular wave field (205 V_{pp}; 3 Hz,) at 95 °C indicates a surface stabilized FE switching; (c,f) circular domains as grown under a DC field at 90 °C (+ 10 V), (d,g) same areas after switching off the electric field; (e,h) circular domains seen after field reversal (–10 V); both domains, those showing a tristable switching (c-e) and those showing a bistable switching (f-h) coexist in the same sample.

2. Conditions for X-ray diffraction

X-ray investigations on powder-like samples kept in glass capillaries (∅ 1 mm) in temperature-controlled heating stages were carried out with 1. a Guinier film camera (Huber) using quartz-monochromatized CuK_α radiation (30 to 60 min exposure time, calibration with the powder pattern of $Pb(NO_3)_2$), 2. a Guinier goniometer (Huber) using quartz-

monochromatized CuK_α radiation, 3. a modified Kratky camera and a position-sensitive linear detector (MBraun) for the small angle region using Ni-filtered CuK_α radiation. 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) using Ni-filtered CuK_α radiation.

3. Analytical data of compounds 2/*n* and 3/*n*

2/2 ^{1}H-NMR ($CDCl_3$; 400 MHz): δ = 8.28 (d, *J* 8.7, 4H, Ar-H), 8.14 (d, *J* 8.9, 4H, Ar-H), 8.13 (d, *J* 8.9, 4H, Ar-H), 7.63 (d, *J* 8.7, 4H, Ar-H), 7.49 (d, *J* 4.9, 4H, Ar-H), 7.43 (s, 2H, Ar-H), 7.36 (d, *J* 8.9, 4H, Ar-H), 7.26 (d, *J* 8.5, 4H, Ar-H), 7.20 (m, 2H, Ar-H), 6.97 (d, *J* 8.9, 4H, Ar-H), 6.96 (d, *J* 9.1, 4H, Ar-H), 4.04 (m, 8H, OCH_2), 3.41 (t, *J* 6.5, 4H, OCH_2), 3.35 (t, *J* 7.2, 4H, OCH_2), 1.82 (m, 8H, OCH_2CH_2), 1.61 (m, 4H, CH_2OCH_2), 1.47 (m, 8H, $OCH_2CH_2CH_2$), 1.26 (m, 36H, CH_2), 0.87 (t, *J* 6.8, 6H, CH_3), 0.46 (m, 4H, $SiCH_2$), 0.36 (s, 4H, $SiCH_2$), -0.06 (s, 12H, $SiCH_3$); ^{13}C-NMR ($CDCl_3$; 125 MHz): δ = 164.90, 164.48, 164.32, 163.83, 163.55, 155.43, 151.33, 150.85, 142.16, 137.76, 132.42, 132.31, 131.83, 129.84, 128.24, 126.87, 124.68, 122.17, 122.11, 121.50, 120.97, 120.54, 120.41, 114.43, 114.31, 74.03, 70.73, 68.40, 68.22, 31.91, 30.90, 29.75, 29.64, 29.62, 29.58, 29.54, 29.35, 29.33, 29.08, 26.02, 25.97, 29.90, 24.18, 22.68, 14.10, 10.67, 7.12, -3.99; ^{29}Si-NMR ($CDCl_3$, 99.3 MHz): δ = 4.53; Calc. for $C_{114}H_{142}O_{18}Si_2$: C 73.75, H 7.71; found: C 73.73, H 7.87 %.

2/4: ^{1}H-NMR ($CDCl_3$; 400 MHz): δ = 8.28 (d, *J* 8.7, 4H, Ar-H), 8.14 (d, *J* 8.9, 8H, Ar-H), 7.63 (d, *J* 8.5, 4H, Ar-H), 7.49 (d, *J* 4.9, 4H, Ar-H), 7.43 (s, 2H, Ar-H), 7.37 (d, *J* 8.7, 4H, Ar-H), 7.27 (d, *J* 8.5, 4H, Ar-H), 7.21 (m, 2H, Ar-H), 6.97 (d, *J* 8.7, 4H, Ar-H), 6.95 (d, *J* 8.9, 4H, Ar-H), 4.04 (m, 8H, OCH_2), 3.42 (t, *J* 6.5 Hz, 4H, OCH_2), 3.36 (t, *J* 7.2, 4H, OCH_2), 1.83 (m, 8H, OCH_2CH_2), 1.65-1.45 (m, 20H, CH_2), 1.35-1.26 (m, 32H, CH_2), 0.87 (t, *J* 6.8, 6H, CH_3), 0.47 (m, 4H, $SiCH_2$), 0.35 (s, 8H, $SiCH_2$), 0.34 (s, 4H, $SiCH_2$), -0.05 (s, 12H, $SiCH_3$), -0.08 (s, 12H, $SiCH_3$); ^{13}C-NMR ($CDCl_3$; 125 MHz): δ = 164.88, 164.45, 164.29, 163.81, 163.53, 155.40, 151.30, 150.83, 142.14, 137.73, 132.39, 132.28, 131.80, 129.81, 128.42, 128.21, 126.84, 124.65, 122.14, 122.08, 121.47, 120.94, 120.51, 120.39, 115.67, 114.40, 114.28, 24.02, 70.70, 68.37, 68.19, 31.87, 29.72, 29.61, 29.59, 29.54, 29.51, 29.30, 29.05, 25.99, 25.94, 25.88, 25.81, 24.15, 22.64, 14.07, 10.65, 7.13, 6.56, -4.01, -4.49; ^{29}Si-NMR ($CDCl_3$, 99.3 MHz): δ = 5.64, 4.50; Calc. for $C_{122}H_{162}O_{18}Si_4$: C 72.22, H 8.05 ; found: C 72.39, H 8.08 %.

2/6: ^{1}H-NMR ($CDCl_3$; 400 MHz): δ = 8.28 (d, *J* 8.5, 4H, Ar-H), 8.14 (d, *J* 8.5, 8H, Ar-H), 7.63 (d, *J* 8.4, 4H, Ar-H), 7.49 (d, *J* 4.9, 4H, Ar-H), 7.44 (s, 2H, Ar-H), 7.36 (d, *J* 8.7, 4H, Ar-H), 7.27 (d, *J* 8.5, 4H, Ar-H), 7.20 (m, 2H, Ar-H), 6.96 (m, 8H, Ar-H), 4.04 (m, 8H, OCH_2), 3.41 (t, *J* 6.6, 4H, OCH_2), 3.35 (t, *J* 7.1, 4H, OCH_2), 1.83 (m, 8H, OCH_2CH_2), 1.62-1.41 (m, 20H, CH_2), 1.32 (m, 32H, CH_2), 0.87 (t, *J* 6.9, 6H, CH_3), 0.45 (m, 4H, $SiCH_2$), 0.35 (s, 8H, Si-CH_2), 0.35 (s, 8H, Si-CH_2), 0.34 (s, 12H, Si-CH_2), -0.06 (s, 12H, Si-CH_3), -0.08 (s, 24H, Si-CH_3); ^{13}C-NMR ($CDCl_3$; 125 MHz): δ = 164.90, 164.48, 164.32, 163.84, 163.56, 155.43, 151.33, 150.86, 142.17, 137.76, 132.42, 132.31, 131.83, 129.84, 128.24, 126.87, 124.68, 122.17, 122.13, 121.51, 120.97, 120.55, 120.42, 115.70, 114.43, 114.3174.05, 70.73, 68.40, 68.22, 32.65, 31.91, 29.75, 29.64, 29.62, 29.57, 29.54, 29.33, 29.08, 26.03, 25.97, 25.91, 24.19, 22.68, 14.10, 10.68, 7.16, 6.60, -3.97, -4.42, -4.45; ^{29}Si-NMR ($CDCl_3$, 99.3 MHz): δ = 5.61, 4.49; Calc. for $C_{130}H_{182}O_{18}Si_6$: C 70.93, H 8.33 ; found: C 71.30, H 8.34 %.

2/8: ^{1}H-NMR ($CDCl_3$; 400 MHz): δ = 8.29 (d, *J* 8.7, 4H, Ar-H), 8.14 (d, *J* 8.5, 8H, Ar-H), 7.63 (d, *J* 8.5, 4H, Ar-H), 7.49 (d, *J* 4.9, 4H, Ar-H), 7.44 (s, 2H, Ar-H), 7.37 (d, *J* 8.7, 4H, Ar-H), 7.27 (d, *J* 8.5, 4H, Ar-H), 7.20 (m, 2H, Ar-H), 6.98 (d, *J* 8.9, 4H, Ar-H), 6.97 (d, *J* 8.7,

4H, Ar-H), 4.04 (m, 8H, OCH_2), 3.41 (t, *J* 6.6, 4H, OCH_2), 3.35 (t, *J* 7.2, 4H, OCH_2), 1.83 (m, 8H, OCH_2CH_2), 1.61-1.26 (m, 52H, CH_2), 0.87 (t, *J* 6.9, 6H, CH_3), 0.47 (m, 4H, $SiCH_2$), 0.34 (m, 28H, $SiCH_2$), -0.05 (s, 12H, $SiCH_3$), -0.08 (s, 36H, $SiCH_3$); ^{13}C-NMR ($CDCl_3$; 125 MHz): δ = 164.91, 164.49, 164.33, 163.84, 163.56, 155.44, 151.34, 137.77, 132.42, 132.31, 131.84, 128.24, 122.18, 122.12, 121.51, 120.97, 120.42, 114.43, 114.32, 74.06, 70.74, 68.41, 68.23, 31.91, 29.76, 29.65, 29.63, 29.58, 29.55, 29.34, 29.09, 26.03, 25.97, 25.92, 24.19, 22.68, 14.11, 10.68, 7.17, 6.61, -3.97, -4.42, -4.45; ^{29}Si-NMR ($CDCl_3$, 99.3 MHz): δ = 5.60, 4.49; Calc. for $C_{144}H_{202}O_{18}Si_8$: C 70.71, H 8.32 ; found: C 71.14, H 8.62 %.

3/3: ^{1}H-NMR ($CDCl_3$; 400 MHz): δ = 8.29 (d, *J* 8.7, 4H, Ar-H), 8.13 (d, *J* 8.7, 8H, Ar-H), 7.63 (d, *J* 8.3, 4H, Ar-H), 7.47 (d, *J* 4.6, 4H, Ar-H), 7.43 (s, 2H, Ar-H), 7.36 (d, *J* 8.3, 4H, Ar-H), 7.27 (d, *J* 8.3, 4H, Ar-H), 7.19 (m, 2H, Ar-H), 6.97 (d, *J* 8.9, 4H, Ar-H), 6.96 (d, *J* 8.9, 4H, Ar-H), 4.04 (m, 8H, OCH_2), 3.41 (t, *J* 6.6, 4H, CH_2), 3.35 (t, *J* 7.0 Hz, 2H, CH_2), 1.81 (m, 8H, CH_2), 1.59 (m, 4H, CH_2), 1.44 (m, 16H, CH_2), 1.31 (m, 40H, CH_2), 0.87 (t, *J* 6.8, 6H, CH_3), 0.53 (m, 8H, $SiCH_2$), 0.45 (m, 4H, $SiCH_2$), -0.05 [s, 12H, Si-$(CH_3)_2$], -0.08 [s, 6H, Si-$(CH_3)_2$]; ^{13}C-NMR ($CDCl_3$; 125 MHz): δ = 164.89, 164.47, 164.31, 163.82, 163.55, 155.42, 151.32, 150.85, 142.15, 137.75, 132.41, 131.83, 129.84, 128.24, 126.86, 124.68, 122.18, 122.11, 121.49, 120.96, 120.54, 120.41, 114.42, 114.30, 74.00, 70.71, 68.39, 68.21, 31.89, 29.74, 29.64, 29.62, 29.57, 29.54, 29.33, 29.07, 26.01, 25.96, 25.89, 24.15, 22.67, 20.10, 19.89, 18.37, 14.10, 11.27, -3.19, -3.36; ^{29}Si-NMR ($CDCl_3$, 99.3 MHz): δ = 2.21, 0.97;
Calc. for $C_{120}H_{156}O_{18}Si_3$: C 73.13, H 7.98 ; found: C 73.34, H 8.13 %.

3/5: ^{1}H-NMR ($CDCl_3$; 400 MHz): δ = 8.28 (d, *J* 8.7, 4H, Ar-H), 8.14 (d, *J* 8.3, 8H, Ar-H), 7.63 (d, *J* 8.7, 4H, Ar-H), 7.49 (d, *J* 4.9, 4H, Ar-H), 7.43 (s, 2H, Ar-H), 7.36 (d, *J* 8.7, 4H, Ar-H), 7.27 (d, *J* 8.7, 4H, Ar-H), 7.20 (m, 2H, Ar-H), 6.97 (d, *J* 8.9, 4H, Ar-H), 6.96 (d, *J* 8.9, 4H, Ar-H), 4.04 (m, 8H, OCH_2), 3.41 (t, *J* 6.6, 4H, OCH_2), 3.35 (t, *J* 7.1, 4H, OCH_2), 1.81 (m, 8H, OCH_2CH_2), 1.53-1.47 (m, 12H, CH_2), 1.26 (m, 44H, CH_2), 0.87 (t, *J* 6.8, 6H, CH_3), 0.55 (m, 12H, $SiCH_2$ CH_2), 0.53 (m, 4H, $SiCH_2$), 0.35 (s, 8H, $SiCH_2$), -0.05 (s, 6H, $SiCH_3$), -0.07 (s, 12H, $SiCH_3$), -0.08 (s, 12H, $SiCH_3$); ^{13}C-NMR ($CDCl_3$; 125 MHz): δ = 164.90, 164.48, 164.31, 163.83, 163.56, 155.43, 151.33, 150.86, 142.16, 137.75, 132.41, 132.03, 131.83, 129.83, 128.23, 126.87, 124.67, 122.17, 122.11, 121.50, 120.97, 120.54, 120.41, 114.42, 114.31, 74.02, 70.71, 68.40, 68.22, 31.91, 29.75, 29.64, 29.62, 29.57, 29.54, 29.34, 29.33, 29.08, 26.02, 25.97, 25.90, 24.15, 23.08, 22.68, 20.11, 19.90, 19.84, 18.37, 17.82, 14.1, 11.28, 0.515, -3.19, -3.22, -3.36; ^{29}Si-NMR ($CDCl_3$, 99.3 MHz): δ = 2.21, 1.01; Calc. for $C_{130}H_{180}O_{18}Si_5$: C 71.91, H 8.36 ; found: C 72.10, H 8.38 %.

3/7: ^{1}H-NMR ($CDCl_3$; 400 MHz): δ = 8.28 (d, *J* 8.9, 4H, Ar-H), 8.14 (d, *J* 8.9, 8H, Ar-H), 7.63 (d, *J* 8.7, 4H, Ar-H), 7.49 (d, *J* 4.9, 4H, Ar-H), 7.43 (s, 2H, Ar-H), 7.36 (d, *J* 8.7, 4H, Ar-H), 7.27 (d, *J* 8.5, 4H, Ar-H), 7.22 (m, 2H, Ar-H), 6.97 (d, *J* 8.9, 4H, Ar-H), 6.96 (d, *J* 8.9, 4H, Ar-H), 4.03 (m, 8H, OCH_2), 3.41 (t, *J* 6.5, 4H, OCH_2), 3.35 (t, *J* 7.1, 4H, OCH_2), 1.81 (m, 8H, OCH_2CH_2), 1.56 (m, 8H, CH_2), 1.48-1.27 (m, 44H, CH_2), 0.87 (t, *J* 6.8, 6H, CH_3), 0.55 (m, 24H, $SiCH_2$ CH_2), 0.43 (m, 4H, $SiCH_2$), -0.05 (s, 12H, $SiCH_3$), -0.07 (s, 30H, $SiCH_3$); ^{13}C-NMR ($CDCl_3$; 125 MHz): δ = 164.92, 164.49, 164.33, 163.85, 163.57, 155.44, 151.34, 150.87, 142.18, 137.77, 132.43, 132.32, 131.84, 129.85, 128.25, 126.88, 124.69, 122.18, 122.12, 121.51, 120.98, 120.55, 120.42, 114.34, 114.32, 74.03, 70.73, 68.41, 68.23, 31.91, 30.91, 29.76, 29.65, 29.63, 29.58, 29.55, 29.34, 29.09, 26.03, 25.98, 25.92, 24.17, 22.68, 20.15, 19.92, 18.43, 18.38, 14.11, 11.29, -3.18, -3.35; ^{29}Si-NMR ($CDCl_3$, 99.3 MHz): δ = 0.97; Calc. for $C_{140}H_{204}O_{18}Si_7$: C 70.90, H 8.67 ; found: C 70.77, H 8.62 %.