Electronic Supplementary Information for:

Design of liquid crystals with 'de Vries-like' properties: The effect of carbosilane nanosegregation in 5-phenyl-1,3,4-thiadiazole mesogens.

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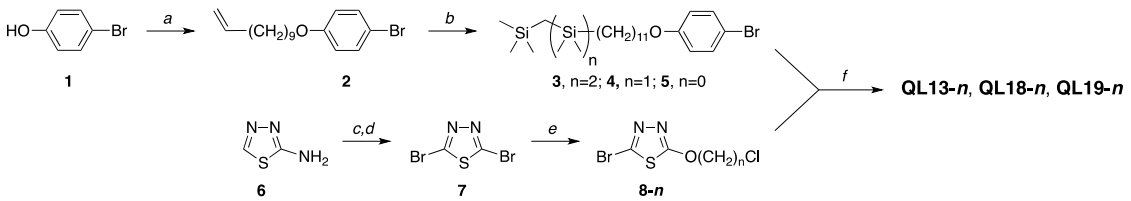
A. EXPERIMENTAL

General

^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance 400 spectrometer; chemical shifts (δ) are reported in parts per million (ppm) relative to TMS. Mass spectra were recorded using Waters/Micromass GC-TOF (low- and high-resolution) and Applied Biosystems/MDS Sciex QSTAR XL QTOF (low-resolution) instruments in electron ionization (EI) mode. Elemental analyses were performed on a Thermo Flash 2000 CHNS analyzer. Differential scanning calorimetry (DSC) analyses were performed using a TA Instruments Q2000 instrument with a scanning rate of 5 K min^{-1}. Texture analyses were performed using a Nikon Eclipse E600 POL polarized microscope fitted with a Linkam LTS 350 hot stage and TMS 93 temperature controller. Optical tilt angles were measured by polarized microscopy in the absence of an electric field by measuring the angle of rotation between dark states in domains of opposite tilt orientation with the sample aligned in glass cells with rubbed nylon alignment layers (5 μm spacing, AWAT, Poland) by slow cooling from the isotropic phase to the SmC phase at 0.1 K min^{-1}. Small-angle X-ray scattering experiments were performed on a SAXSess system from Anton Paar GmbH. Unaligned samples (filled into Hilgenberg Mark capillary tubes of 0.7 mm diameter) were mounted in a temperature controlled sample holder unit (TSC 120). The X-ray beam from a ceramic tube generator was focused by a bent multilayer mirror and shaped by a line collimation block. The X-ray scattering was recorded with a CCD detector (Princeton Instruments SCX-TE-4300K/2) and processed and analysed using the SAXSquant 3.5 software. The monodomain 2D X-ray scattering analyses were performed on a Bruker Nanostar X-ray diffractometer (CuKα radiation, beam diameter 100 μm, HiStar 2D-detector). The samples were filled into Hilgenberg Mark capillary tubes of 0.7 mm in diameter and placed in a temperature-controlled sample holder. After gently cooling the sample from the isotropic to the smectic phase in the presence of a magnetic field of 1 T, several large smectic monodomains with different directions of **z** grew inside the capillary. Using the motorized *x,y* position control of the sample holder, the sample was screened until the X-ray beam probed a scattering volume containing either a single monodomain or several monodomains having the same directions of **z** and **n**. All air sensitive reactions were carried out under dry N_2. Chemicals were obtained from commercial sources unless otherwise noted. 2,2,4,4,6-Pentamethyl-2,4,6-trisilaheptane, 2,2,4-trimethyl-2,4-disilapentane, 2,5-dibromo-1,3,4-thiadiazole (**7**), 2-(6-chlorohexyloxy)-5-(4-(12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecyloxy)phenyl)-1,3,4-thiadiazole (**QL13-6**), 1-bromo-4-

hexyloxybenzene (**9**) and 1-bromo-4-undecyloxybenzene (**10**) were prepared according to literature procedures and shown to have the expected physical and spectral properties.[1-6]

Synthesis



Scheme S1. *Reagents and conditions*: (a) CH_2=$CH(CH_2)_9OH$, DIAD, Ph_3P, THF; (b) 2,2,4,4,6-pentamethyl-2,4,6-trisilaheptane or 2,2,4-trimethyl-2,4-disilapentane, Karsted's catalyst, toluene (for n=2 and n=1, respectively); or (i) chlorodimethylsilane, Karsted's catalyst, toluene, (ii) CH_3MgBr (for n=0); (c) Br_2, NaOAc, AcOH; (d) HBr, $NaNO_2$, CuBr; (e) $Cl(CH_2)_nOH$, NaH, CuO, KI, THF; (f) *n*-BuLi, $ZnCl_2$(TMEDA), $Pd(PPh_3)_4$, THF.

1-Bromo-4-(10-undecenyloxy)benzene (2). Under a N_2 atmosphere, DIAD (23.3 g, 115.6 mmol) was added dropwise to a solution of 10-undecen-1-ol (9.8 g, 57.8 mmol), 4-bromophenol (**1**, 10.0 g, 57.8 mmol) and triphenylphosphine (30.3 g, 115.6 mmol) in dry THF (300 mL). After stirring overnight at room temperature, the reaction mixture was concentrated and purified by flash chromatography on silica gel (hexanes) to give **2** (16.5 g, 87%) as a colourless oil: ^{1}H NMR (400 MHz, CDCl3) δ 7.35 (d, J = 8.7 Hz, 2H), 6.79 (d, J = 8.7 Hz, 2H), 5.82 (tdd, J = 6.7, 10.2, 17.0 Hz, 1H), 4.93-5.03 (m, 2H), 3.92 (t, J = 6.6 Hz, 2H), 2.06 (q, J = 6.8 Hz, 2H), 1.77 (dt, J = 6.8, 14.5 Hz, 2H), 1.23-1.51 (m, 12H).

1-Bromo-4-(12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecyloxy)benzene (3). Under an N_2 atmosphere, a 3 wt% solution of Karsted's catalyst in xylenes (0.8 mL, 0.8 mmol) was added dropwise to a solution of **2** (5.0 g, 15.3 mmol) and 2,2,4,4,6-pentamethyl-2,4,6-trisilaheptane (4.36 g, 20.0 mmol) in dry toluene (100 mL) and the mixture was stirred at room temperature for 72 h. The mixture was then concentrated, and the residue purified by flash chromatography on silica gel (hexanes) to give **3** (5.58 g, 67%) as a clear liquid: ^{1}H NMR (400 MHz, CDCl3) δ 7.35 (d, J = 8.8 Hz, 2H), 6.79 (d, J = 8.8 Hz, 2H), 3.92 (t, J = 6.5 Hz, 2H), 1.72-1.84 (m, 2H), 1.41-1.51 (m, 2H), 1.22-1.40 (m, 14H), 0.50 (m, 2H), 0.05 (s, 6H), 0.03 (s, 9H), 0.00 (s, 6H), –0.25 (s, 2H), –0.28 (s, 2H).

1-Bromo-4-(12,12,14,14-tetramethyl-12,14-disilapentadecyloxy)benzene (4). The procedure used for the preparation of **3** was repeated with **2** (3.42 g, 10.5 mmol) and 2,2,4-trimethyl-2,4-disilapentane (2.0 g, 13.6 mmol) to give **4** (3.35 g, 68%) as a colourless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.8 Hz, 2H), 6.78 (d, J = 8.8 Hz, 2H), 3.92 (t, J = 6.6 Hz, 2H), 1.69-1.87 (m, 2H), 1.39-1.50 (m, 2H), 1.28 (br s, 12H), 0.89 (t, J = 6.7 Hz, 2H), 0.49 (t, J = 6.5 Hz, 2H), 0.02 (s, 6H), 0.00 (s, 9H), –0.29 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 132.2, 116.3, 112.5, 68.3, 33.7, 31.6, 29.6-29.2 (several overlapping peaks), 26.0, 24.0, 22.7, 18.0, 14.1, 2.6, 1.4, –0.6; LRMS (EI) *m/z* 472 ([M]$^+$, 11), 318 (18), 303 (46), 145 (100), 131 (14), 73 (14); HRMS (EI) calcd for $C_{23}H_{43}BrOSi_2$ 472.2019, found 472.2030.

1-Bromo-4-(12,12-dimethyl-12-silatridecyloxy)benzene (5). Under a N_2 atmosphere, a 3 wt% solution of Karsted's catalyst in xylenes (0.6 mL, 0.6 mmol) was added dropwise to a

solution of **2** (4.0 g, 12.3 mmol) and chlorodimethylsilane (1.40 g, 14.7 mmol) in dry toluene (40 mL). After the mixture was stirred at room temperature for 18 h, it was concentrated and the dark residue was redissolved in dry THF (30 mL) and cooled to 0 °C. A 3.0 M solution of CH_3MgBr in diethyl ether (4.5 mL, 13.5 mmol) was added dropwise and the mixture was stirred at room temperature for 2 h, and then refluxed for an additional 2 h. After cooling, the mixture was diluted with hexane (100 mL) and washed with water (100 mL). The aqueous layer was extracted with hexane (3 × 100 mL) and the combined extracts were dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography on silica gel (hexanes) to give **5** (3.37 g, 67%) as a colourless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 9.1 Hz, 2H), 6.79 (d, J = 8.8 Hz, 2H), 3.92 (t, J = 6.6 Hz, 2H), 1.66-1.91 (m, 2H), 1.14-1.53 (m, 14H), 0.92 (t, J = 6.7 Hz, 2H), 0.52 (t, J = 6.6 Hz, 2H), 0.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 132.2, 116.3, 112.5, 68.2, 33.6, 29.5-26.0 (several overlapping peaks), 23.9, 16.7, –1.6; LRMS (EI) *m/z* 400 ([M]$^+$, 24), 245 (17), 230 (18), 173 (68), 73 (100), 59 (30); HRMS (EI) calcd for $C_{20}H_{35}BrOSi$ 400.1623, found 400.1628.

2-Bromo-5-(3-chloropropyloxy)-1,3,4-thiadiazole (8-3). To a suspension of NaH (0.98 g, 16.4 mmol) in dry THF (100 mL) cooled to 0 °C was added 3-chloropropan-1-ol (1.55 g, 16.4 mmol) dropwise. The resulting solution was warmed to room temperature and stirred for 1 h. After adding KI (0.03 g, 0.2 mmol) and CuO (0.46 g, 5.7 mmol) to the solution, 2,5-dibromo-1,3,4-thiadiazole (**7**, 4.0 g, 16.4 mmol) was added and the reaction mixture was refluxed for 72 h. After cooling to room temperature, the mixture was diluted with CH_2Cl_2 (100 mL), filtered through Celite and the residue washed with EtOAc (3 × 200 mL). The combined filtrate was concentrated and purified by flash chromatography on silica get (10:1 hexanes/EtOAc) to give **8-3** (2.96 g, 70%) as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.65 (t, J = 5.9 Hz, 2H), 3.65 (t, J = 6.7 Hz, 2H), 2.26 (m, J = 6.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 130.8, 69.8, 40.5, 31.3; LRMS (EI) *m/z* 259 (2), 257 ([M]$^{4+}$, 5), 255 (2), 182 (24), 181 (100), 180 (25), 179 (94), 178 (28), 176 (71), 124 (43), 122 (40), 121 (20), 119 (21), 78 (13), 77 (21), 76 (18); HRMS (EI) calcd for $C_5H_6N_2OSBrCl$ 257.9050, found 257.9059.

2-Bromo-5-(4-chlorobutyloxy)-1,3,4-thiadiazole (8-4). The procedure used for the preparation of **8-3** was repeated with 4-chlorobutan-1-ol (1.78 g, 16.4 mmol) and **7** (4.0 g, 16.4 mmol) to give **8-4** (1.12 g, 25%) as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.57 (t, J = 6.0 Hz, 2H), 3.60 (t, J = 6.1 Hz, 2H), 1.89-2.14 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 130.8, 72.6, 44.2, 28.7, 26.1; LRMS (EI) *m/z* 271 ([M]$^+$, 0.3), 182 (17), 181 (43), 180 (16), 179 (41), 124 (27), 122 (27), 93 (36), 91 (100), 62 (11); HRMS (EI) calcd for $C_6H_8N_2OSBrCl$ 271.9206, found 271.9201.

2-Bromo-5-(5-chloropentyloxy)-1,3,4-thiadiazole (8-5) The procedure used for the preparation of **8-3** was repeated with 5-chloropentan-1-ol (3.0 g, 24.6 mmol) and **7** (6.0 g, 24.6 mmol) to give **8-5** (2.88 g, 41%) as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.54 (t, J = 6.4 Hz, 2H), 3.56 (t, J = 6.5 Hz, 2H), 1.76-1.94 (m, 4H), 1.55-1.66 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 130.7, 73.2, 44.6, 31.8, 27.9, 23.1; LRMS (EI) *m/z* 286 ([M+H]$^+$, 2), 208 (5), 206 (12), 205 (22), 182 (21), 181 (24), 180 (20), 179 (23), 107 (10), 105 (19), 70 (7), 69 (100), 68 (25); HRMS (EI) calcd for $C_7H_{10}N_2OSBrClH$ 286.9441, found 286.9485.

2-Bromo-5-(6-chlorohexyloxy)-[1,3,4]thiadiazole (8-6) The procedure used for the preparation of **8-3** was repeated with 6-chlorohexan-1-ol (2.21 g, 16.2 mmol) and **7** (3.95 g, 16.2

mmol) to give **8-6** (2.88 g, 59%) as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.49 (t, J = 5.7 Hz, 2H), 3.51 (t, J = 6.4 Hz, 2H), 1.67-1.90 (m, 4H), 1.31-1.64 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 130.5, 73.4, 44.8, 32.3, 28.4, 26.3, 24.9; LRMS (EI) *m/z* 300 ([M+H]$^+$, 4), 221 (19), 219 (41), 182 (34), 181 (27), 180 (33), 179 (25), 124 (18), 122 (17), 118 (13), 83 (81), 82 (30), 77 (13), 69 (19), 67 (24), 57 (19), 56 (21), 55 (100), 53 (10); HRMS (EI) calcd for $C_8H_{12}N_2OSBrClH$ 300.9598, found 300.9590.

2-(5-Chloropentyloxy)-5-(4-(12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecyl-oxy)phenyl)-1,3,4-thiadiazole (QL13-5). Under a N_2 atmosphere, a solution of *n*-BuLi (2.5 M in hexanes, 0.8 mL, 2.06 mmol) was added dropwise by syringe to a solution of **3** (1.0 g, 1.83 mmol) in dry THF (100 mL) cooled to –78°C. After stirring for 1 h at –78°C, $ZnCl_2$(TMEDA) (0.48 g, 1.84 mmol) was added and the mixture was allowed to warm to room temperature. $Pd(PPh_3)_4$ (0.1 g, 0.092 mmol) and **8-5** (0.54 g, 1.89 mmol) were then added and the mixture was refluxed overnight. After cooling, the mixture was concentrated and the residue purified by flash chromatography on silica gel (10:1 hexanes/EtOAc) to give **QL13-5** as a white solid (0.50 g, 41%). Recrystallization from HPLC-grade ethanol produced a white solid with sharp phase transitions: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.6 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 4.57 (t, J = 6.3 Hz, 2H), 4.00 (t, J = 6.4 Hz, 2H), 3.58 (t, J = 6.6 Hz, 2H), 1.69-2.01 (m, 2H), 1.53-1.69 (m, 6H), 1.41-1.51 (m, 6H), 1.28 (br s, 12H), 0.49 (t, J = 6.7 Hz, 2H), 0.05 (s, 6H), 0.03 (s, 9H), 0.00 (s, 6H), –0.25 (s, 2H), –0.28 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 165.4, 161.1, 128.5, 123.1, 114.9, 72.8, 68.2, 44.7, 33.7, 32.1, 29.2-26.0 (several overlapping peaks), 24.0, 23.2, 18.1, 5.8, 4.0, 2.0, –0.4; LRMS (EI) *m/z* 668 ([M]$^+$, 100), 653 (48), 581 (20), 549 (37), 527 (25), 514 (33), 509 (24), 451 (19), 395 (10), 347 (16), 217 (55), 194 (30), 145 (41), 129 (100), 73 (95), 69 (44); HRMS (EI) calcd for $C_{33}H_{61}N_2O_2SSi_3$ 668.3450, found 668.3435.

Anal. Calcd for $C_{33}H_{61}N_2O_2SSi_3$: C, 59.19; H, 9.18; N, 4.18. Found: C, 59.15; H, 9.22; N, 4.20.

2-(4-Chlorobutyloxy)-5-(4-(12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecyl-oxy)phenyl)-1,3,4-thiadiazole (QL13-4). The procedure used for the preparation of **QL13-5** was repeated with **3** (1.0 g, 1.83 mmol) and **8-4** (0.51 g, 1.89 mmol) to give **QL13-4** (0.45 g, 37%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.8 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 4.60 (t, J = 5.9 Hz, 2H), 4.00 (t, J = 6.4 Hz, 2H), 3.63 (t, J = 6.2 Hz, 2H), 1.90-2.14 (m, 6H), 1.71-1.87 (m, 6H), 1.11-1.55 (m, 10H), 0.49 (t, J = 6.7 Hz, 2H), 0.04 (s, 6H), 0.00 (s, 9H), –0.24 (s, 6H), –0.28 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 161.1, 128.5, 123.2, 114.9, 100.0, 72.2, 68.2, 44.4, 33.7, 29.4-26.1 (several overlapping peaks), 24.0, 18.1, 5.8, 4.0, 2.5, –0.4; LRMS (EI) *m/z* 654 ([M]$^+$, 44), 639 (44), 567 (16), 549 (18), 500 (18), 474 (27), 217 (69), 145 (29), 129 (100), 91 (50), 73 (86); HRMS (EI) calcd for $C_{32}H_{59}N_2O_2SSi_3$ 654.3293, found 654.3279.

Anal. Calcd for $C_{32}H_{59}N_2O_2SSi_3$: C, 58.62; H, 9.07; N, 4.27. Found: C, 58.58; H, 9.02; N, 4.20.

2-(3-Chloropropyloxy)-5-(4-(12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecyl-oxy)phenyl)-1,3,4-thiadiazole (QL13-3). The procedure used for the preparation of **QL13-5** was repeated with **3** (0.76 g, 1.40 mmol) and **8-3** (0.35 g, 1.42 mmol) to give **QL13-3** (0.33 g, 37%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.8 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H), 4.73 (t, J = 5.9 Hz, 2H), 4.00 (t, J = 6.4 Hz, 2H), 3.73 (t, J = 6.3 Hz, 2H), 2.33 (m, 2H),

1.67-1.90 (m, 6H), 1.09-1.55 (m, 8H), 0.49 (t, J = 6.6 Hz, 2H), 0.05 (s, 2H), 0.03 (s, 6H), 0.00 (s, 9H), –0.25 (s, 6H), –0.28 (s, 2H); ^{13}C NMR (100 MHz, CDCl3) δ 174.0, 162.6, 161.2, 128.5, 123.1, 114.9, 69.5, 68.2, 40.8, 33.7, 31.7, 29.5-28.0 (several overlapping peaks), 26.0, 24.0, 18.1, 5.8, 4.0, 2.5, 1.5, –0.4; LRMS (EI) *m/z* 640 ([M]$^+$, 86), 627 (48), 625 (80), 553 (30), 499 (27), 486 (32), 270 (11), 217 (100), 203 (14), 147 (14), 145 (22), 137 (26), 129 (98), 73 (57); HRMS (EI) calcd for $C_{31}H_{57}N_2O_2SSi_3$ 640.3137, found 640.3147.

Anal. Calcd for $C_{31}H_{57}N_2O_2SSi_3$: C, 58.03; H, 8.95; N, 4.37. Found: C, 58.15; H, 8.89; N, 4.29.

2-(6-Chlorohexyloxy)-5-(4-(12,12,14,14-tetramethyl-12,14-disilapentadecyloxy)phenyl)-1,3,4-thiadiazole (QL18-6). The procedure used for the preparation of **QL13-5** was repeated with **4** (0.57 g, 1.20 mmol) and **8-6** (0.35 g, 1.17 mmol) to give **QL18-6** (0.13 g, 17%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.8 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 4.56 (t, J = 6.6 Hz, 2H), 4.00 (t, J = 6.6 Hz, 2H), 3.56 (t, J = 6.7 Hz, 2H), 1.67-2.01 (m, 6H), 1.05-1.64 (m, 20H), 0.49 (t, J = 6.6 Hz, 2H), 0.02 (s, 9H), 0.00 (s, 6H), –0.29 (s, 2H); ^{13}C NMR (100 MHz, CDCl3) δ 174.4, 162.2, 161.1, 128.4, 123.2, 114.8, 73.0, 68.2, 44.8, 33.7, 32.4, 29.2-26.4 (several overlapping peaks), 26.0, 25.0, 23.9, 17.9, 2.6, 1.4, –0.6; LRMS (EI) *m/z* 610 ([M]$^+$, 43), 580 (5), 477 (12), 469 (14), 456 (11), 351 (12), 145 (100), 131 (13), 73 (23), 55 (16); HRMS (EI) calcd for $C_{31}H_{55}ClN_2O_2SSi_2$ 610.3211, found 610.3201.

Anal. Calcd for $C_{31}H_{55}ClN_2O_2SSi_2$: C, 60.89; H, 9.07; N, 4.58. Found: C, 60.79; H, 9.27; N, 4.63.

2-(5-Chloropentyloxy)-5-(4-(12,12,14,14-tetramethyl-12,14-disilapentadecyloxy)-phenyl)-1,3,4-thiadiazole (QL18-5). The procedure used for the preparation of **QL13-5** was repeated with **4** (0.80 g, 1.70 mmol) and **8-5** (0.50 g, 1.75 mmol) to give **QL18-5** (0.42 g, 42%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.6 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 4.57 (t, J = 6.4 Hz, 2H), 4.00 (t, J = 6.6 Hz, 2H), 3.58 (t, J = 6.6 Hz, 2H), 1.71-2.03 (m, 4H), 1.09-1.69 (m, 20H), 0.49 (t, J = 6.6 Hz, 2H), 0.02 (s, 9H), 0.00 (s, 6H), –0.29 (s, 2H); ^{13}C NMR (100 MHz, CDCl3) δ 174.3, 162.3, 161.1, 128.5, 123.2, 114.9, 72.8, 68.2, 44.7, 33.7, 32.1, 29.4-28.1 (several overlapping peaks), 26.0, 24.0, 23.2, 18.0, 2.6, 1.4, –0.6; LRMS (EI) *m/z* 596 ([M]$^+$, 35), 581 (14), 477 (15), 455 (14), 451 (13), 442 (15), 194 (14), 145 (100), 137 (14), 131 (22), 73 (25), 69 (19); HRMS (EI) calcd for $C_{30}H_{53}ClN_2O_2SSi_2$ 596.3055, found 596.3044.

Anal. Calcd for $C_{30}H_{53}ClN_2O_2SSi_2$: C, 60.31; H, 8.94; N, 4.69. Found: C, 60.51; H, 8.97; N, 4.74.

2-(4-Chlorobutyloxy)-5-(4-(12,12,14,14-tetramethyl-12,14-disilapentadecyloxy)phenyl)-1,3,4-thiadiazole (QL18-4). The procedure used for the preparation of **QL13-5** was repeated with **4** (0.84 g, 1.79 mmol) and **8-4** (0.41 g, 1.84 mmol) to give **QL18-4** (0.45 g, 50%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.6 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 4.60 (t, J = 5.9 Hz, 2H), 4.00 (t, J = 6.6 Hz, 2H), 3.62 (t, J = 6.2 Hz, 2H), 1.90-2.11 (m, 2H), 1.74-1.87 (m, 2H), 1.26-1.53 (m, 18H), 0.48 (t, J = 6.5 Hz, 2H), 0.02 (s, 9H), –0.01 (s, 6H), –0.30 (s, 2H); ^{13}C NMR (100 MHz, CDCl3) δ 174.2, 162.4, 161.1, 128.5, 123.2, 114.9, 72.2, 68.2, 58.4, 44.4, 33.7, 29.4-26.3 (several overlapping peaks), 26.0, 24.0, 18.4, 18.0, 2.6, 1.4, –0.6; LRMS (EI) *m/z* 582 ([M]$^+$, 63), 567 (30), 552 (14), 539 (12), 495 (15), 477 (16), 441 (27), 437 (23), 428 (29), 413 (15), 284 (17), 145 (100), 91 (65), 73 (24), 55 (19); HRMS (EI) calcd for $C_{29}H_{51}ClN_2O_2SSi_2$ 582.2899, found 582.2911.

Anal. Calcd for $C_{29}H_{51}ClN_2O_2SSi_2$: C, 59.70; H, 8.81; N, 4.80. Found: C, 59.92; H, 8.78; N, 4.89.

2-(3-Chloropropyloxy)-5-(4-(12,12,14,14-tetramethyl-12,14-disilapentadecyloxy)-phenyl)-1,3,4-thiadiazole (QL18-3). The procedure used for the preparation of **QL13-5** was repeated with **4)** (0.66 g, 1.40 mmol) and **8-3** (0.35 g, 1.36 mmol) to give **QL18-3** (0.55 g, 69%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.6 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H), 4.73 (t, J = 5.8 Hz, 2H), 4.01 (t, J = 6.6 Hz, 2H), 3.73 (t, J = 6.3 Hz, 2H), 2.34 (m, 2H), 1.71-1.89 (m, 2H), 1.14-1.64 (m, 16H), 0.49 (t, J = 6.5 Hz, 2H), 0.02 (s, 9H), 0.00 (s, 6H), –0.29 (s, 2H); ^{13}C NMR (100 MHz, CDCl3) δ 174.0, 162.6, 161.2, 128.5, 123.1, 114.9, 69.5, 68.2, 40.8, 33.7, 31.7, 29.5-26.0 (several overlapping peaks), 24.0, 18.0, 2.6, 1.4, –0.6; LRMS (EI) *m/z* 568 ([M]$^+$, 99), 553 (45), 525 (13), 481 (12), 427 (34), 414 (40), 270 (10), 145 (100), 73 (6); HRMS (EI) calcd for $C_{28}H_{49}ClN_2O_2SSi_2$ 568.2742, found 568.2763.

Anal. Calcd for $C_{28}H_{49}ClN_2O_2SSi_2$: C, 59.06; H, 8.67; N, 4.92. Found: C, 59.10; H, 8.72; N, 4.82.

2-(6-Chlorohexyloxy)-5-(4-(12,12-dimethyl-12-silatridecyloxy)phenyl)-1,3,4-thiadiazole (QL19-6). The procedure used for the preparation of **QL13-5** was repeated with **5** (0.48 g, 1.20 mmol) and **8-6** (0.35 g, 1.10 mmol) to give **QL19-6** (0.23 g, 38%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.6 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 4.56 (t, J = 6.4 Hz, 2H), 4.00 (t, J = 6.6 Hz, 2H), 3.56 (t, J = 6.7 Hz, 2H), 1.67-2.01 (m, 6H), 1.05-1.67 (m, 20H), 0.49 (t, J = 6.7 Hz, 2H), –0.02 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 162.2, 161.1, 128.5, 123.3, 114.9, 73.0, 68.2, 44.9, 33.6, 32.4, 31.6, 29.3-26.5 (several overlapping peaks), 26.0, 25.2, 23.9, 22.6, 16.7, 14.1, –1.6; LRMS (EI) *m/z* 538 ([M]$^+$, 32), 420 (5), 397 (2), 312 (6), 266 (2), 194 (25), 83 (4), 73 (100), 59 (11), 55 (16); HRMS (EI) calcd for $C_{28}H_{47}ClN_2O_2SSi$ 538.2816, found 538.2837.

Anal. Calcd for $C_{28}H_{47}ClN_2O_2SSi$: C, 62.36; H, 8.78; N, 5.19. Found: C, 62.46; H, 8.91; N, 5.32.

2-(5-Chloropentyloxy)-5-(4-(12,12-dimethyl-12-silatridecyloxy)phenyl)-1,3,4-thiadiazole (QL19-5). The procedure used for the preparation of **QL13-5** was repeated with **5** (0.68 g, 1.70 mmol) and **8-5** (0.50 g, 1.75 mmol) to give **QL19-5** (0.34 g, 37%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.6 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 4.57 (t, J = 6.4 Hz, 2H), 4.00 (t, J = 6.6 Hz, 2H), 3.38-3.71 (m, 2H), 1.73-2.05 (m, 6H), 1.07-1.73 (m, 18H), 0.49 (t, J = 6.7 Hz, 2H), –0.02 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 162.4, 160.9, 128.5, 123.4, 114.9, 72.8, 68.2, 44.7, 33.6, 32.1, 29.5-28.1 (several overlapping peaks), 26.0, 23.9, 23.2, 16.7, –1.6; LRMS (EI) *m/z* 524 ([M]$^+$, 49), 451 (15), 347 (9), 311 (10), 298 (17), 194 (38), 137 (24), 73 (100), 59 (22), 55 (15); HRMS (EI) calcd for $C_{27}H_{45}ClN_2O_2SSi$ 524.2659, found 524.2648.

Anal. Calcd for $C_{27}H_{45}ClN_2O_2SSi$: C, 61.74; H, 8.64; N, 5.33. Found: C, 61.82; H, 8.61; N, 5.53.

2-(4-Chlorobutyloxy)-5-(4-(12,12-dimethyl-12-silatridecyloxy)phenyl)-1,3,4-thiadiazole (QL19-4). The procedure used for the preparation of **QL13-5** was repeated with **5** (0.50 g, 1.25 mmol) and **8-4** (0.33 g, 1.22 mmol) to give **QL19-4** (0.20 g, 31%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.6 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H), 4.61 (t, J = 5.9 Hz, 2H),

4.01 (t, J = 6.6 Hz, 2H), 3.63 (t, J = 6.1 Hz, 2H), 1.90-2.15 (m, 4H), 1.67-1.87 (m, 2H), 1.09-1.62 (m, 16H), 0.49 (t, J = 6.7 Hz, 2H), –0.02 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 162.5, 161.8, 158.1, 128.5, 114.9, 75.6, 72.1, 44.4, 33.6, 32.1, 29.6-28.9 (several overlapping peaks), 26.0, 23.9, 23.2, 18.8, 13.9, –1.6; LRMS (EI) *m/z* 510 ([M]$^+$, 61), 495 (10), 437 (15), 356 (9), 297 (10), 284 (26), 249 (24), 194 (29), 137 (39), 134 (23), 120 (15), 91 (43), 73 (100), 59 (34), 55 (46); HRMS (EI) calcd for $C_{26}H_{43}ClN_2O_2SSi$ 510.2503, found 510.2521.

Anal. Calcd for $C_{26}H_{43}ClN_2O_2SSi$: C, 61.08; H, 8.48; N, 5.48. Found: C, 61.02; H, 8.65; N, 5.35.

2-(3-Chloropropyloxy)-5-(4-(12,12-dimethyl-12-silatridecyloxy)phenyl)-1,3,4-thiadiazole (QL19-3). The procedure used for the preparation of **QL13-5** was repeated with **5** (0.56 g, 1.39 mmol) and **8-3** (0.35 g, 1.35 mmol) to give **QL19-3** (0.51 g, 73%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.6 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H), 4.73 (t, J = 5.9 Hz, 2H), 4.01 (t, J = 6.4 Hz, 2H), 3.73 (t, J = 6.3 Hz, 2H), 2.34 (m, 2H), 1.73-1.94 (m, 2H), 1.09-1.66 (m, 16H), 0.49 (t, J = 6.6 Hz, 2H), –0.02 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 162.6, 161.2, 128.5, 123.1, 114.9, 99.9, 69.5, 68.2, 40.8, 33.6, 31.7, 29.6-29.1 (several overlapping peaks), 26.0, 23.9, 16.7, –1.6; LRMS (EI) *m/z* 496 ([M]$^+$, 83), 481 (19), 423 (21), 355 (12), 351 (25), 342 (17), 283 (13), 272 (17), 270 (43), 194 (21), 147 (11), 137 (31), 120 (10), 73 (100), 69 (13), 59 (19), 57 (16); HRMS (EI) calcd for $C_{25}H_{41}ClN_2O_2SSi$ 496.2346, found 496.2361.

Anal. Calcd for $C_{25}H_{41}ClN_2O_2SSi$: C, 60.39; H, 8.31; N, 5.63. Found: C, 60.42; H, 8.12; N, 5.55.

2-(6-Chlorohexyloxy)-5-(4-hexyloxyphenyl)-1,3,4-thiadiazole (QL28-6/6)). The procedure used for the preparation of **QL13-5** was repeated with **8-6** (0.47 g, 1.55 mmol) and **9** (0.39 g, 1.52 mmol) to give **QL28-6/6** (0.27 g, 45%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.6 Hz, 2H), 6.94 (d, J = 8.6 Hz, 2H), 4.56 (t, J = 6.4 Hz, 2H), 4.00 (t, J = 6.6 Hz, 2H), 3.56 (t, J = 6.6 Hz, 2H), 1.74-1.93 (m, 6H), 1.27-1.59 (m, 10H), 0.92 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 162.2, 161.1, 128.5, 123.3, 114.9, 73.0, 68.2, 44.9, 32.4, 31.5, 29.1, 28.6, 26.5, 25.6, 25.1, 22.6, 14.0; LRMS (EI) *m/z* 398 ([M+2]$^+$, 14), 396 (M$^+$, 33), 279 (15), 278 (69), 195 (14), 194 (100), 137 (33), 134 (36), 120 (13), 55 (20); HRMS (EI) calcd for $C_{20}H_{29}N_2O_2SCl^{35}$ 396.1638, found 396.1621.

Anal. Calcd for $C_{20}H_{29}N_2O_2SCl$: C, 62.90; H, 9.94; N, 4.32. Found: C, 63.15; H, 9.72; N, 4.35.

2-(6-Chlorohexyloxy)-5-(4-undecyloxyphenyl)-1,3,4-thiadiazole (QL28-11/6). The procedure used for the preparation of **QL13-5** as repeated with **8-6** (0.30 g, 1.00 mmol) and **10** (0.35 g, 1.07 mmol) to give **QL28-11/6** (0.19 g, 41%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.5 Hz, 2H), 6.94 (d, J = 8.6 Hz, 2H), 4.56 (t, J = 6.4 Hz, 2H), 4.01 (t, J = 6.6 Hz, 2H), 3.56 (t, J = 6.5 Hz, 2H), 1.74-1.93 (m, 6H), 1.27-1.59 (m, 20H), 0.92 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 162.2, 161.1, 128.5, 123.3, 114.9, 73.0, 68.2, 44.9, 32.4, 31.5, 29.4-29.1 (several overlapping peaks), 28.6, 26.5, 25.6, 25.1, 22.6, 14.0; LRMS (EI) *m/z* 468 ([M+2]$^+$, 21), 466 (M$^+$, 51), 349 (18), 348 (65), 195 (19), 194 (100), 137 (40), 134 (30), 120 (14), 57 (16), 55 (33); HRMS (EI) *m/z* calcd for $C_{25}H_{39}N_2O_2SCl^{35}$ 466.2421, found 466.2410.

Anal. Calcd for $C_{25}H_{39}N_2O_2SCl$: C, 64.28; H, 8.42; N, 6.00. Found: C, 64.57; H, 8. 20; N, 6.29.

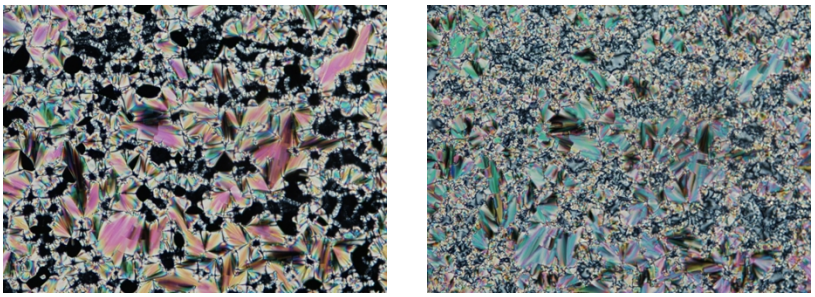


Fig. S1. Polarized photomicrographs of compound **QL13-3** at 65 °C in the SmA phase (left) and at 58 °C in the SmC phase (right).

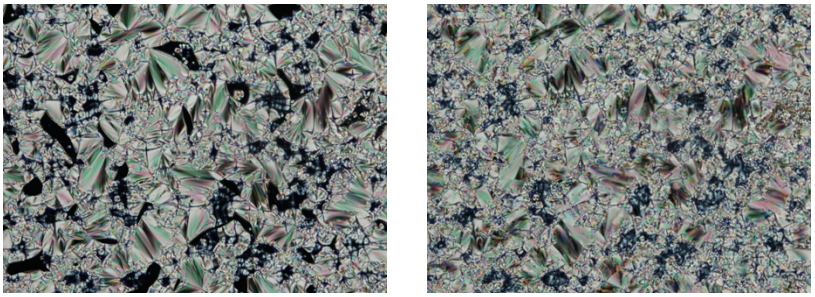


Fig. S2. Polarized photomicrographs of compound **QL18-3** at 72 °C in the SmA phase (left) and at 64 °C in the SmC phase (right).

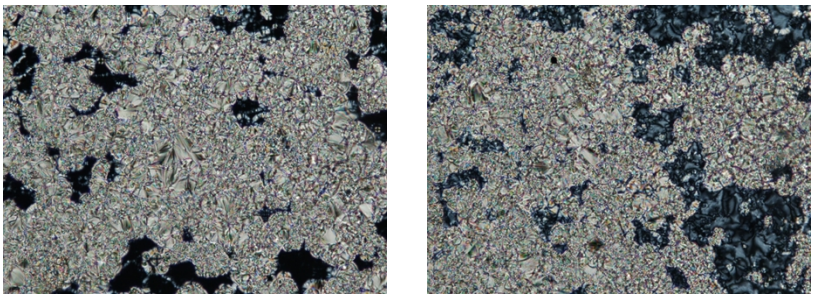


Fig. S3. Polarized photomicrographs of compound **QL19-6** at 75 °C in the SmA phase (left) and at 60 °C in the SmC phase (right).

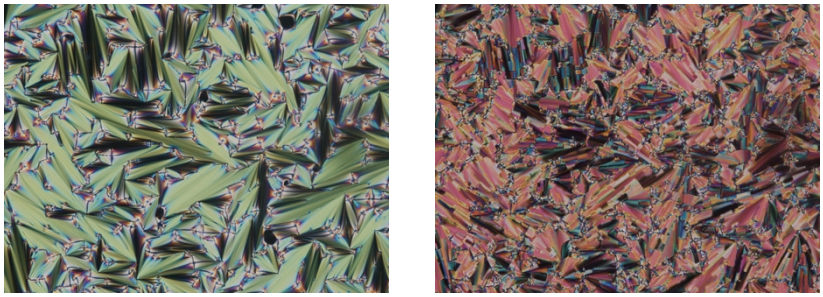


Fig. S4. Polarized photomicrographs of compound **QL13-3** as an unaligned 10 μm film at $T–T_{AC}$ = +1K (left) and at $T–T_{AC}$ = –15 K (right).

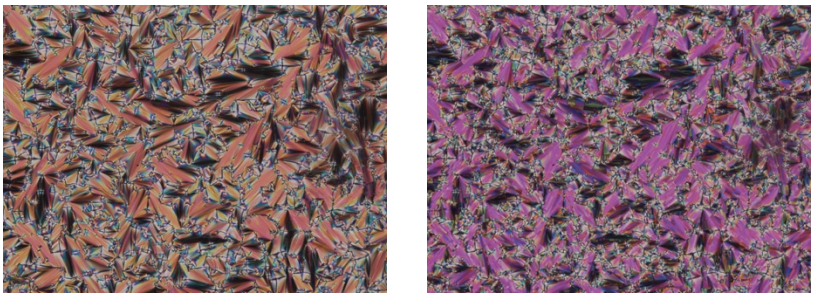


Fig. S5. Polarized photomicrographs of compound **QL18-3** as an unaligned 10 μm film at $T–T_{AC}$ = +1K (left) and at $T–T_{AC}$ = –15 K (right).

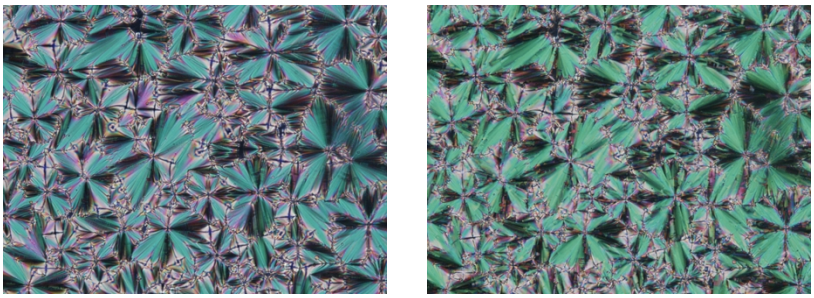


Fig. S6. Polarized photomicrographs of compound **QL19-6** as an unaligned 10 μm film at $T–T_{AC}$ = +1K (left) and at $T–T_{AC}$ = –15 K (right).

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