Electronic Supplementary Information for:

Tuning 'de Vries-like' properties in siloxane- and carbosilane-terminated smectic liquid crystals

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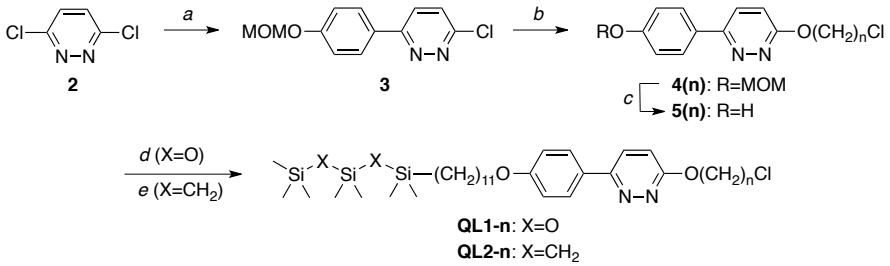
A. EXPERIMENTAL

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 as internal standard. 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 3 K min^{-1}, unless otherwise noted. 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 a rubbed polyimide alignment layer (4 μm spacing, E. H. C. Co., Japan) by slow cooling from the isotropic phase to the SmC phase at 2 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 123). 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 (KAF 2084x2083 SCX) and processed and analysed using the SAXSquant 3.5 software. Chemicals were obtained from commercial sources unless otherwise noted. 11-(1,1,1,3,3,5,5-Heptamethyltrisiloxanyl)undecan-1-ol,[1] 2,2,4,4,6-pentamethyl-2,4,6-trisilaheptane,[2] 4-(methoxymethoxy)phenylboronic acid,[3] 7-chloroheptanoyl chloride, 8-chlorooctanoyl chloride, 9-chlorononanoyl chloride and 10-chlorodecanoyl chloride[4, 5] were prepared according to literature procedures and shown to have the expected physical and spectral properties.

12,12,14,14,16,16-Hexamethyl-12,14,16-trisilaheptadecan-1-ol. Under an Ar atmosphere, a 3 wt% solution of platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in xylenes (1.0 mL, 0.1 mmol) was added to a solution of 10-undecen-1-ol (1.19 g, 7 mmol), and 2,2,4,4,6-pentamethyl-2,4,6-trisilaheptane (2.18 g, 10 mmol) in toluene (30 mL). The mixture was stirred at 0 ºC for 30 min, then concentrated, and the residue purified by flash chromatography on silica gel, first with 50% EtOAc/hexanes and then with 20% EtOAc/hexanes, to give the product (1.77 g, 65%) as a clear liquid: ^{1}H NMR (400MHz, $CDCl_3$) δ 3.65 (t, J = 6.5 Hz, 2H), 1.16-1.41 (m,

18H), 0.48 (t, J = 7.5 Hz, 2H), 0.05 (s, 6H), 0.03 (s, 9H), 0.00 (s, 6H), -0.25 (s, 2 H), -0.28 (s, 2 H);[13]C NMR (125 MHz, $CDCl_3$) δ 63.4, 34.1, 33.2, 30.0-29.8 (several overlapping peaks), 26.2, 24.4, 18.5, 6.2, 4.4, 2.9, 1.9, 0.0; HRMS (ESI(–)) calcd for $C_{20}H_{47}OSi_3$ ([M-H]$^-$) 387.2935, found 387.2943.



[a] 4-(Methoxymethoxy)phenylboronic acid, $Pd_2(dba)_3$, Cy_3P, aq K_3PO_4; [b] $Cl(CH_2)_nOH$, NaH, THF; [c] aq 6 M HCl, IPA; [d] 11-(1,1,1,3,3,5,5-heptamethyltrisiloxanyl)undecan-1-ol, DIAD, Ph_3P, THF; [e] 12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecan-1-ol, DIAD, Ph_3P, THF.

3-Chloro-6-(4-(methoxymethoxy)phenyl)pyridazine (3). A 50 mL Schlenk flask was charged with 3,6-dichloropyridazine (**2**, 0.73 g, 3.0 mmol), 4-(methoxymethoxy)phenylboronic acid (0.70 g, 3.9 mmol), $Pd_2(dba)_3$ (27.6 mg, 0.030 mmol) and Cy_3P (20.1 mg, 0.072 mmol), then evacuated and filled with Ar (5×). Degassed dioxane (15 mL) and aq K_3PO_4 (1.27 M, 4.0 mL, 5.08 mmol) were added by syringe, the Schlenk flask was sealed and heated in an oil bath at 100 °C for 18 h with vigorous stirring. The mixture was then filtered through a pad of silica gel and washed with EtOAc. The filtrate was concentrated and the aqueous residue extracted three times with EtOAc. The combined extracts were dried ($MgSO_4$), concentrated, and the residue purified by flash chromatography on silica gel (20% EtOAc/hexanes) to give **3** (0.52 g, 70%) as a white solid: mp 123-125 °C; ^{1}H NMR (400 MHz ,$CDCl_3$) δ 8.00 (d, J = 8.6 Hz, 2H), 7.78 (d, J = 9.1 Hz, 1H), 7.52 (d, J = 8.8 Hz, 1H), 7.17 (d, J = 8.3 Hz, 2H), 5.25 (s, 2H), 3.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 158.1, 155.0, 128.6, 128.5, 128.4, 125.6, 116.7, 94.3, 56.2; LRMS (EI) *m/z* 250 (M^+, 100), 222 (15), 220 (45), 192 (15), 149 (19), 132 (24), 117 (13), 89 (18); HRMS (EI) calcd for $C_{12}H_{11}N_2O_2{}^{35}Cl$ 250.0509, found 250.0511.

General procedure for the synthesis of 4(n). The procedure described for the synthesis of 3-(6-chlorohexyloxy)-6-(4-(methoxymethoxy)phenyl)pyridazine **(4(6))** is representative: A mixture of 6-chloro-1-hexanol (0.55 g, 4 mmol) and NaH (60% oil suspension, 0.16 g, 4 mmol) in dry THF (10 mL) was stirred for 1 hour, and a suspension of **3** (0.25 g, 1.0 mmol) in dry THF (20 mL) was added in one portion. The mixture was stirred overnight at room temperature and then slowly quenched with sat aq NH_4Cl. The mixture was poured into H_2O (30 mL) and extracted with CH_2Cl_2 (100 mL, then 3 × 10 mL). The combined extracts were washed with brine, dried ($MgSO_4$), concentrated and the residue was purified by flash chromatography on silica gel (25% EtOAc/hexanes) to give **4(6)** (0.21 g, 60%) as a white solid: mp 78-80 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.8 Hz, 2H), 7.74 (d, J = 9.1 Hz, 1H), 7.15 (d, J = 8.6 Hz, 2H), 7.00 (d, J = 9.3 Hz, 1H), 5.24 (s, 2 H), 4.57 (t, J = 6.6 Hz, 2H), 3.55 (t, J = 6.7 Hz, 2H), 3.51 (s, 3H), 1.70-1.95 (m, 4H), 1.42-1.61 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 158.4, 154.6, 130.0, 127.9, 126.7, 117.8, 116.4, 94.3, 67.3, 56.1, 45.0, 32.5, 28.8, 26.6, 25.4; LRMS

(EI) *m/z* 350 (M^+, 28), 315 (16), 306 (12), 233 (20), 232 (100), 230 (14), 202 (25), 200 (21), 189 (10), 188 (54); HRMS (EI) *m/z* calcd for $C_{18}H_{23}N_2O_3{}^{35}Cl$ 350.1397, found 350.1395.

3-(7-Chloroheptyloxy)-6-(4-(methoxymethoxy)phenyl)pyridazine (4(7)). Yield of 60%, white solid: mp 82-83 °C; ^{1}H NMR (400 MHz ,$CDCl_3$) δ 7.96 (d, *J* = 8.8 Hz, 2 H), 7.73 (d, *J* = 9.3 Hz, 1 H), 7.15 (d, *J* = 8.6 Hz, 2 H), 7.00 (d, *J* = 9.3 Hz, 1 H), 5.24 (s, 2 H), 4.56 (t, *J* = 6.6 Hz, 2 H), 3.54 (t, *J* = 6.7 Hz, 2 H), 3.51 (s, 3 H), 1.70-1.95 (m, 4 H), 1.32-1.60 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 158.4, 154.6, 130.0, 127.8, 126.7, 117.8, 116.5, 94.3, 67.4, 56.1, 45.1, 32.6, 28.8, 28.6, 26.8, 25.9; LRMS (EI) *m/z* 364 (M^+, 19), 299 (22), 245(11), 233 (24), 232 (100), 202 (39), 200 (32), 189 (12), 188(55); HRMS (EI) calcd for $C_{19}H_{25}N_2O_3{}^{35}Cl$ 364.1554, found 364.1552.

3-(8-Chlorooctyloxy)-6-(4-(methoxymethoxy)phenyl)pyridazine (4(8)). Yield of 65%, white solid: mp 80-81 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.95 (d, *J* = 8.8 Hz, 2H), 7.73 (d, *J* = 9.1 Hz, 1H), 7.15 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 9.1 Hz, 1H), 5.23 (s, 2H), 4.56 (t, *J* = 6.7 Hz, 2H), 3.49-3.58 (m, 5H), 1.71-1.91 (m, 4H), 1.30-1.53 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 162.9, 157.3, 153.4, 128.8, 126.7, 125.6, 116.7, 115.5, 93.2, 66.4, 55.0, 44.0, 31.5, 28.0, 27.7, 27.6, 25.7, 24.8; LRMS (EI) *m/z* 378 (M^+, 24), 353 (15), 352 (67), 343 (12), 322 (13), 313 (18), 308 (21), 279 (10), 233 (21), 232(100), 202 (25), 200 (20), 189 (11), 188 (54), 167 (11), 149 (14); HRMS (EI) *m/z* calcd for $C_{20}H_{27}N_2O_3{}^{35}Cl$ 378.1710, found 378.1708.

3-(9-Chlorononyloxy)-6-(4-(methoxymethoxy)phenyl)pyridazine (4(9)). Yield of 61%, white solid: mp 84-85 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.95 (d, *J* = 8.6 Hz, 2H), 7.73 (d, *J* = 9.1 Hz, 1H), 7.15 (d, *J* = 8.6 Hz, 2H), 6.99 (d, *J* = 9.1 Hz, 1H), 5.23 (s, 2H), 4.55 (t, *J* = 6.6 Hz, 2H), 3.45-3.62 (m, 5H), 1.71-1.93 (m, 4H), 1.23-1.60 (m, 10H); ^{13}C NMR (100MHz, $CDCl_3$) δ 164.0, 158.4, 154.5, 130.0, 127.8, 126.6, 117.8, 116.5, 94.3, 67.5, 56.1, 45.2, 32.6, 29.4, 29.2, 28.9, 28.8, 26.9, 26.0; LRMS (EI) *m/z* 392 (M^+, 44), 357 (29), 233 (18), 232 (100), 202 (16); HRMS (EI) *m/z* calc'd for $C_{21}H_{29}{}^{35}ClN_2O_3$ 392.1867, found 392.1865.

General procedure for the synthesis of 5(n). The procedure described for the synthesis of 3-(6-chlorohexyloxy)-6-(4-hydroxyphenyl)pyridazine **(5(6))** is representative: To a solution of **4(6)** (0.2 g, 0.57 mmol) in isopropanol (20 mL) was add 6 M aq HCl (0.5 mL, 3.0 mmol). After stirred for 5 hours at 50 °C, the solution was concentrated and diluted with CH_2Cl_2 (20 mL) and H_2O (20 mL). The layers were separated the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined extracts were dried ($MgSO_4$), concentrated and the residue was purified by flash chromatography on silica gel (33% EtOAc/hexanes) to give **5(6)** (0.16 g, 92%) as a white solid: mp 103-105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.82 (d, *J* = 8.6 Hz, 2H), 7.74 (d, *J* = 9.3 Hz, 1H), 7.04 (d, *J* = 9.1 Hz, 1H), 7.00 (d, *J* = 8.6 Hz, 2H), 4.55 (t, *J* = 6.4 Hz, 2H), 3.54 (t, *J* = 6.7 Hz, 2H), 1.72-1.94 (m, 4H), 1.38-1.61 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 164.0, 158.2, 155.2, 128.1, 127.8, 127.5, 118.5, 116.3, 67.5, 45.0, 32.5, 28.8, 26.6, 25.4; LRMS (EI) *m/z* 306 (M^+, 13), 189 (18), 188(100), 131 (11); HRMS (EI) *m/z* calcd for $C_{16}H_{19}N_2O_2{}^{35}Cl$ 306.1135, found 306.1133.

3-(7-Chloroheptyloxy)-6-(4-hydroxyphenyl)pyridazine (5(7)). Yield of 91%, white solid: mp 102-103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.6 Hz, 2 H), 7.74 (d, *J* = 9.3 Hz, 1 H), 6.92-7.05 (m, 3 H), 4.54 (t, *J* = 6.6 Hz, 2 H), 3.53 (t, *J* = 6.7 Hz, 2 H), 1.70-1.92 (m, 4 H),

1.33-1.54 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 158.3, 155.2, 128.1, 127.7, 127.6, 118.5, 116.3, 67.6, 45.1, 32.5, 28.8, 28.6, 26.8, 25.9; LRMS (EI) *m/z* 320 (M^+, 13), 279 (5), 255 (8), 189 (17), 188(100), 167 (6), 149 (8), 131 (5); HRMS (EI) calcd for $C_{17}H_{21}N_2O_2{}^{35}Cl$ 320.1292, found 320.1290.

3-(8-Chlorooctyloxy)-6-(4-hydroxyphenyl)pyridazine (5(8)). Yield of 90%, white solid: mp 102-104 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.8 Hz, 2H), 7.77 (d, J = 9.1 Hz, 1H), 7.08 (d, J = 9.1 Hz, 1H), 7.01 (d, J = 8.6 Hz, 2H), 4.53 (t, J = 6.6 Hz, 2H), 3.53 (t, J = 6.8 Hz, 2H), 1.68-1.91 (m, 4H), 1.23-1.55 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 158.5, 154.9, 128.3, 127.9, 127.0, 119.2, 116.4, 67.9, 45.2, 32.6, 29.2, 28.8, 28.7, 26.8, 25.9; LRMS (EI) *m/z* 334 (M^+, 11), 299 (8), 269 (7), 189 (16), 188 (100); HRMS (EI) *m/z* calcd for $C_{18}H_{23}N_2O_2{}^{35}Cl$ 334.1448, found 334.1446.

3-(9-Chlorononyloxy)-6-(4-hydroxyphenyl)pyridazine (5(9)). Yield of 91%, white solid: mp 105-107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.6 Hz, 2H), 7.74 (d, J = 9.1 Hz, 1H), 7.02 (m, 3H), 4.54 (t, J = 6.6 Hz, 2H), 3.53 (t, J = 6.8 Hz, 2H), 1.68-1.94 (m, 4H), 1.21-1.56 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 158.1, 155.1, 128.1, 127.8, 127.4, 118.5, 116.3, 67.7, 45.2, 32.6, 29.4, 29.2, 28.9, 28.8, 26.9, 26.0; LRMS (EI) *m/z* 348 (M^+, 8), 189 (23), 188 (100), 131 (11); HRMS (EI) *m/z* calcd for $C_{19}H_{25}N_2O_2{}^{35}Cl$ 348.1605, found 348.1603.

General procedure for the synthesis of QL1-n. The procedure described for the synthesis of 3-(6-chlorohexyloxy)-6-(4-(11-(1,1,1,3,3,5,5-heptamethyltrisiloxanyl)undecyloxy)phenyl) pyridazine **(QL1-6)** is representative: Under an Ar atmosphere, DIAD (202 mg, 0.20 mL, 1.0 mmol) was added to a solution of 11-(1,1,1,3,3,5,5-heptamethyltrisiloxanyl)undecanol (200 mg, 0.52 mmol), **5(6)** (160 mg, 0.52 mmol) and triphenylphosphine (262 mg, 1.0 mmol) in dry THF (25 mL). The yellow solution was stirred overnight at room temperature, then concentrated and purified by flash chromatography on silica gel (10% EtOAc/hexanes) to give **QL1-6** (230 mg, 68%) as a yellow solid contaminated with traces of DIAD. Recrystallization from HPLC-grade acetonitrile (3×) gave a white solid with sharp phase transitions: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.8 Hz, 2H), 7.73 (d, J = 9.3 Hz, 1 H), 6.97 - 7.03 (m, 3H), 4.57 (t, J = 6.6 Hz, 2H), 4.02 (t, J = 6.6 Hz, 2H), 3.56 (t, J = 6.7 Hz, 2H), 1.73-1.98 (m, 8H), 1.19-1.59 (m, 24H), 0.51-0.56 (t, J = 7.2 Hz, 2H), 0.10 (s, 9H), 0.07 (s, 6H), 0.03 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 158.6, 152.9, 126.8, 125.9, 124.7, 115.9, 113.1, 66.3, 65.4, 43.2, 31.6, 30.7, 27.8-27.4 (several overlapping peaks), 27.0, 24.8, 24.2, 23.6, 21.4, 16.5, 0.0, –0.5, –1.6; LRMS (EI) *m/z* 680 (M^+, 100), 665 (34), 562 (25), 561 (25), 319 (30), 306 (39), 221 (51); HRMS (EI) *m/z* calcd for $C_{34}H_{61}N_2O_4Si_3{}^{35}Cl$ 680.3628, found 680.3626.

Anal. Calcd for $C_{34}H_{61}N_2O_4Si_3Cl$: C, 59.92; H, 9.02; N, 4.11. Found: C, 59.70; H, 9.12; N, 4.29.

3-(7-Chloroheptyloxy)-6-(4-(11-(1,1,1,3,3,5,5-heptamethyltrisiloxanyl)undecyloxy) phenyl)pyridazine (QL1-7). Yield of 68%, white solid: ^{1}H NMR (400 MHz ,$CDCl_3$) δ 7.95 (d, J = 8.8 Hz, 2H), 7.73 (d, J = 9.3 Hz, 1H), 6.88-7.11 (m, 3H), 4.56 (t, J = 6.6 Hz, 2H), 4.02 (t, J = 6.6 Hz, 2H), 3.55 (t, J = 6.7 Hz, 2H), 1.72-1.98 (m, 6H), 1.20-1.60 (m, 22H), 0.54 (t, J = 7.4 Hz, 2H), 0.09 (s, 9H), 0.07 (s, 6H), 0.03 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 158.5, 152.9, 126.8, 125.9, 124.7, 115.9, 113.0, 66.3, 65.5, 43.3, 31.6, 30.7, 27.8-27.4 (several overlapping peaks), 27.0, 26.8, 25.0, 24.2, 24.0, 21.4, 16.5, 0.0, –0.5, –1.6; LRMS (EI) *m/z* 694 (M^+, 100),

681 (14), 680 (16), 679 (29), 562 (18), 561 (20), 473 (11), 333 (27), 322 (11), 320 (38), 222 (12), 221 (60); HRMS (EI) calcd for $C_{35}H_{63}N_2O_4Si_3{}^{35}Cl$ 694.3784, found 694.3781.

Anal. Calcd for $C_{35}H_{63}N_2O_4Si_3Cl$: C, 60.43; H, 9.13; N, 4.03. Found: C, 60.70; H, 9.28; N, 4.23.

3-(8-Chlorooctyloxy)-6-(4-(11-(1,1,1,3,3,5,5-heptamethyltrisiloxanyl)undecyloxy) phenyl)pyridazine (QL1-8). Yield of 60%, white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.8 Hz, 2H), 7.73 (d, J = 9.1 Hz, 1H), 6.94-7.07 (m, 3H), 4.56 (t, J = 6.7 Hz, 2H), 4.02 (t, J = 6.4 Hz, 2H), 3.54 (t, J = 6.8 Hz, 2H), 1.72-1.92 (m, 6H), 1.23-1.62 (m, 24H), 0.54 (t, J = 7.0 Hz, 2H), 0.09 (s, 9H), 0.07 (s, 6H), 0.03 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 158.6, 152.8, 126.8, 125.9, 124.7, 115.9, 113.0, 66.3, 65.6, 43.3, 31.6, 30.8, 27.8-27.0 (several overlapping peaks), 25.0, 24.2, 24.1, 21.4, 16.5, 0.0, –0.5, –1.6; LRMS (EI) *m/z* 708 (M^+, 58), 693 (34), 562 (26), 561 (23), 347 (33), 334 (42), 222 (22), 221(100); HRMS (EI) *m/z* calcd for $C_{36}H_{65}N_2O_4Si_3{}^{35}Cl$ 708.3941, found 708.3937.

Anal. Calcd for $C_{36}H_{65}N_2O_4Si_3Cl$: C, 60.93; H, 9.23; N, 3.95. Found: C, 60.80; H, 9.32; N, 4.00.

3-(9-Chlorononyloxy)-6-(4-(11-(1,1,1,3,3,5,5-heptamethyltrisiloxanyl)undecyloxy) phenyl)pyridazine (QL1-9). Yield of 70%, white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.6 Hz, 2H), 7.73 (d, J = 9.1 Hz, 1H), 6.94-7.10 (m, 3H), 4.56 (t, J = 6.5 Hz, 2H), 4.02 (t, J = 6.5 Hz, 2H), 3.54 (t, J = 6.7 Hz, 2H), 1.72-1.94 (m, 6H), 1.24-1.60 (m, 26H), 0.55 (t, J = 6.1 Hz, 2H), 0.10 (s, 9H), 0.07 (s, 6H), 0.03 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 158.6, 152.8, 126.8, 125.9, 124.7, 115.9, 113.0, 66.3, 65.7, 43.3, 31.6, 30.8, 27.8-27.0 (several overlapping peaks), 25.0, 24.2, 24.1, 21.4, 16.5, 0.0, –0.5, –1.6; LRMS (EI) *m/z* 722 (M^+, 94), 709 (21), 708 (22), 707 (38), 687 (25), 562 (39), 561 (25), 361 (38), 348 (53), 222 (22), 221 (100), 167 (36), 149 (48); HRMS (EI) *m/z* calcd for $C_{37}H_{67}N_2O_4Si_3{}^{35}Cl$ 722.4097, found 722.4093.

Anal. Calcd for $C_{37}H_{67}N_2O_4Si_3Cl$: C, 61.41; H, 9.33; N, 3.87. Found: C, 61.56; H, 9.45; N, 4.04.

General procedure for the synthesis of QL2-n. The procedure described for the synthesis of 3-(6-chlorohexyloxy)-6-(4-(12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecyloxy) phenyl)pyridazine (**QL2-6**) is representative: Under an Ar atmosphere, DIAD (202 mg, 0.20 mL, 1.0 mmol) was added to a solution of **5(6)** (160 mg, 0.52 mmol), 12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecan-1-ol (202 mg, 0.52 mmol) and triphenylphosphine (262 mg, 1.0 mmol) in dry THF (25 mL). The yellow solution was stirred overnight at room temperature, then concentrated and purified by flash chromatography on silica gel (10% EtOAc/hexanes) to give **QL2-6** (246 mg, 70%). Recrystallization from HPLC-grade acetonitrile (3×) gave a white solid with sharp phase transitions: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.8 Hz, 2H), 7.73 (d, J = 9.1 Hz, 1H), 6.98-7.01 (m, 3H), 4.56 (t, J = 6.6 Hz, 2H), 4.02 (t, J = 6.6 Hz, 2H), 3.56 (t, J = 6.7 Hz, 2H), 1.73-1.96 (m, 6H), 1.20-1.60 (m, 20H), 0.49 (t, J = 8.3 Hz, 2H), 0.05 (s, 6H), 0.03 (s, 9H), 0.00 (s, 6H), –0.25 (s, 2 H), –0.28 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 160.3, 154.7, 128.5, 127.7, 126.5, 117.7, 114.8, 68.1, 67.2, 45.0, 33.7, 32.5, 29.6-29.2 (several overlapping peaks), 28.8, 26.6, 26.0, 25.3, 24.0, 18.0, 5.8, 4.0, 2.5, 1.5, –0.4; LRMS (EI) *m/z* 676 (M^+, 67), 663 (26), 662 (25), 661 (44), 640 (23), 558 (33), 557 (51), 543 (27), 461 (24), 460 (22), 459 (64), 319 (33), 306 (37), 217 (59), 203 (21), 189 (28), 188 (40), 145 (25), 131 (39), 130 (20),

129 (100), 73 (92), 55 (25); HRMS (EI) *m/z* calcd for $C_{36}H_{65}N_2O_2Si_3{}^{35}Cl$ 676.4042, found 676.4057.

Anal. Calcd for $C_{36}H_{65}N_2O_2Si_3Cl$: C, 63.81; H, 9.67; N, 4.13. Found: C, 63.67; H, 9.50; N, 3.93.

3-(7-Chloroheptyloxy)-6-(4-(12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecyl-oxy)phenyl)pyridazine (QL2-7). Yield of 65%, white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.6 Hz, 2H), 7.73 (d, J = 9.3 Hz, 1H), 6.92-7.07 (m, 3H), 4.56 (t, J = 6.6 Hz, 2H), 4.02 (t, J = 6.6 Hz, 2H), 3.55 (t, J = 6.7 Hz, 2H), 1.74-1.97 (m, 6H), 1.18-1.59 (m, 22H), 0.49 (t, J = 8.3 Hz, 2H), 0.05 (s, 6H), 0.03 (s, 9H), 0.00 (s, 6H), –0.26 (s, 2 H), –0.28 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 158.9, 153.2, 127.1, 126.2, 125.1, 116.2, 113.4, 66.7, 65.9, 43.6, 32.2, 31.1, 28.2-27.1 (several overlapping peaks), 25.3, 24.6, 24.4, 22.5, 16.6, 4.3, 2.6, 1.0, 0.0, –1.9; LRMS (EI) *m/z* 690 (M^+, 100), 677 (24), 676 (22), 675 (42), 656 (30), 655 (22), 654 (33), 558 (42), 557 (57), 543 (25), 475 (30), 474 (27), 473 (80), 333 (41), 320 (53), 219 (24), 217 (74), 203 (20), 167 (35), 149 (51), 129 (27); HRMS (EI) *m/z* calcd for $C_{37}H_{67}N_2O_2Si_3{}^{35}Cl$ 690.4199, found 690.4193.

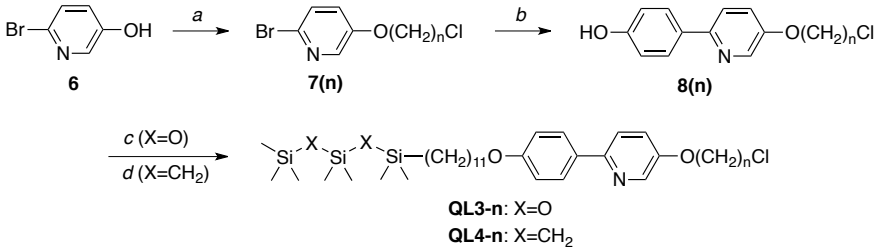
Anal. Calcd for $C_{37}H_{67}N_2O_2Si_3Cl$: C, 64.25; H, 9.76; N, 4.05; Found: C, 64.47; H, 9.60; N, 3.87.

3-(8-Chlorooctyloxy)-6-(4-(12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecyl-oxy)phenyl)pyridazine (QL2-8). Yield of 63%, white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.8 Hz, 2H), 7.73 (d, J = 9.3 Hz, 1H), 6.92-7.08 (m, 3H), 4.56 (t, J = 6.7 Hz, 2H), 4.02 (t, J = 6.6 Hz, 2H), 3.54 (t, J = 6.7 Hz, 2H), 1.72-1.95 (m, 6H), 1.19-1.57 (m, 24H), 0.49 (t, J = 7.8 Hz, 2H), 0.05 (s, 6H), 0.03 (s, 9H), 0.00 (s, 6H), –0.23 (s, 2 H), –0.25 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 158.9, 153.2, 127.1, 126.2, 125.0, 116.2, 113.4, 66.7, 66.0, 43.6, 32.2, 31.1, 28.2-27.3 (several overlapping peaks), 25.3, 24.6, 24.4, 22.5, 16.6, 4.3, 2.6, 1.0, 0.0, –1.9; LRMS (EI) *m/z* 704 (M^+, 100), 691 (25), 690 (23), 689 (41), 558 (30), 557 (46), 489 (22), 488 (21), 487 (71), 347 (33), 334 (43), 217 (42); HRMS (EI) *m/z* calcd for $C_{38}H_{69}N_2O_2Si_3{}^{35}Cl$ 704.4355, found 704.4351.

Anal. Calcd for $C_{38}H_{69}N_2O_2Si_3Cl$: C, 64.68; H, 9.86; N, 3.97; Found: C, 64.53; H, 9.70; N, 3.79.

3-(9-Chlorononyloxy)-6-(4-(12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecyl-oxy)phenyl)pyridazine (QL2-9). Yield of 57%, white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.9 Hz, 2H), 7.73 (d, J = 9.3 Hz, 1H), 6.87 - 7.09 (m, 3H), 4.55 (t, J = 6.7 Hz, 2H), 4.02 (t, J = 6.6 Hz, 2H), 3.54 (t, J = 6.7 Hz, 2H), 1.71-1.90 (m, 6H), 1.22-1.53 (m, 26H), 0.49 (t, J = 9.0 Hz , 2H), 0.05 (s, 6H), 0.03 (s, 9H), 0.00 (s, 6H), –0.22 (s, 2 H), –0.27 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 158.9, 153.2, 127.2, 126.2, 125.0, 116.2, 113.4, 66.7, 66.0, 43.7, 32.2, 31.2, 28.1-27.3 (several overlapping peaks), 25.4, 24.6, 24.5, 22.5, 16.6, 4.3, 2.6, 1.0, 0.0, –1.9; LRMS (EI) *m/z* 718 (M^+, 100), 705 (21), 704 (23), 703 (31), 558 (33), 557 (44), 502 (20), 501 (63), 361 (31), 348 (45), 217 (48), 167 (24), 149 (38); HRMS (EI) *m/z* calcd for $C_{39}H_{71}N_2O_2Si_3{}^{35}Cl$ 718.4512, found 718.4509.

Anal. Calcd for $C_{39}H_{71}N_2O_2Si_3Cl$: C, 65.08; H, 9.94; N, 3.89; Found: C, 64.96; H, 9.80; N, 3.75.



[a] $Cl(CH_2)_nOH$, DIAD, Ph_3P, THF; [b] 4-hydroxyphenylboronic acid, $Pd_2(dba)_3$, Cy_3P, aq K_3PO_4; [c] 11-(1,1,1,3,3,5,5-heptamethyltrisiloxanyl)undecan-1-ol, DIAD, Ph_3P, THF; [d] 12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecan-1-ol, DIAD, Ph_3P, THF.

General procedure for the synthesis of 7(n). The procedure described for the synthesis of 2-bromo-5-(6-chlorohexyloxy)pyridine (**7(6)**) is representative: Under an Ar atmosphere, DIAD (1.22 g, 1.20 mL, 6.0 mmol) was added to a solution of 2-bromopyridin-5-ol (**6**, 0.87 g, 5.0 mmol), 6-chloro-1-hexanol (0.84 g, 6.0 mmol) and triphenylphosphine (1.84 g, 7.0 mmol) in dry THF (30 mL). The yellow solution was stirred overnight at room temperature, then concentrated and purified by flash chromatography on silica gel (10% EtOAc/hexanes) to give **7(6)** (1.17 g, 80%) as a white solid: mp 54-56 ºC; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.02 (d, J = 3.0 Hz, 1H), 7.36 (d, J = 8.8 Hz, 1H), 7.10 (dd, J = 3.2, 8.7 Hz, 1H), 3.98 (t, J = 6.4 Hz, 2H), 3.56 (t, J = 6.7 Hz, 2H), 1.71-1.99 (m, 4H), 1.39-1.68 (m, 4H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 155.6, 138.1, 132.3, 128.6, 125.3, 69.2, 45.7, 33.1, 29.4, 27.1, 25.7; LRMS (EI) m/z 291 (M^+, 25), 175 (27), 174 (27), 173 (100), 119 (21), 117 (10), 94 (33), 83(54), 55 (68); HRMS (EI) m/z calcd for $C_{11}H_{15}NO^{35}Cl^{79}Br$ 291.0026, found 291.0017.

2-Bromo-5-(7-chloroheptyloxy)pyridine (7(7)). Yield of 78%, white solid: mp 56-57 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.02 (d, J = 3.0 Hz, 1H), 7.36 (d, J = 8.3 Hz, 1H), 7.10 (dd, J = 3.0, 8.6 Hz, 1H), 3.98 (t, J = 6.4 Hz, 2H), 3.55 (t, J = 6.7 Hz, 2H), 1.68-1.92 (m, 4H), 1.27-1.52 (m, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 155.7, 138.1, 132.2, 128.6, 125.3, 69.4, 45.8, 33.1, 29.5, 29.1, 27.3, 26.3; LRMS (EI) m/z 305 (M^+, 24), 176 (43), 175 (100), 174 (43), 173 (98), 158 (14), 156 (14), 146 (13), 144 (13), 119 (14), 117 (14), 97 (29), 84(11), 72 (11), 69 (14), 67 (10), 57 (14), 55 (83); HRMS (EI) m/z calcd for $C_{12}H_{17}NO^{35}Cl^{79}Br$ 305.0182, found 305.0193.

2-Bromo-5-(8-chlorooctyloxy)pyridine (7(8)). Yield of 75%, white solid: mp 63-65 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.02 (d, J = 3.0 Hz, 1H), 7.35 (d, J = 8.8 Hz, 1H), 7.10 (dd, J = 3.2, 8.7 Hz, 1H), 3.98 (t, J = 6.4 Hz, 2H), 3.54 (t, J = 6.8 Hz, 2H), 1.69-1.98 (m, 6H), 1.19-1.60 (m, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 155.7, 138.1, 132.2, 128.6, 125.3, 69.4, 45.9, 33.2, 29.7, 29.6, 29.3, 27.3, 26.3; LRMS (EI) m/z 319 (M^+, 27), 176 (60), 175 (99), 174 (63), 173 (100), 158 (17), 156 (17), 146 (17), 144 (14), 119 (14), 117 (15), 94 (32), 84(11), 72 (11), 69 (60), 67 (14); HRMS (EI) m/z calcd for $C_{13}H_{19}NO^{35}Cl^{79}Br$ 319.0339, found 319.0329.

2-Bromo-5-(9-chlorononyloxy)pyridine (7(9)). Yield of 80%, white solid: mp 65-67 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.02 (d, J = 2.8 Hz, 1H), 7.35 (d, J = 8.6 Hz, 1H), 7.10 (dd, J = 3.2, 8.7 Hz, 1H), 3.97 (t, J = 6.4 Hz, 2H), 3.54 (t, J = 6.7 Hz, 2H), 1.69-1.92 (m, 6H), 1.25-1.50 (m, 8H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 155.7, 138.1, 132.2, 128.6, 125.3, 69.5, 45.9, 33.2, 29.9, 29.7, 29.6, 29.3, 27.4, 26.4; LRMS (EI) m/z 333 (M^+, 26), 262 (16), 186 (11), 183 (14), 176 (72), 175 (96), 174 (74), 173 (100), 158 (17), 156 (17), 146 (13), 144 (13), 119 (19), 117 (14), 94

(30), 83 (25), 71 (11), 69 (44), 67 (13), 57 (32), 56 (11), 55 (73); HRMS (EI) *m/z* calcd for $C_{14}H_{21}NO^{35}Cl^{79}Br$ 333.0495, found 333.0506.

General procedure for the synthesis of 8(n). The procedure described for the synthesis of 5-(6-chlorohexyloxy)-2-(4-hydroxyphenyl)pyridine (**8(6)**) is representative: A 50 mL Schlenk flask was charged with **7(6)** (0.88 g, 3.0 mmol), 4-hydroxyphenylboronic acid (0.62 g, 4.5 mmol), $Pd_2(dba)_3$ (27.6 mg, 0.030 mmol) and Cy_3P (20.1 mg, 0.072 mmol), then evacuated and refilled with Ar (5×). Degassed dioxane (15 mL) and aq K_3PO_4 (1.27 M, 4.0 mL, 5.1 mmol) were added by syringe, and the flask was sealed and heated in an oil bath at 100 °C for 18 h with vigorous stirring. The mixture was then filtered through a pad of silica gel and washed with EtOAc. The filtrate was concentrated and the aqueous residue extracted with EtOAc (3×). The combined extracts were dried ($MgSO_4$), concentrated and the residue was purified by flash chromatography on silica gel (33% EtOAc/Hexanes) to give **8(6)** (0.70 g, 77%) as a white solid: 95-97 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.97 (s, 1H), 8.28 (d, J = 2.3 Hz, 1H), 7.69 (d, J = 8.3 Hz, 2H), 7.59 (d, J = 8.6 Hz, 1H), 7.30 (dd, J = 2.8, 8.6 Hz, 1H), 6.78 (d, J = 8.6 Hz, 2H), 4.03 (t, J = 6.3 Hz, 2H), 3.56 (t, J = 6.6 Hz, 2H), 1.64-1.90 (m, 4H), 1.31-1.58 (m, 4H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 157.9, 154.7, 150.5, 137.0, 131.1, 128.4, 123.4, 121.4, 116.2, 69.0, 45.7, 33.1, 29.6, 27.1, 25.8; LRMS (EI) *m/z* 305 (M^+, 36), 188 (15), 187 (100), 158 (11), 131 (20), 55 (10); HRMS (EI) *m/z* calcd for $C_{17}H_{20}NO_2{}^{35}Cl$ 305.1183, found 305.1192.

5-(7-Chloroheptyloxy)-2-(4-hydroxyphenyl)pyridine (8(7)). Yield of 68%, white solid: mp 96-98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (s, 1H), 8.30 (d, J = 3.0 Hz, 1H), 7.66 (d, J = 8.6 Hz, 2H), 7.57 (d, J = 8.8 Hz, 1H), 7.30 (dd, J = 2.7, 8.5 Hz, 1H), 6.77 (d, J = 8.8 Hz, 2H), 4.03 (t, J = 6.4 Hz, 2H), 3.56 (t, J = 6.7 Hz, 2H), 1.81 (dq, J = 6.7, 14.1 Hz, 4H), 1.31-1.63 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 154.0, 150.3, 136.1, 130.3, 128.0, 123.3, 121.2, 115.8, 68.5, 45.0, 32.5, 29.0, 28.6, 26.7, 25.8; LRMS (EI) *m/z* 319 (M^+, 44), 188 (16), 187 (100), 186 (12), 158 (14), 131 (28), 55 (20); HRMS (EI) *m/z* calcd for $C_{18}H_{22}NO_2{}^{35}Cl$ 319.1339, found 319.1328.

5-(8-Chlorooctyloxy)-2-(4-hydroxyphenyl)pyridine (8(8)). Yield of 65%, white solid: mp 92-94 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 3.0 Hz, 1H), 7.67 (d, J = 8.6 Hz, 2H), 7.57 (d, J = 8.8 Hz, 1H), 7.30 (dd, J = 2.7, 8.7 Hz, 1H), 6.78 (d, J = 8.6 Hz, 2H), 4.03 (t, J = 6.4 Hz, 2H), 3.55 (t, J = 6.8 Hz, 2H), 1.80 (dq, J = 7.3, 15.1 Hz, 4H), 1.29-1.56 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 154.1, 150.4, 136.2, 130.4, 128.1, 123.3, 121.2, 115.9, 68.6, 45.2, 32.6, 29.3, 29.2, 28.8, 26.8, 25.9; LRMS (EI) *m/z* 333 (M^+, 64), 188 (19), 187 (100), 186 (12), 158 (14), 131 (20), 55 (11); HRMS (EI) *m/z* calcd for $C_{19}H_{24}NO_2{}^{35}Cl$ 333.1496, found 333.1491.

5-(9-Chlorononyloxy)-2-(4-hydroxyphenyl)pyridine (8(9)). Yield of 70%, white solid: mp 97-99 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 3.0 Hz, 1 H), 7.66 (d, J = 8.6 Hz, 2H), 7.57 (d, J = 8.8 Hz, 1H), 7.29 (d, J = 9.6 Hz, 1H), 6.77 (d, J = 8.6 Hz, 2H), 4.03 (t, J = 6.3 Hz, 2H), 3.55 (t, J = 6.7 Hz, 2H), 1.72-1.90 (m, 4H), 1.27-1.57 (m, 10 H); ^{13}C NMR (100MHz, $CDCl_3$) δ 157.4, 154.1, 150.4, 136.2, 130.4, 128.1, 123.3, 121.2, 115.9, 68.6, 45.2, 32.6, 29.4-28.8 (several overlapping peaks), 26.9, 25.9; LRMS (EI) *m/z* 347 (M^+, 39), 187 (100), 158 (11), 131 (18), 55 (11); HRMS (EI) *m/z* calcd for $C_{20}H_{26}NO_2{}^{35}Cl$ 347.1652, found 347.1649.

General procedure for the synthesis of QL3-n. The procedure described for the synthesis of 5-(7-chloroheptyloxy)-2-(4-(11-(1,1,1,3,3,5,5-heptamethyltrisiloxanyl)undecyl)oxy)phenyl) pyridine (**QL3-7**) is representative: Under an Ar atmosphere, DIAD (244 mg, 0.24 mL, 1.2 mmol) was added to a solution of 11-(1,1,1,3,3,5,5-heptamethyltrisiloxanyl)undecan-1-ol (385 mg, 1.0 mmol), **8(7)** (320 mg, 1.0 mmol) and triphenylphosphine (393 mg, 1.5 mmol) in dry THF (25 mL). The yellow solution was stirred overnight at room temperature, then concentrated and purified by flash chromatography on silica gel (10% EtOAc/hexanes) to give **QL3-7** (451 mg, 65%). Recrystallization from HPLC-grade acetonitrile (3×) gave a white solid with sharp phase transitions: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 3.0 Hz, 1H), 7.76 (d, J = 7.3 Hz, 2H), 7.49 (d, J = 8.6 Hz, 1H), 7.16 (d, J = 12.4 Hz, 1H), 6.87 (d, J = 7.6 Hz, 2H), 3.82 - 3.99 (m, 4H), 3.43 (t, J = 6.7 Hz, 2H), 1.72 (d, J = 6.8 Hz, 6H), 1.07-1.48 (m, 22H), 0.44 ((t, J = 6.3 Hz, 2H), 0.00 (s, 9H), –0.03 (s, 6H), –0.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 153.8, 149.9, 137.2, 131.7, 127.5, 122.0, 120.0, 114.6, 68.4, 68.1, 45.1, 33.4, 32.5, 29.6, 29.4, 29.3, 29.1, 28.6, 26.8, 26.1, 25.8, 23.2, 18.3, 1.8, 1.3, 0.2; LRMS (EI) m/z 693 (M^+, 100), 678 (18), 472 (14), 319 (17), 223 (11), 222 (20), 221 (93), 207 (27), 188 (12), 187 (60), 186 (12), 73 (32), 55(16); HRMS (EI) m/z calcd for $C_{36}H_{64}NO_4Si_3{}^{35}Cl$ 693.3832, found 693.3841.

Anal. Calcd for $C_{36}H_{64}NO_4Si_3Cl$: C, 62.25; H, 9.29; N, 2.02; Found: C, 62.12; H, 9.32; N, 2.04.

5-(8-Chlorooctyloxy)-2-(4-(11-(1,1,1,3,3,5,5-heptamethyltrisiloxanyl)undecyl)oxy) phenyl)pyridine (QL3-8). Yield of 60%, white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 3.0 Hz, 1H), 7.76 (d, J = 8.6 Hz, 2H), 7.49 (d, J = 8.8 Hz, 1H), 7.13 (dd, J = 2.9, 8.7 Hz, 1H), 6.87 (d, J = 8.8 Hz, 1H), 3.87-4.00 (m, 4H), 3.45 (t, J = 6.7 Hz, 2H), 1.65-1.82 (m, 6H), 1.15-1.50 (m, 24H), 0.45 (t, J = 7.3 Hz, 2H), 0.00 (s, 9H), –0.03 (s, 6H), –0.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 153.8, 149.9, 137.2, 131.7, 127.5, 122.0, 120.0, 114.6, 77.0, 76.9, 76.7, 76.6, 68.4, 68.1, 45.1, 33.4, 32.6, 29.6-29.1 (several overlapping peaks), 28.8, 26.8, 26.0, 25.9, 23.2, 18.3, 1.8, 1.3, 0.2; LRMS (EI) m/z 707 (M^+, 100), 694 (10), 693 (11), 692 (14), 486 (12), 333 (15), 222 (16), 221 (75), 207 (15), 187 (47), 73 (14); HRMS (EI) m/z calcd for $C_{37}H_{66}NO_4Si_3{}^{35}Cl$ 707.3988, found 707.3981.

Anal. Calcd for $C_{37}H_{66}NO_4Si_3Cl$: C, 62.71; H, 9.39; N, 1.98; Found: C, 62.62; H, 9.36; N, 2.04.

5-(9-Chlorononyloxy)-2-(4-(11-(1,1,1,3,3,5,5-heptamethyltrisiloxanyl)undecyl)oxy) phenyl)pyridine (QL3-9). Yield of 63%, white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 2.8 Hz, 1H), 7.76 (d, J = 8.6 Hz, 2H), 7.49 (d, J = 8.6 Hz, 1H), 7.13 (dd, J = 2.8, 8.6 Hz, 2H), 6.87 (d, J = 8.6 Hz, 1H), 3.80-4.08 (m, 4H), 3.45 (t, J = 7.7 Hz, 2H), 1.64-1.83 (m, 6H), 1.05-1.52 (m, 26H), 0.45 (t, J = 6.6 Hz, 3H), 0.00 (s, 9H), –0.03 (s, 6H), –0.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 153.8, 149.9, 137.2, 131.7, 127.5, 122.0, 120.0, 114.6, 68.5, 68.1, 45.1, 33.4, 32.6, 29.6-28.8 (several overlapping peaks), 26.8, 26.0, 25.9, 23.2, 18.3, 1.8, 1.3, 0.2; LRMS (EI) m/z 721 (M^+, 100), 706 (14), 500 (10), 347 (13), 222 (11), 221 (53), 187 (31); HRMS (EI) m/z calcd for $C_{38}H_{68}NO_4Si_3{}^{35}Cl$ 721.4145, found 721.4133.

Anal. Calcd for $C_{38}H_{68}NO_4Si_3Cl$: C, 63.16; H, 9.48; N, 1.94; Found: C, 63.03; H, 9.40; N, 1.93.

General procedure for the synthesis of QL4-n. The procedure described for the synthesis of 5-(6-chlorohexyloxy)-2-(4-(12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecyloxy)-

phenyl)pyridine (**QL4-6**) is representative: Under an Ar atmosphere, DIAD (244 mg, 0.24 mL, 1.2 mmol) was added to a solution of **8(6)** (306 mg, 1.0 mmol), 12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecan-1-ol (466 mg, 1.0 mmol) and triphenylphosphine (393 mg, 1.5 mmol) in dry THF (25 mL). The yellow solution was stirred overnight at room temperature, then concentrated and purified by flash chromatography on silica gel (10% EtOAc/hexanes) to give **QL4-6** (406 mg, 60%). Recrystallization from HPLC-grade acetonitrile (3×) gave a white solid with sharp phase transitions: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.30 (d, J = 2.8 Hz, 1H), 7.87 (d, J = 8.8 Hz, 2H), 7.61 (d, J = 8.6 Hz, 1H), 7.23 (dd, J = 2.8, 8.6 Hz, 2H), 6.95 (d, J = 8.8 Hz, 1H), 4.04 (t, J = 6.4 Hz, 2H), 4.00 (t, J = 6.5 Hz, 2H), 3.57 (t, J = 6.7 Hz, 2H), 1.72-1.92 (m, 6H), 1.14-1.58 (m, 20H), 0.51 (t, J = 7.8 Hz, 2H), 0.06 (s, 6H), 0.03 (s, 9H), 0.00 (s, 6H), –0.25 (s, 2 H), –0.28 (s, 2 H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 160.1, 154.6, 149.7, 137.7, 132.1, 127.6, 122.2, 120.2, 114.8, 68.9, 68.7, 45.7, 34.3, 33.1, 30.3-29.8 (several overlapping peaks), 27.3, 26.6, 25.9, 24.6, 18.6, 6.2, 4.5, 2.8, 1.7, –0.1; LRMS (EI) m/z 675 (M^+, 100), 662 (17), 661 (16), 660 (29), 460 (11), 459 (13), 458 (29), 305 (18), 217 (23), 188 (10), 187 (39), 131 (11), 129 (45), 73 (37), 55 (12); HRMS (EI) m/z calcd for $C_{37}H_{66}NO_2Si_3{}^{35}Cl$ 675.4090, found 675.4103.

Anal. Calcd for $C_{37}H_{66}NO_2Si_3Cl$: C, 65.68; H, 9.83; N, 2.07; Found: C, 65.62; H, 9.86; N, 2.05.

5-(7-Chloroheptyloxy)-2-(4-(12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecyl-oxy)phenyl)pyridine (QL4-7). Yield of 58%, white solid: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.30 (d, J = 2.8 Hz, 1H), 7.87 (d, J = 8.6 Hz, 2H), 7.61 (d, J = 8.8 Hz, 1H), 7.25 (dd, J = 2.6, 8.4 Hz, 1H), 6.95 (d, J = 8.6 Hz, 2H), 3.98-4.05 (m, 4H), 3.58 (t, J = 6.7 Hz, 2H), 1.73-1.96 (m, 6H), 1.21-1.57 (m, 22H), 0.49 (t, J = 7.8 Hz, 2H), 0.05 (s, 6H), 0.03 (s, 9H), 0.00 (s, 6H), –0.23 (s, 2 H), –0.26 (s, 2 H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 160.0, 154.5, 150.0, 137.9, 132.2, 127.9, 122.3, 120.3, 115.0, 69.0, 68.7, 45.8, 34.3, 33.2, 31.2, 30.2-29.9 (several overlapping peaks), 29.7, 29.2, 27.4, 26.6, 26.4, 24.5, 18.6, 6.2, 4.4, 2.8, 1.7, –0.2; LRMS (EI) m/z 689 (M^+, 100), 676 (17), 675 (18), 674 (28), 474 (14), 473 (17), 472 (29), 332 (10), 319 (18), 217 (25), 188 (15), 187 (58), 186 (12), 131 (15), 130 (11), 129 (56), 73 (47), 55 (18); HRMS (EI) m/z calcd for $C_{38}H_{68}NO_2Si_3{}^{35}Cl$ 689.4246, found 689.4257.

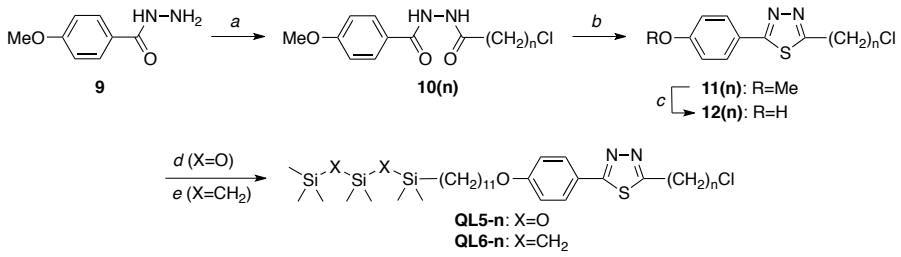
Anal. Calcd for $C_{38}H_{68}NO_2Si_3Cl$: C, 66.08; H, 9.92; N, 2.03; Found: C, 65.83; H, 9.94; N, 2.00.

5-(8-Chlorooctyloxy)-2-(4-(12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecyl-oxy)phenyl)pyridine (QL4-8). Yield of 65%, white solid: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.30 (d, J = 2.8 Hz, 1H), 7.87 (d, J = 8.8 Hz, 2H), 7.62 (d, J = 8.8 Hz, 1H), 7.25 (m, 1H), 6.95 (d, J = 8.8 Hz, 2H), 4.03 (t, J = 7.6 Hz, 2H), 3.96-4.02 (m, 2H), 1.70-1.95 (m, 6H), 1.18-1.57 (m, 24H), 0.50 (t, J = 7.8 Hz, 2H), 0.08 (s, 6H), 0.03 (s, 9H), 0.00 (s, 6H), –0.23 (s, 2 H), –0.27 (s, 2 H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 160.0, 154.5, 150.0, 137.9, 132.2, 127.9, 122.3, 120.2, 115.0, 69.1, 68.7, 45.9, 34.3, 33.2, 30.2-29.7 (several overlapping peaks), 29.4, 27.4, 26.6, 26.4, 24.6, 18.6, 6.2, 4.4, 2.8, 1.7, –0.2; LRMS (EI) m/z 703 (M^+, 100), 690 (16), 689 (17), 688 (25), 488 (10), 486 (24), 333 (12), 217 (16), 187 (24), 129 (27), 73 (19); HRMS (EI) m/z calcd for $C_{39}H_{70}NO_2Si_3{}^{35}Cl$ 703.4403, found 703.4410.

Anal. Calcd for $C_{39}H_{70}NO_2Si_3Cl$: C, 66.47; H, 10.01; N, 1.99; Found: C, 66.62; H, 9.96; N, 1.97.

5-(9-Chlorononyloxy)-2-(4-(12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecyl-oxy)phenyl)pyridine (QL4-9). Yield of 60%, white solid: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.30 (d, J = 3.0 Hz, 1H), 7.87 (d, J = 8.8 Hz, 2H), 7.61 (d, J = 8.6 Hz, 1H), 7.23 (dd, J = 3.0, 8.8 Hz, 1H), 6.95 (d, J = 9.1 Hz, 2H), 4.03 (t, J = 7.5 Hz, 2H), 3.98 (t, J = 8.3 Hz, 2H), 3.55 (t, J = 6.8 Hz, 2H), 1.69-1.89 (m, 6H), 1.21-1.56 (m, 26H), 0.50 (t, J = 7.8 Hz, 2H), 0.05 (s, 6H), 0.03 (s, 9H), 0.00 (s, 6H), –0.23 (s, 2 H), –0.28 (s, 2 H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 160.0, 154.5, 150.0, 137.9, 132.2, 127.9, 122.3, 120.2, 115.0, 69.1, 68.7, 45.9, 34.3, 33.3, 30.2, 30.0-29.8 (several overlapping peaks), 29.4, 27.4, 26.6, 26.5, 24.5, 18.6, 6.2, 4.4, 2.8, 1.7, –0.2; LRMS (EI) m/z 717 (M^+, 100), 705 (10), 704 (18), 703 (20), 702 (25), 502 (11), 501 (12), 500 (28), 217 (19), 187 (36), 129 (39), 73 (28); HRMS (EI) m/z calcd for $C_{40}H_{72}NO_2Si_3{}^{35}Cl$ 717.4559, found 717.4530.

Anal. Calcd for $C_{40}H_{72}NO_2Si_3Cl$: C, 66.85; H, 10.10; N, 1.95; Found: C, 66.72; H, 10.03; N, 1.94.



[a] $Cl(CH_2)_nCOCl$, Na_2CO_3, CH_2Cl_2; [b] Lawesson's reagent, toluene; [c] BBr_3, CH_2Cl_2; [d] 11-(1,1,1,3,3,5,5-heptamethyl-trisiloxanyl)undecan-1-ol, DIAD, Ph_3P, THF; [e] 12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecan-1-ol, DIAD, Ph_3P, THF.

General procedure for the synthesis of 10(n). The procedure described for the synthesis of N'-(7-chloroheptanoyl)-4-methoxybenzohydrazide (**10(6)**) is representative: 7-chloroheptanoyl chloride (1.65 g, 9 mmol) was added dropwise to a solution of 4-methoxybenzohydrazide (**9**, 1.4 g, 8.1 mmol) and Na_2CO_3 (3.4 g) in CH_2Cl_2 (60 mL) at 0 °C. The reaction mixture was stirred for 1h, and then allowed to warm to room temperature. After 18 h, the mixture was filtered and the solid residue washed with CH_2Cl_2 (100 mL) and EtOAc (100 mL). The filtrate was concentrated and the residue purified by flash chromatography on silica gel (3:1 CH_2Cl_2/EtOAc) to give **10(6)** (1.2 g, 48%) as a white solid: mp 115-116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (d, J = 4.5 Hz, 1H), 9.74 (d, J = 4.3 Hz, 1H), 7.82 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 3.82 (s, 3H), 3.48 (t, J = 6.7 Hz, 2H), 2.28 (t, J = 7.6 Hz, 2H), 1.54-1.81 (m, 4H), 1.22-1.48 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 164.7, 162.8, 129.3, 123.4, 113.8, 55.4, 44.9, 33.9, 32.3, 28.3, 26.5, 25.2; LRMS (EI) m/z 312 (M^+, 17), 166 (16), 136 (80), 135 (100), 107 (27), 92 (21), 77 (29); HRMS (EI) m/z calcd for $C_{15}H_{21}N_2O_3{}^{35}Cl$ 312.1241, found 312.1233.

N'-(8-Chlorooctanoyl)-4-methoxybenzohydrazide (10(7)). Yield of 45%, white solid: mp 126-128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.86 (d, J = 4.5 Hz, 1H), 9.62 (d, J = 4.5 Hz, 1H), 7.82 (d, J = 7.8 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 3.83 (s, 3H), 3.50 (t, J = 6.7 Hz, 2H), 2.29 (t, J = 7.5 Hz, 2H), 1.53-1.81 (m, 4H), 1.16-1.46 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 164.5, 162.8, 129.3, 123.5, 113.8, 55.4, 45.0, 34.0, 32.5, 28.9, 28.5, 26.6, 25.3; LRMS (EI) m/z 326 (M^+, 13), 166 (12), 136 (10), 135 (100); HRMS (EI) m/z calcd for $C_{16}H_{23}N_2O_3{}^{35}Cl$ 326.1397, found 326.1389.

N'-(9-Chlorononanoyl)-4-methoxybenzohydrazide (10(8)). Yield of 52%, white solid: mp 107-109 °C; ^{1}H NMR (400 MHz ,$CDCl_3$) δ 9.83 (d, J = 4.8 Hz, 1H), 9.58 (d, J = 4.8 Hz, 1H), 7.81 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 3.83 (s, 3H), 3.51 (t, J = 6.7 Hz, 2H), 2.29 (t, J = 7.6 Hz, 2H), 1.54-1.73 (m, 4H), 1.27-1.44 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 164.5, 162.8, 129.3, 123.6, 113.8, 55.4, 45.1, 34.1, 32.6, 29.1, 29.0, 28.7, 26.8, 25.4; LRMS (EI) *m/z* 340 (M^+, 17), 322 (12), 166 (41), 135 (100); HRMS (EI) calcd for $C_{17}H_{25}N_2O_3{}^{35}Cl$ 340.1554, found 340.1549.

N'-(10-Chlorodecanoyl)-4-methoxybenzohydrazide (10(9)). Yield of 50%, white solid, mp 129-130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (d, J = 4.0 Hz, 1H), 9.55 (d, J = 4.2 Hz, 1H), 7.81 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 3.83 (s, 3H), 3.52 (t, J = 6.7 Hz, 2H), 2.29 (t, J = 7.5 Hz, 2H), 1.54-2.03 (m, 4H), 1.13-1.54 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 164.4, 162.8, 129.3, 123.6, 113.9, 55.4, 45.2, 34.2, 32.6, 29.3, 29.2, 29.1, 28.8, 26.9, 25.5; LRMS (EI) *m/z* 354 (M^+, 9), 166 (17), 136 (12), 135 (100); HRMS (EI) *m/z* calcd for $C_{18}H_{27}N_2O_3{}^{35}Cl$ 354.1710, found 354.1701.

General procedure for the synthesis of 11(n). The procedure described for the synthesis of 2-(6-chlorohexyl)-5-(4-methoxyphenyl)-1,3,4-thiadiazole **(11(6))** is representative: Under a N_2 atmosphere, a mixture of **10(6)** (1.0 g, 3.2 mmol) and Lawesson's reagent (1.5 g, 3.7 mmol) in toluene (80 mL) was heated to reflux and stirred for 2 h. After cooling to room temperature, the mixture was poured into water (60 mL) and extracted with $CHCl_3$ (3×30 mL). The combined extracts were washed with water, dried ($MgSO_4$), concentrated and the crude product was purified by flash chromatography on silica gel (9:1 CH_2Cl_2/EtOAc) to give **11(6)** (0.60 g, 60%) as a white solid: mp 72-73 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.6 Hz, 2H), 6.98 (d, J = 8.6 Hz, 2H), 3.87 (s, 3H), 3.54 (t, J = 6.6 Hz, 2H), 3.12 (t, J = 7.6 Hz, 2H), 1.69-1.94 (m, 4H), 1.39-1.59 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 168.1, 161.7, 129.3, 123.0, 114.4, 55.4, 44.9, 32.3, 30.0, 29.8, 28.2, 26.4; LRMS (EI) *m/z* 310 (M^+, 30), 276 (22), 275 (75), 261 (21), 220 (24), 219 (59), 207 (45), 206 (100), 151 (56), 150 (21), 134 (39), 133 (43), 122 (25), 108 (21), 90 (20); HRMS (EI) *m/z* calcd for $C_{15}H_{19}N_2OS^{35}Cl$ 310.0907, found 310.0903.

2-(7-Chloroheptyl)-5-(4-methoxyphenyl)-1,3,4-thiadiazole (11(7)). Yield of 58%, white solid: mp 75-76 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.8 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H), 3.53 (t, J = 6.6 Hz, 2H), 3.13 (t, J = 7.6 Hz, 2H), 1.85-1.75 (m, 4H), 1.32-1.56 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 168.5, 162.0, 129.5, 122.5, 114.6, 55.5, 45.1, 32.5, 30.0, 29.9, 28.8, 28.5, 26.7; LRMS (EI) *m/z* 324 (M^+, 14), 290 (40), 261 (13), 220 (15), 219 (48), 207 (18), 206 (100), 151 (34), 134 (21), 133 (22), 122 (12); HRMS (EI) *m/z* calcd for $C_{16}H_{21}N_2OS^{35}Cl$ 324.1063, found 324.1057.

2-(8-Chlorooctyl)-5-(4-methoxyphenyl)-1,3,4-thiadiazole (11(8)). Yield of 60%, white solid: mp 70-71 °C; ^{1}H NMR (400 MHz ,$CDCl_3$) δ 7.88 (d, J = 8.8 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H), 3.53 (t, J = 6.7 Hz, 2H), 3.11 (t, J = 7.6 Hz, 2H), 1.67-2.00 (m, 4H), 1.22-1.57 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 168.1, 161.7, 129.4, 123.1, 114.5, 55.5, 45.1, 32.6, 30.2, 30.0, 29.0, 28.9, 28.7, 26.8; LRMS (EI) *m/z* 338 (M^+, 32), 303 (14), 219 (40), 206 (100); HRMS (EI) calcd for $C_{17}H_{23}N_2OS^{35}Cl$ 338.1220, found 338.1227.

2-(9-Chlorononyl)-5-(4-methoxyphenyl)-1,3,4-thiadiazole (11(9)). Yield of 57%, white solid: mp 79-81 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.8 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H), 3.53 (t, J = 6.7 Hz, 2H), 3.11 (t, J = 7.7 Hz, 2H), 1.66-1.99 (m, 4H), 1.16-1.55 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 168.1, 161.7, 129.4, 123.1, 114.5, 55.5, 45.2, 32.6, 30.2, 30.0, 29.3, 29.1, 28.9, 28.8, 26.9; LRMS (EI) *m/z* 352 (M^+, 41), 317 (28), 261 (20), 220 (21), 219 (67), 207 (23), 206 (100), 151 (25), 134 (21), 133 (22); HRMS (EI) *m/z* calcd for $C_{18}H_{25}N_2OS^{35}Cl$ 352.1376, found 352.1368.

General procedure for the synthesis of 12(n). The procedure described for the synthesis of 2-(6-chlorohexyl)-5-(4-hydroxyphenyl)-1,3,4-thiadiazole **(12(6))** is representative: A solution of BBr_3 in CH_2Cl_2 (1.0 M, 8.35 mL, 8.35 mmol) was added to a solution of **11(6)** (0.52 g, 1.67 mmol) in CH_2Cl_2 (30 mL) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 3 h, then poured into 10% aq HCl and stirred for another 30 min. The organic and aqueous layers were separated and the aqueous layer was extracted with Et_2O (4×30 mL). The combined organic layers were dried ($MgSO_4$), concentrated, and the residue was purified by flash chromatography on silica gel (2:1 hexane/EtOAc) to give **12(6)** (0.45 g, 90%) as a white solid: mp 82-84 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.6 Hz, 2H), 7.09 (d, J = 8.6 Hz, 2H), 3.52 (t, J = 6.6 Hz, 2H), 3.13 (t, J = 7.6 Hz, 2H), 1.66-1.96 (m, 4H), 1.38-1.61 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 169.1, 159.8, 129.6, 121.5, 116.5, 44.9, 32.3, 29.9, 29.7, 28.2, 26.4; LRMS (EI) *m/z* 296 (M^+, 23), 261 (72), 247 (20), 206 (23), 205 (59), 193 (44), 192 (100), 137 (57), 120 (41), 119 (50), 65 (30); HRMS (EI) *m/z* calcd for $C_{14}H_{17}N_2OS^{35}Cl$ 296.0750, found 296.0743.

2-(7-Chloroheptyl)-5-(4-hydroxyphenyl)-1,3,4-thiadiazole (12(7)). Yield of 87%, white solid: mp 85-86 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (s, 1H), 7.80 (d, J = 8.6 Hz, 2H), 7.09 (d, J = 7.3 Hz, 2H), 3.51 (t, J = 6.7 Hz, 2H), 3.12 (t, J = 7.5 Hz, 2H), 1.66-2.03 (m, 4H), 1.44-1.40 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 169.2, 159.9, 129.6, 121.6, 116.6, 45.1, 32.5, 30.0, 29.9, 28.8, 28.5, 26.7; LRMS (EI) *m/z* 310 (M^+, 11), 275 (31), 205 (35), 192 (100); HRMS (EI) *m/z* calcd for $C_{15}H_{19}N_2OS^{35}Cl$ 310.0907, found 310.0906.

2-(8-Chlorooctyl)-5-(4-hydroxyphenyl)-1,3,4-thiadiazole (12(8)). Yield of 87%, white solid: mp 77-79 °C; ^{1}H NMR (400 MHz ,$CDCl_3$) δ 8.95 (s, 1H), 7.81 (d, J = 8.6 Hz, 2H), 7.10 (d, J = 8.6 Hz, 2H), 3.52 (t, J = 6.7 Hz, 2H), 3.12 (t, J = 7.6 Hz, 2H), 1.63-1.92 (m, 4H), 1.16-1.53 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 166.6, 157.4, 127.1, 119.1, 114.1, 42.6, 30.1, 27.6, 27.5, 26.5, 26.4, 26.2, 24.3; LRMS (EI) *m/z* 324 (M^+, 13), 289 (13), 247 (11), 206 (11), 205 (49), 192 (100); HRMS (EI) calcd for $C_{16}H_{21}N_2OS^{35}Cl$ 324.1063, found 324.1053.

2-(9-chlorononyl)-5-(4-hydroxyphenyl)-1,3,4-thiadiazole (12(9)). Yield of 89%, white solid: mp 86-87 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.6 Hz, 2H), 7.09 (d, J = 8.6 Hz, 2H), 3.52 (t, J = 6.7 Hz, 2H), 3.12 (t, J = 7.6 Hz, 2H), 1.65-2.04 (m, 4H), 1.12-1.65 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 169.2, 160.0, 129.6, 121.5, 116.6, 45.2, 32.6, 30.1, 30.0, 29.2, 29.1, 28.9, 28.8, 26.8; LRMS (EI) *m/z* 338 (M^+, 30), 303 (30), 261 (20), 247 (25), 206 (25), 205 (75), 193 (27), 192 (100), 137 (40), 120 930), 119 (30), 55 (22); HRMS (EI) *m/z* calcd for $C_{17}H_{23}N_2OS^{35}Cl$ 338.1220, found 338.1209.

General procedure for the synthesis of QL5-n. The procedure described for the synthesis of 2-(6-chlorohexyl)-5-(4-(11-(1,1,1,3,3,5,5-heptamethyltrisiloxanyl)undecyloxy)phenyl)-1,3,4-thiadiazole **(QL5-6)** is representative: Under an Ar atmosphere, DIAD (244 mg, 0.24 mL, 1.2 mmol) was added to a solution of 11-(1,1,1,3,3,5,5-heptamethyltrisiloxanyl)undecan-1-ol (385 mg, 1.0 mmol), **12(6)** (300 mg, 1.0 mmol) and triphenylphosphine (393 mg, 1.5 mmol) in dry THF (25 mL). The yellow solution was stirred overnight at room temperature, then concentrated and purified by flash chromatography on silica gel (10% EtOAc/hexanes) to give **QL5-6** (436 mg, 65%). Recrystallization from HPLC-grade acetonitrile (3×) gave a white solid with sharp phase transitions: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.6 Hz, 2H), 6.96 (d, J = 8.6 Hz, 2H), 4.01 (t, J = 6.6 Hz, 2H), 3.54 (t, J = 6.7 Hz, 2H), 3.12 (t, J = 7.6 Hz, 2H), 1.88-1.78 (m, 6H), 1.17-1.62 (m, 20H), 0.53 (t, J = 7.2 Hz, 2H), 0.09 (s, 9H), 0.06 (s, 6H), 0.03 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 168.2, 161.3, 129.3, 122.7, 114.9, 68.2, 44.9, 33.4, 32.3, 30.0, 29.8-29.4 (several overlapping peaks), 29.1, 28.2, 26.5, 26.0, 23.2, 18.3, 1.8, 1.3, 0.2; LRMS (EI) m/z 670 (M^+, 41), 657 (18), 656 (14), 655 (38), 640 (12), 636 (13), 635 (25), 529 (16), 516 (20), 309 (23), 298 (12), 296 (38), 223 (12), 222 (24), 221(100); HRMS (EI) m/z calcd for $C_{32}H_{59}N_2O_3SSi_3{}^{35}Cl$ 670.3243, found 670.3256.

Anal. Calcd for $C_{32}H_{59}N_2O_3SSi_3Cl$: C, 57.23; H, 8.85; N, 4.17; S, 4.77. Found: C, 57.36; H, 8.98; N, 4.13; S, 4.64.

2-(7-Chloroheptyl)-5-(4-(11-(1,1,1,3,3,5,5-heptamethyltrisiloxanyl)undecyloxy)phenyl)-1,3,4-thiadiazole (QL5-7). Yield of 60%, white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 7.8 Hz, 2H), 6.96 (d, J = 8.1 Hz, 2H), 4.01 (t, J = 6.2 Hz, 2H), 3.53 (t, J = 6.4 Hz, 2H), 3.11 (t, J = 7.3 Hz, 2H), 1.69-2.01 (m, 6H), 1.17-1.59 (m, 22H), 0.48 (t, J = 7.1 Hz, 2H), 0.09 (s, 9H), 0.06 (s, 6H), 0.02 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 166.4, 159.5, 127.5, 121.0, 113.1, 66.5, 43.2, 31.6, 30.7, 28.3, 28.1, 27.8-27.4 (several overlapping peaks), 27.0, 26.7, 24.9, 24.2, 21.4, 16.5, 0.0, –0.5, –1.6; LRMS (EI) m/z 684 (M^+, 52), 671 (36), 670 (33), 669 (74), 649 (22), 543 (21), 530 (21), 323 (28), 310 (44), 222 (21), 221(100); HRMS (EI) m/z calcd for $C_{33}H_{61}N_2O_3SSi_3{}^{35}Cl$ 684.3399, found 684.3393.

Anal. Calcd for $C_{33}H_{61}Cl\,N_2O_3SSi_3$: C, 57.81; H, 8.97; N, 4.09; S, 4.68. Found: C, 57.76; H, 8.94; N, 4.12; S, 4.54.

2-(8-Chlorooctyl)-5-(4-(11-(1,1,3,3,5,5,5-heptamethyltrisiloxanyl)undecyloxy)phenyl) 1,3,4-thiadiazole (QL5-8). Yield of 58%, white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.8 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 4.01 (t, J = 6.6 Hz, 2H), 3.53 (t, J = 6.8 Hz, 2H), 3.11 (t, J = 7.6 Hz, 2H), 1.69-1.92 (m, 6H), 1.13-1.56 (m, 24H), 0.54 (t, J = 7.5 Hz, 2H), 0.09 (s, 9H), 0.07 (s, 6H), 0.03 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 166.4, 159.5, 127.5, 121.0, 113.1, 66.4, 43.3, 31.6, 30.8, 28.3, 28.2, 27.8-27.6 (several overlapping peaks), 27.4, 27.2, 27.0, 26.9, 25.0, 24.2, 21.4, 16.5, 0.0, –0.5, –1.6; LRMS (EI) m/z 698 (M^+, 14), 683 (12), 324 (13), 223 (13), 222 (20), 221 (100), 207 (16), 205 (10), 73 (23); HRMS (EI) calcd for $C_{34}H_{63}N_2O_3Si_3S^{35}Cl$ 698.3556, found 698.3561.

Anal. Calcd for $C_{34}H_{63}N_2O_3Si_3SCl$: C, 58.37; H, 9.08; N, 4.00; S, 4.58. Found: C, 58.48; H, 9.23; N, 4.14; S, 4.74.

2-(9-Chlorononyl)-5-(4-(11-(1,1,1,3,3,5,5-heptamethyltrisiloxanyl)undecyloxy)phenyl)-1,3,4-thiadiazole (QL5-9): yield of 67%, white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 7.8 Hz, 2H), 6.96 (d, J = 8.1 Hz, 2H), 4.01 (t, J = 6.1 Hz, 2 H), 3.53 (t, J = 6.6 Hz, 2H), 3.11 (t, J

= 7.4 Hz, 2H), 2.00-1.63 (m, 6H), 1.21-1.58 (m, 26H), 0.53 (t, *J* = 6.3 Hz, 2H), 0.09 (s, 9H), 0.06 (s, 6H), 0.03 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 166.4, 159.5, 127.5, 121.0, 113.1, 66.5, 43.3, 31.7, 30.8, 28.4, 28.2, 27.8-27.0 (several overlapping peaks), 25.0, 24.2, 21.4, 16.5, 0.0, –0.5, –1.6; LRMS (EI) *m/z* 712 (M^+, 100), 699 (19), 698 (17), 697 (38), 682 (13), 677 (11), 676 (12), 571 (12), 558 (17), 478 (16), 351 (15), 338 (25), 223 (12), 222 (17), 221(79); HRMS (EI) *m/z* calcd for $C_{35}H_{65}N_2O_3SSi_3{}^{35}Cl$ 712.3712, found 712.3723.

Anal. Calcd for $C_{35}H_{65}N_2O_3SSi_3Cl$: C, 58.90; H, 9.18; N, 3.93; S, 4.49. Found: C, 58.76; H, 9.08; N, 4.03; S, 4.65.

General procedure for the synthesis of QL6-n. The procedure described for the synthesis of 2-(6-chlorohexyl)-5-(4-(12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecyloxy)-phenyl)-1,3,4-thiadiazole (**QL6-6)** is representative: Under an Ar atmosphere, DIAD (244 mg, 0.24 mL, 1.2 mmol) was added to a solution of **12(6)** (300 mg, 1.0 mmol), 12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecan-1-ol (466 mg, 1.0 mmol) and triphenylphosphine (393 mg, 1.5 mmol) in dry THF (25 mL). The yellow solution was stirred overnight at room temperature, then concentrated and purified by flash chromatography on silica gel (10% EtOAc/hexanes) to give **QL6-6** (470 mg, 70%). Recrystallization from HPLC-grade acetonitrile (3×) gave a white solid with sharp phase transitions: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.6 Hz, 2H), 4.01 (t, *J* = 6.6 Hz, 2H), 3.54 (t, *J* = 6.7 Hz, 2H), 3.13 (t, *J* = 7.6 Hz, 2H), 1.90-1.76 (m, 6H), 1.16-1.68 (m, 20H), 0.49 (t, *J* = 9.0 Hz , 2H), 0.05 (s, 6H), 0.03 (s, 9H), 0.00 (s, 6H), –0.25 (s, 2 H), –0.29 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 168.2, 161.3, 129.3, 122.7, 114.9, 68.2, 44.9, 33.7, 32.3, 30.0, 29.8, 29.4-29.1(several overlapping peaks), 28.2, 26.5, 26.0, 24.0, 18.0, 5.8, 4.0, 2.5, 1.5, –0.4; LRMS (EI) *m/z* 666 (M^+, 91), 654 (26), 653 (63), 652 (54), 651 (100), 638 (27), 637 (26), 636 (37), 632 (24), 631 (39), 630 (32), 581 (30), 580 (24), 579 (45), 527 (27), 526 (25), 525 (51), 514 (50), 513 (39), 512 (95), 510 (20), 509 (29), 508 (23), 507 (61), 474 (22), 449 (25), 296 (30), 217 (43); HRMS (EI) *m/z* calcd for $C_{34}H_{63}N_2OSSi_3{}^{35}Cl$ 666.3657, found 666.3646.

Anal. Calcd for $C_{34}H_{63}N_2OSSi_3Cl$: C, 61.16; H, 9.51; N, 4.20; S, 4.80. Found: C, 61.20; H, 9.44; N, 4.10; S, 4.76.

2-(7-Chloroheptyl)-5-(4-(12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecyloxy) phenyl)-1,3,4-thiadiazole (QL6-7): yield of 50%, white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 4.01 (t, *J* = 6.6 Hz, 2H), 3.54 (t, *J* = 6.7 Hz, 2H), 3.12 (t, *J* = 7.6 Hz, 2H), 1.72-1.90 (m, 6H), 1.14-1.56 (m, 22H), 0.49 (t, *J* = 8.6 Hz, 2H), 0.05 (s, 6H), 0.03 (s, 9H), 0.00 (s, 6H), –0.25 (s, 2 H), –0.29 (s, 2 H);^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 168.2, 161.3, 129.3, 122.8, 114.9, 68.2, 45.0, 33.7, 32.5, 30.1, 29.9, 29.6, 29.4-29.1 (several overlapping peaks), 28.8, 28.5, 26.7, 26.0, 24.0, 18.0, 5.8, 4.0, 2.5, 1.5, –0.4; LRMS (EI) *m/z* 680 (M^+, 34), 667 (42), 666 (43), 665 (72), 593 (29), 539 (32), 528 (23), 526 (42), 521 (32), 463 (31), 217 (59), 203 (24), 131 (23), 129 (100), 73 (65); HRMS (EI) *m/z* calcd for $C_{35}H_{65}N_2OSSi_3{}^{35}Cl$ 680.3814, found 680.3831.

Anal. Calcd for $C_{35}H_{65}N_2OSSi_3Cl$: C, 61.67; H, 9.61; N, 4.11; S, 4.70. Found: C, 61.48; H, 9.54; N, 4.08; S, 4.67.

2-(8-Chlorooctyl)-5-(4-(12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecyloxy) phenyl)-1,3,4-thiadiazole (QL6-8): yield of 62%, white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 4.01 (t, *J* = 6.6 Hz, 2H), 3.53 (t, *J* = 6.7 Hz,

2H), 3.11 (t, J = 7.6 Hz, 2H), 1.69-1.90 (m, 6H), 1.15-1.54 (m, 24H), 0.49 (t, J = 8.3 Hz, 2H), 0.05 (s, 6H), 0.03 (s, 9H), 0.00 (s, 6H), –0.25 (s, 2 H), –0.29 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 168.2, 161.3, 129.3, 122.8, 114.9, 68.2, 45.1, 33.7, 32.6, 30.1, 30.0, 29.6, 29.4-29.1 (several overlapping peaks), 29.0, 28.8, 28.7, 26.8, 26.0, 24.0, 18.0, 5.8, 4.0, 2.5, 1.5, –0.4; LRMS (EI) m/z 694 (M^+, 91), 682 (28), 681 (65), 680 (63), 679 (100), 666 (23), 665 (26), 664 (32), 609 (31), 608 (20), 607 (43), 555 (25), 554 (26), 553 (53), 542 (43), 541 (37), 540 (76), 537 (27), 536 (22), 535 (55), 477 (30), 337 (22), 324 (32), 217 (38), 129 (22); HRMS (EI) m/z calcd for $C_{36}H_{67}N_2OSSi_3{}^{35}Cl$ 694.3971, found 694.3959.

Anal. Calcd for $C_{36}H_{67}N_2OSSi_3Cl$: C, 62.15; H, 9.71; N, 4.03; S, 4.61. Found: C, 62.17; H, 9.74; N, 4.00; S, 4.63.

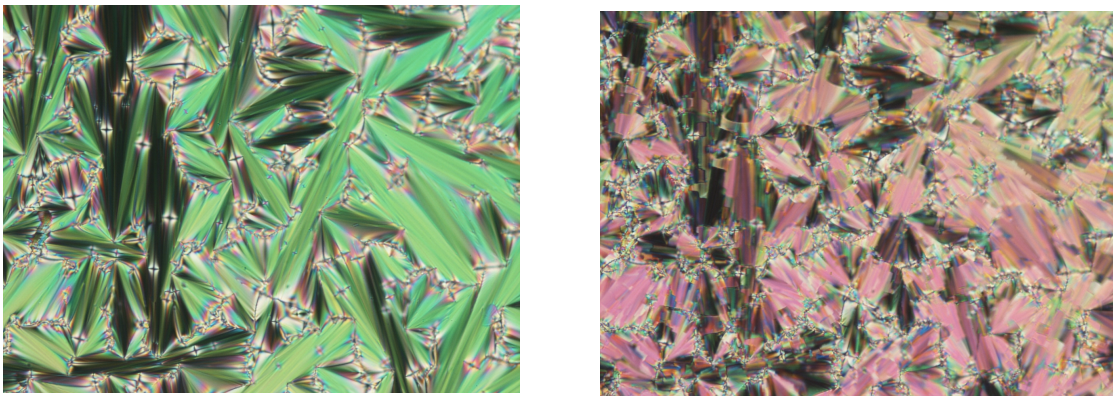


Fig S1. Polarized photomicrographs of compound **QL1-8** at 87 °C in the SmA phase (left) and at 73 °C in the SmC phase (right).

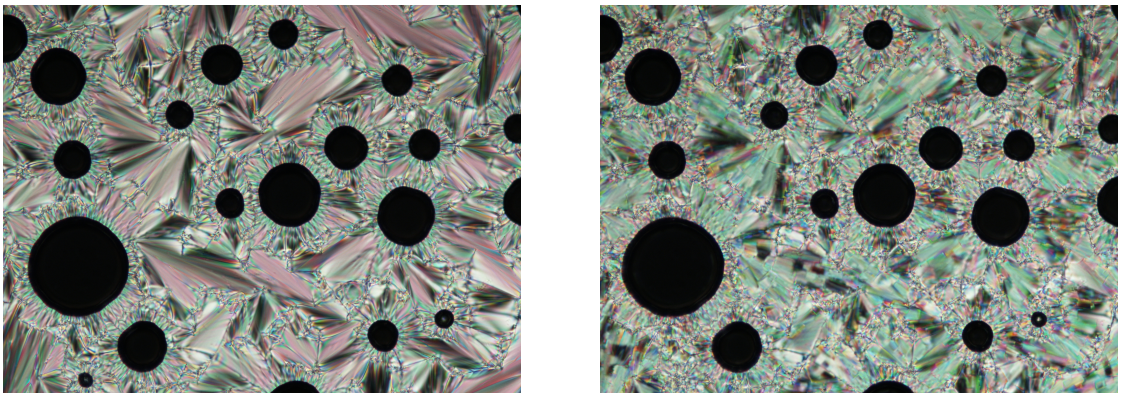


Fig S2. Polarized photomicrographs of compound **QL2-8** at 78 °C in the SmA phase (left) and at 74 °C in the SmC phase (right).

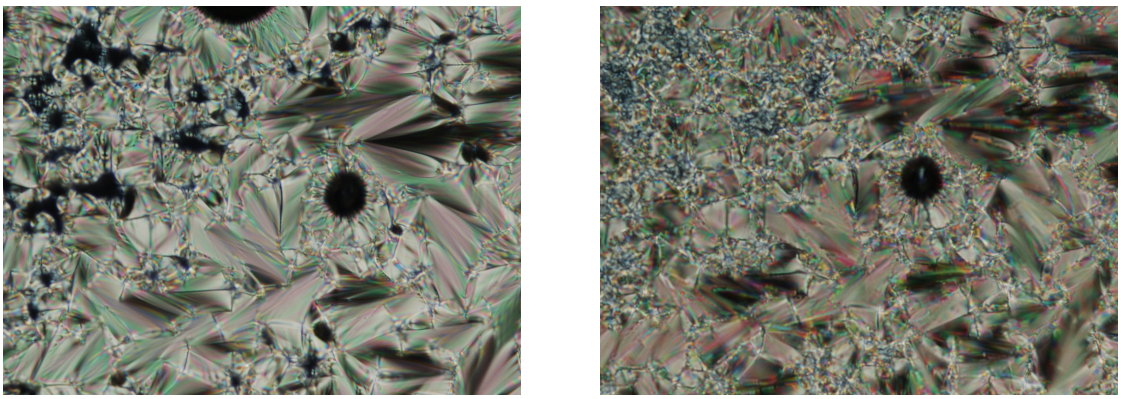


Fig S3. Polarized photomicrographs of compound **QL3-8** at 95 °C in the SmA phase (left) and at 85 °C in the SmC phase (right).

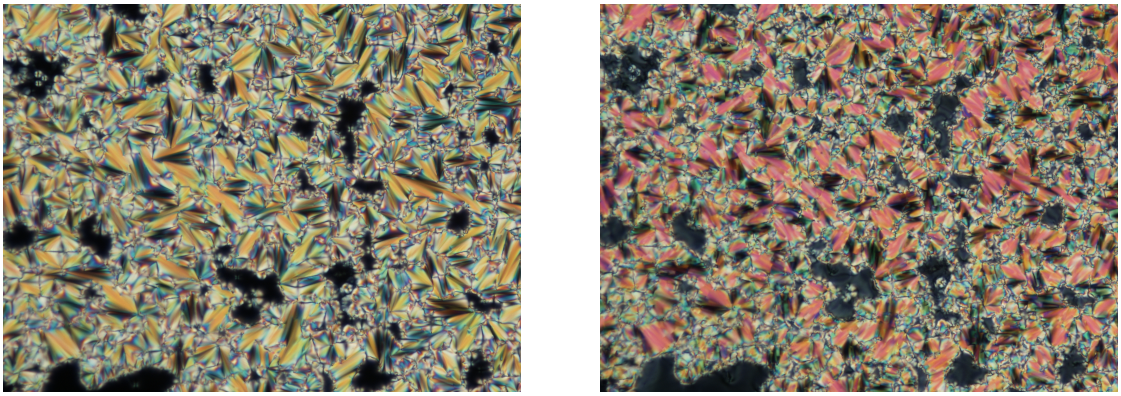


Fig S4. Polarized photomicrographs of compound **QL4-8** at 89 °C in the SmA phase (left) and at 83 °C in the SmC phase (right).

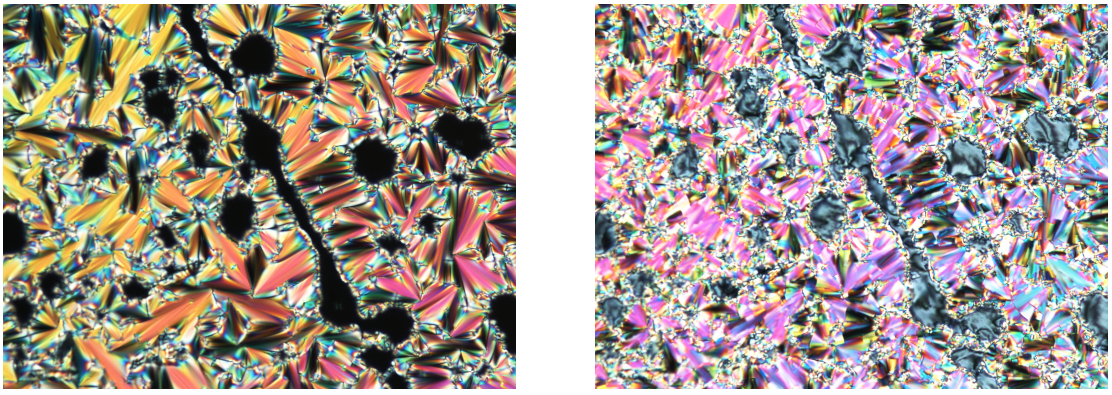


Fig S5. Polarized photomicrographs of compound **QL5-8** at 74 °C in the SmA phase (left) and at 71 °C in the SmC phase (right).

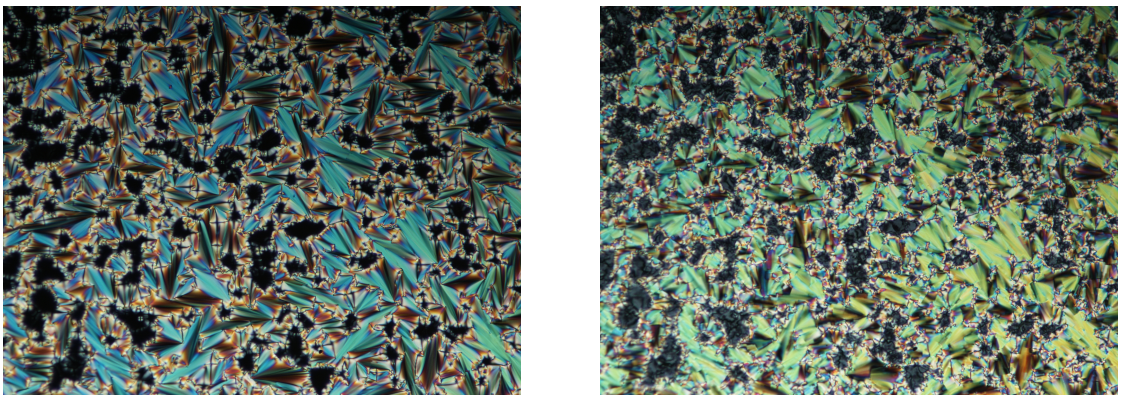


Fig S6. Polarized photomicrographs of compound **QL6-8** at 65 °C in the SmA phase (left) and at 67 °C in the SmC phase (right).

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