Electronic Supplementary Information for:

Design of liquid crystals with 'de Vries-like' properties: Carbosilane-terminated 5-phenylpyrimidine mesogens suitable for chevron-free FLC formulations.

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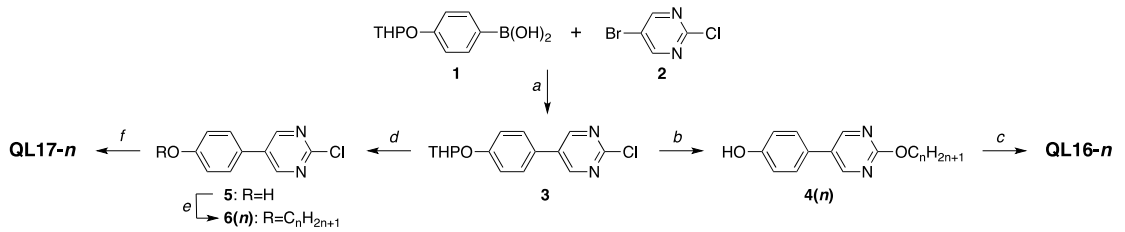
EXPERIMENTAL

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-resolution 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}, 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 analyses 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**. Chemicals were obtained from commercial sources unless otherwise noted. 12,12,14,14,16,16-Hexamethyl-12,14,16-trisilaheptadecan-1-ol, 1-bromo-12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecane, 2,2,4,4,6-pentamethyl-2,4,6-trisilaheptane and 5-(4-butyloxyphenyl)-2-chloropyrimidine **6(4)** were prepared according to literature procedures and shown to have the expected physical and spectral properties.[1-3]



Scheme 1. *Reagents and conditions*: (a) $Pd_2(dba)_3$, Cy_3P, K_3PO_4, 1,4-dioxane, 76%; (b) (i) $C_nH_{2n+1}OH$, NaH, THF; (ii) H_3O^+, 70-80%; (c) 1-bromo-12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecane, Cs_2CO_3, acetone, 85-95%; (d) TsOH, 1:1 CH_2Cl_2/EtOH, 99%; (e) $C_nH_{2n+1}Br$, Cs_2CO_3, acetone, 75-90%; (f) 12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecan-1-ol, NaH, THF, 60-70%.

2-Chloro-5-[4-(tetrahydro-2H-pyran-2-yloxy)phenyl]pyrimidine (3). 5-Bromo-2-chloropyrimidine (2.02 g, 10.45 mmol), 4-(tetrahydro-2H-pyran-2-yloxy)phenylboronic acid (3.48 g, 15.67 mmol), $Pd_2(dba)_3$ (0.092 g, 0.10 mmol), tricyclohexylphosphine (0.073 g, 0.26 mmol) and K_3PO_4 (2.22 g, 15.67 mmol) were purged under nitrogen. Degassed 1,4-dioxane (40 mL) was added and the reaction mixture heated to reflux for 24 h. After cooling, the mixture was concentrated and the solid residue was diluted with DCM (40 mL). The solution was washed with water (40 mL), brine (40 mL), dried ($MgSO_4$) and concentrated. Purification by silica gel column chromatography (hexane/ethyl acetate 4:1) gave **3** as a white crystalline solid (2.32 g, 76%): ^{1}H NMR δ (400 MHz, $CDCl_3$) 8.79 (s, 2H), 7.49 (d, J = 8.8 Hz, 2H), 7.20 (d, J = 8.8 Hz, 2H), 3.90 (ddd, J = 11.3, 9.9, 3.0 Hz, 1H), 3.61-3.71 (m, 1H), 1.83-1.93 (m, 2H), 1.59-1.78 (m, 4H); ^{13}C NMR δ (101 MHz, $CDCl_3$) 159.7, 157.2, 133.0, 128.2, 128.0, 126.1, 117.7, 96.5, 62.3, 30.4, 25.3, 18.8; LRMS (EI) *m/z* 290 (M^+, 2), 264 (100), 207 (37), 85 (58); HRMS (EI) *m/z* calcd for $C_{15}H_{15}ClN_2O_2$ 290.0822, found 290.0834.

General procedure for the synthesis of 4(*n*). The procedure described for the synthesis of 4-(2-butyloxypyrimid-5-yl)phenol (**4(4)**) is representative: To a suspension of NaH in mineral oil (60% w/w, 140 mg, 3.45 mmol) in dry THF (10 mL) was added 1-butanol (255 mg, 3.45 mmol), and the mixture was stirred at room temperature for 30 min under nitrogen. The mixture was cooled to 0 ºC and a solution of **3** (250 mg, 0.86 mmol) in dry THF (10 mL) was added dropwise. The mixture was allowed to warm to room temperature and stirred for 12 h. The reaction was quenched with sat aq NH_4Cl (5 mL) before adding water (40 mL). The crude product was extracted with ethyl acetate (3×20 mL) and the combined extracts were washed with 2M aq HCl (2×30 mL), water (40 mL), brine (40 mL), dried ($MgSO_4$) and concentrated. Purification by silica gel column chromatography (hexane/ethyl acetate 3:1) gave **4(4)** (190 mg, 90%) as a white solid: ^{1}H NMR δ (400 MHz, $CDCl_3$) 8.61 (s, 2H), 7.28 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 4.36 (t, J = 6.6 Hz, 2H), 1.63-1.76 (m, 2H), 1.32-1.45 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H); ^{13}C NMR δ (101 MHz, $CDCl_3$) 164.0, 156.9, 156.7, 128.2, 127.7, 126.0, 116.5, 67.5, 30.8, 19.1, 13.7; LRMS (EI) *m/z* 244 (M^+, 77), 188 (100), 146 (94); HRMS (EI) *m/z* calcd for $C_{14}H_{16}N_2O_2$ 244.1212, found 244.1205.

4-(2-Pentyloxypyrimid-5-yl)phenol (4(5)). Yield of 87%, white solid: ^{1}H NMR δ (400 MHz, $CDCl_3$) 8.59 (s, 2H), 7.31 (d, J = 8.3 Hz, 2H), 6.91 (d, J = 8.3 Hz, 2H), 6.24 (s, 1H), 4.32 (t, J = 6.7 Hz, 2H), 1.68-1.79 (m, 2H), 1.29-1.43 (m, 4H), 0.84 (t, J = 6.8 Hz, 3H); ^{13}C NMR δ (101 MHz, $CDCl_3$) 164.0, 157.6, 156.7, 128.1, 127.7, 116.4, 68.0, 28.5, 28.0, 22.3, 13.9; LRMS (EI) *m/z* 258 (M^+, 61), 188 (100), 146 (84); HRMS (EI) *m/z* calcd for $C_{15}H_{19}N_2O_2$ 258.1368, found 258.1357.

4-(2-Hexyloxypyrimid-5-yl)phenol (4(6)). Yield of 77%, white solid: ^{1}H NMR δ (400 MHz, $CDCl_3$) 8.48 (s, 2H), 7.22 (d, J = 8.8 Hz, 2H), 6.78 (d, J = 8.8 Hz, 2H), 4.21 (t, J = 6.7 Hz, 2H), 1.58-1.68 (m, 2H), 1.27-1.39 (m, 2H), 1.11-1.23 (m, 4H), 0.72 (t, J = 7.9 Hz, 3H); ^{13}C NMR δ (101 MHz, $CDCl_3$) 164.1, 156.7, 156.7, 128.1, 127.7, 126.1, 116.4, 68.0, 31.5, 28.80, 25.5, 22.5, 13.9; LRMS (EI) *m/z* 272 (M^+, 54), 188 (100), 146 (73); HRMS (EI) *m/z* calcd for $C_{16}H_{20}N_2O_2$ 272.1525, found 272.1518.

4-(2-Heptyloxypyrimid-5-yl)phenol (4(7)). Yield of 87%, white solid: ^{1}H NMR δ (400 MHz, $CDCl_3$) 8.67 (s, 2H), 7.39 (d, J = 8.8 Hz, 2H), 6.98 (d, J = 8.8 Hz, 2H), 4.40 (t, J = 6.7 Hz, 2H), 1.75-1.89 (m, 2H), 1.42-1.54 (m, 2H), 1.28-1.40 (m, 6H), 0.88 (t, J = 7.9 Hz, 3H); ^{13}C NMR δ (101 MHz, $CDCl_3$) 164.0, 156.9, 156.7, 128.2, 127.7, 125.9, 116.5, 68.1, 31.7, 28.9, 28.8, 25.8, 22.5, 14.0; LRMS (EI) *m/z* 286 (M^+, 37), 188 (100), 146 (75); HRMS (EI) *m/z* calcd for $C_{17}H_{22}N_2O_2$ 286.1681, found 286.1693.

4-(2-Octyloxypyrimid-5-yl)phenol (4(8)). Yield of 85%, white solid: ^{1}H NMR δ (400 MHz, $CDCl_3$) 8.67 (s, 2H), 7.39 (d, J = 8.8 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 4.40 (t, J = 6.7 Hz, 2H), 1.73-1.85 (m, 2H), 1.39-1.51 (m, 2H), 1.25-1.38 (m, 8H), 0.85 (t, J = 7.9 Hz, 3H); ^{13}C NMR δ (101 MHz, $CDCl_3$) 163.9, 157.0, 156.6, 128.2, 127.7, 125.8, 116.5, 68.1, 31.7, 29.2, 29.1, 28.8, 25.8, 22.5, 14.0; LRMS (EI) *m/z* 300 (M^+, 48), 189 (56), 188 (100), 146 (60); HRMS (EI) *m/z* calcd for $C_{18}H_{24}N_2O_2$ 300.1838, found 300.1826.

4-(2-Nonyloxypyrimid-5-yl)phenol (4(9)). Yield of 86%, white solid: ^{1}H NMR δ (400 MHz, $CDCl_3$) 8.67 (s, 2H), 7.39 (d, J = 8.6 Hz, 2H), 6.97 (d, J = 8.6 Hz, 2H), 4.39 (t, J = 6.7 Hz, 2H), 1.75-1.91 (m, 2H), 1.39-1.49 (m, 2H), 1.23-1.38 (m, 10H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR δ (101 MHz, $CDCl_3$) 164.0, 156.9, 156.7, 128.2, 127.7, 125.9, 116.5, 68.1, 31.8, 29.4, 29.3, 29.2, 28.8, 25.9, 22.6, 14.0; LRMS (EI) *m/z* 314 (M^+, 50), 188 (100), 146 (54); HRMS (EI) *m/z* calcd for $C_{20}H_{26}N_2O_2$ 314.1994, found 314.1982.

General procedure for the synthesis of QL16-*n*. The procedure described for the synthesis of 2-butyloxy-5-[4-(12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecyloxy)-phenyl]pyrimidine (**QL16-4**) is representative: A solution of **4(4)** (90 mg, 0.37 mmol), Cs_2CO_3 carbonate (360 mg, 1.1 mmol) and 1-bromo-12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecane (250 mg, 0.74 mmol) in acetone (10 mL) was stirred for 30 min at room temperature and then heated to reflux for 16 h. The mixture was then filtered and the filtrate concentrated. The solid residue was dissolved in DCM (10 mL) and washed with 1M aq HCl (20 mL), water (20 mL), dried ($MgSO_4$) and concentrated. Purification by silica gel column chromatography (hexane/ethyl acetate 7:1) gave **QL16-4** (0.23 g, 99%) as a white solid. The product was further purified by two recrystallizations, first from hexanes and then from EtOH: ^{1}H NMR δ (400 MHz, $CDCl_3$) 8.66 (s, 2H), 7.43 (d, J = 8.8 Hz, 2H), 7.01 (d, J = 8.8 Hz, 2H), 4.37 (t, J = 6.6 Hz, 2H), 4.00 (t, J = 6.6 Hz, 2H), 1.75-1.86 (m, 4H), 1.46-1.58 (m, 4H), 1.26-1.38 (m, 14H), 0.99 (t, J = 7.3 Hz, 3H), 0.48-0.50 (m, 2H), 0.05 (s, 6H), 0.03 (s, 9H), 0.00 (s, 6H), -0.25 (s, 2H), -0.28 (s, 2H); ^{13}C NMR δ (101 MHz, $CDCl_3$) 164.4, 159.3, 156.8, 127.9, 127.5, 126.6, 115.2, 68.1, 67.5, 33.7, 30.9, 29.63, 29.60, 29.5, 29.4, 29.3, 29.2, 26.0, 23.9, 19.1, 18.0, 13.8, 5.7, 4.0, 2.4, 1.4, -0.4; LRMS (EI) *m/z* 614 (M^+, 100), 599 (55), 217 (37), 129 (48), 73 (35); HRMS (EI) *m/z* calcd for $C_{34}H_{62}N_2O_2Si_3$ 614.4119, found 614.4139.

Anal. calcd for $C_{34}H_{62}N_2O_2Si_3$: C, 66.39; H, 10.16; N, 4.55, Found C, 66.46; H, 9.95; N, 4.54.

5-[4-(12,12,14,14,16,16-Hexamethyl-12,14,16-trisilaheptadecyloxy)phenyl]-2-pentyloxypyrimidine (QL16-5). Yield of 86%, white solid: ^{1}H NMR δ (400 MHz, $CDCl_3$) 8.66 (s, 2H), 7.43 (d, J = 8.6 Hz, 2H), 7.00 (d, J = 8.6 Hz, 2H), 4.39 (t, J = 6.7 Hz, 2H), 4.00 (t, J = 6.6 Hz, 2H), 1.75-1.86 (m, 4H), 1.41-1.55 (m, 4H), 1.26-1.33 (m, 6H), 0.94 (t, J = 7.6 Hz, 3H), 0.48-0.50 (m, 2H), 0.05 (s, 6H), 0.03 (s, 9H), 0.00 (s, 6H), -0.25 (s, 2H), -0.27 (s, 2H); ^{13}C NMR δ (101 MHz, $CDCl_3$) 164.4, 159.3, 152.8, 127.8, 127.5, 126.6, 115.2, 68.1, 67.8, 33.7, 29.6, 29.59, 29.57, 29.39, 29.38, 29.2, 28.5, 28.1, 26.0, 23.9, 22.4, 18.0, 13.9, 5.7, 4.0, 2.4, 1.4, -0.4; LRMS (EI) *m/z* 628 (M^+, 100), 613 (49), 217 (25), 129 (38), 73 (28); HRMS (EI) *m/z* calcd for $C_{35}H_{64}N_2O_2Si_3$ 628.4276, found 628.4265.

Anal. calcd for $C_{35}H_{64}N_2O_2Si_3$: C, 66.82; H, 10.25; N, 4.45, Found C, 66.55; H, 10.18; N, 4.36.

5-[4-(12,12,14,14,16,16-Hexamethyl-12,14,16-trisilaheptadecyloxy)phenyl]-2-hexyloxypyrimidine (QL16-6). Yield of 86%, white solid: ^{1}H NMR δ (400 MHz, $CDCl_3$) 8.66 (s, 2H), 7.43 (d, J = 8.8 Hz, 2H), 7.00 (d, J = 8.8 Hz, 2H), 4.39 (t, J = 6.7 Hz, 2H), 4.00 (t, J = 6.6 Hz, 2H), 1.75-1.86 (m, 4H), 1.40-1.52 (m, 4H), 1.29-1.38 (m, 18H), 0.91 (t, J = 6.8 Hz, 3H), 0.48-0.50 (m, 2H), 0.05 (s, 6H), 0.03 (s, 9H), 0.00 (s, 6H), -0.25 (s, 2H), -0.28 (s, 2H); ^{13}C NMR δ (101 MHz, $CDCl_3$) 164.4, 159.3, 156.8, 127.8, 127.5, 126.6, 115.2, 68.1, 67.8, 33.7, 31.5, 29.6, 29.59, 29.57, 29.39, 29.38, 29.2, 28.8, 26.0, 25.6, 23.9, 22.5, 18.0, 14.0, 5.7, 4.0, 2.4, 1.4, -0.4; LRMS (EI) *m/z* 642 (M^+, 100), 627 (45), 217 (27), 129 (38), 73 (26); HRMS (EI) *m/z* calcd for $C_{36}H_{66}N_2O_2Si_3$ 642.4432, found 642.4461.

Anal. calcd for $C_{36}H_{66}N_2O_2Si_3$: C, 67.23; H, 10.34; N, 4.36, Found C, 66.94; H, 10.29; N, 4.29.

2-Heptyloxy-5-[4-(12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecyloxy)phenyl]-pyrimidine (QL16-7). Yield of 75%, white solid: ^{1}H NMR δ (400 MHz, $CDCl_3$) 8.66 (s, 2H), 7.43 (d, J = 8.8 Hz, 2H), 7.00 (d, J = 8.8 Hz, 2H), 4.38 (t, J = 6.7 Hz, 2H), 4.00 (t, J = 6.6 Hz, 2H), 1.74-1.85 (m, 4H), 1.41-1.54 (m, 4H), 1.23-1.41 (m, 20H), 0.89 (t, J = 6.8 Hz, 3H), 0.48-0.50 (m, 2H), 0.05 (s, 6H), 0.03 (s, 9H), 0.00 (s, 6H), -0.25 (s, 2H), -0.28 (s, 2H); ^{13}C NMR δ (101 MHz, $CDCl_3$) 164.4, 159.3, 156.8, 127.8, 127.5, 126.6, 115.2, 68.1, 67.8, 33.7, 31.7, 29.6, 29.59, 29.57, 29.39, 29.38, 29.2, 29.0, 28.9, 26.0, 25.9, 23.9, 22.5, 18.0, 14.0, 5.7, 4.0, 2.4, 1.4, -0.4; LRMS (EI) *m/z* 656 (M^+, 100), 641 (80), 543 (45), 217 (57), 129 (88), 73.0 (60); HRMS (EI) *m/z* calcd for $C_{37}H_{68}N_2O_2Si_3$ 656.4589, found 656.4612.

Anal. calcd for $C_{37}H_{68}N_2O_2Si_3$: C, 67.62; H, 10.43; N, 4.26, Found C, 67.54; H, 10.56; N, 4.18.

5-[4-(12,12,14,14,16,16-Hexamethyl-12,14,16-trisilaheptadecyloxy)phenyl]-2-octyloxy-pyrimidine (QL16-8). Yield of 97%, white solid: ^{1}H NMR δ (400 MHz, $CDCl_3$) 8.66 (s, 2H), 7.43 (d, J = 8.8 Hz, 2H), 7.00 (d, J = 8.8 Hz, 2H), 4.38 (t, J = 6.7 Hz, 2H), 4.00 (t, J = 6.6 Hz, 2H), 1.75-1.85 (m, 4H), 1.40-1.52 (m, 4H), 1.25-1.36 (m, 22H), 0.89 (t, J = 6.8 Hz, 3H), 0.48-0.50 (m, 2H), 0.05 (s, 6H), 0.03 (s, 9H), 0.00 (s, 6H), -0.25 (s, 2H), -0.28 (s, 2H); ^{13}C NMR δ (101 MHz, $CDCl_3$) 164.4, 159.3, 156.8, 127.8, 127.5, 126.6, 115.2, 68.1, 67.8, 33.6, 31.7, 29.6, 29.58, 29.56, 29.38, 29.37, 29.32, 29.2, 28.9, 26.0, 25.9, 23.9, 22.6, 18.0, 14.0, 5.7, 4.0, 2.4, 1.4, -0.4; LRMS (EI) *m/z* 670 (M^+, 100), 655 (43), 217 (34), 129 (59), 73 (54); HRMS (EI) *m/z* calcd for $C_{38}H_{70}N_2O_2Si_3$ 670.4745, found 670.4766.

Anal. calcd for $C_{38}H_{70}N_2O_2Si_3$: C, 68.00; H, 10.51; N, 4.17. Found C, 67.95; H, 10.58; N, 4.15.

5-[4-(12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecyloxy)phenyl]-2-nonyloxy-pyrimidine (QL16-9). Yield of 91%, white solid: ^{1}H NMR δ (400 MHz, $CDCl_3$) 8.66 (s, 2H), 7.42 (d, J = 8.8 Hz, 2H), 7.00 (d, J = 8.8 Hz, 2H), 4.38 (t, J = 6.7 Hz, 2H), 4.00 (t, J = 6.6 Hz, 2H), 1.75-1.85 (m, 4H), 1.42-1.54 (m, 4H), 1.26-1.37 (m, 24H), 0.88 (t, J = 7.2 Hz, 3H), 0.48-0.50 (m, 2H), 0.05 (s, 6H), 0.03 (s, 9H), 0.00 (s, 6H), -0.25 (s, 2H), -0.28 (s, 2H); ^{13}C NMR δ (101 MHz, $CDCl_3$) 164.4, 159.3, 156.8, 127.8, 127.5, 126.6, 115.2, 68.1, 67.8, 33.7, 31.8, 29.6, 29.59, 29.57, 29.52, 29.39, 29.38, 29.25, 29.22, 28.9, 26.0, 25.9, 23.9, 22.6, 18.0, 14.0, 5.7, 4.0, 2.4, 1.4, -0.4; LRMS (EI) *m/z* 684 (M^+, 100), 669 (39), 543 (26), 217 (26), 129 (38); HRMS (EI) *m/z* calcd for $C_{39}H_{72}N_2O_2Si_3$ 684.4902, found 684.4883.

Anal. calcd for $C_{39}H_{82}N_2O_2Si_3$: C, 68.36; H, 10.59; N, 4.09, Found C, 68.61; H, 10.75; N, 4.09.

4-(2-Chloropyrimidin-5-yl)phenol (5). To a solution of **3** (1.01 g, 3.47 mmol) in 1:1 DCM/EtOH (50 mL) was added *p*-toluenesulphonic acid (33 mg, 0.17 mmol). The mixture was stirred at room temperature for 16 h and monitored by TLC. The mixture was then concentrated and the residue purified by silica gel column chromatography (hexane/ethyl acetate 4:1) to give **5** (0.71 g, 99%) as a white solid: ^{1}H NMR δ (400 MHz, CD_3OD) 7.33 (s, 2H). 5.99 (d, J = 8.6 Hz, 2H), 5.37 (d, J = 8.6 Hz, 2H); ^{13}C NMR δ (101 MHz, $CDCl_3$) 158.8, 158.3, 156.8, 133.0, 128.1, 123.8, 116.5; LRMS (EI) *m/z* 206 (M^+, 100), 149 (20), 118 (44), 89 (31), 61 (19); HRMS (EI) *m/z* calcd for $C_{10}H_7ClN_2O$ 206.0247, found 206.0239.

General procedure for the synthesis of 6(*n*). The procedure described for the synthesis of 2-chloro-5-(4-pentyloxyphenyl)pyrimidine **6(5)** is representative: To a solution of **5** (330 mg, 1.6 mmol) and K_2CO_3 (662 mg, 4.8 mmol) in acetone (20 mL) was added 1-bromopentane (725 mg, 4.8 mmol) and the mixture was heated to reflux for 24 h. The mixture was filtered and the filtrate concentrated. The residue was diluted with ethyl acetate (20 mL) and washed with 1M aq HCl (20 mL), brine (20 mL), dried ($MgSO_4$) and concentrated. Purification by silica gel column chromatography (hexane/ethyl acetate 7:1) gave **6(5)** (380 mg, 86%) as a white solid: ^{1}H NMR δ (400 MHz, $CDCl_3$) 8.79 (s, 2H), 7.49 (d, J = 8.8 Hz, 2H), 7.03 (d, J = 8.8 Hz, 2H), 4.02 (t, J = 6.6 Hz, 2H), 1.77-1.87 (m, 2H), 1.36-1.46 (m, 4H), 0.95 (t, J = 6.9 Hz, 3H); ^{13}C NMR δ (101 MHz, $CDCl_3$) 160.2, 159.3, 156.8, 132.6, 127.9, 124.7, 115.5, 68.1, 28.8, 28.1, 22.3, 13.9; LRMS (EI) *m/z* 276 (26), 206 (100); HRMS (EI) *m/z* calcd for $C_{15}H_{17}ClN_2O$ 276.1021, found 276.0129.

2-Chloro-5-(4-hexylyloxyphenyl)pyrimidine 6(6). Yield of 86%, white solid: ^{1}H NMR δ (400 MHz, $CDCl_3$) 8.78 (s, 2H), 7.47 (d, J = 8.8 Hz, 2H); 7.03 (d, J = 8.8 Hz, 2H), 4.01 (t, J = 6.6 Hz, 2H), 1.78-1.85 (m, 2H), 1.45-1.52 (m, 2H), 1.34-1.38 (m, 4H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR δ (101 MHz, $CDCl_3$) 160.2, 159.3, 156.8, 132.7, 128.0, 124.8, 115.5, 68.2, 31.5, 29.1, 25.6, 22.5, 13.9; HRMS (EI) *m/z* calcd for $C_{16}H_{19}ClN_2O$ 290.1186, found 290.1175.

2-Chloro-5-(4-heptyloxyphenyl)pyrimidine 6(7). Yield of 73%, white solid: ^{1}H NMR δ (400 MHz, $CDCl_3$) 8.79 (s, 2H), 7.48 (d, J = 8.8 Hz, 2H), 7.03 (d, J = 8.8 Hz, 2H), 4.01 (t, J = 6.6 Hz, 2H), 1.74-1.83 (m, 2H), 1.41-1.51 (m, 2H), 1.30-1.48 (m, 6H), 0.90 (t, J = 6.9 Hz, 3H); ^{13}C NMR δ (101 MHz, $CDCl_3$) 160.2, 159.3, 156.8, 132.7, 128.0, 124.8, 115.5, 68.2, 63.0, 33.6, 32.8, 31.7, 29.6, 29.59, 29.57, 29.4, 29.3, 29.1, 29.0, 25.9, 25.7, 22.5, 18.0, 14.0, 5.7, 4.0, 2.4, 1.4, -0.4; LRMS (EI) *m/z* 304 (M^+, 25), 206 (100); HRMS (EI) *m/z* calcd for $C_{17}H_{21}ClN_2O$ 304.1342, found 304.1333.

2-Chloro-5-(4-octyloxyphenyl)pyrimidine 6(8). Yield of 77%, white solid: ^{1}H NMR δ (400 MHz, $CDCl_3$) 8.79 (s, 2H), 7.48 (d, J = 8.8 Hz, 2H), 7.03 (d, J = 8.8 Hz, 2H), 4.01 (t, J = 6.6 Hz, 2H), 1.76-1.86 (m, 2H), 1.42-1.52 (m, 2H), 1.25-1.41 (m, 8H), 0.90 (t, J = 6.9 Hz, 3H); ^{13}C NMR δ (101 MHz, $CDCl_3$) 160.2, 159.3, 156.8, 132.7, 128.0, 124.8, 115.5, 68.2, 31.7, 29.3, 29.19, 21.14, 25.9, 22.6, 14.0; LRMS (EI) *m/z* 318 (32), 206 (100); HRMS (EI) *m/z* calcd for $C_{18}H_{23}ClN_2O$ 318.1499, found 318.1488.

2-Chloro-5-(4-nonyloxyphenyl)pyrimidine 6(9). Yield of 81%, white solid: ^{1}H NMR δ (400 MHz, $CDCl_3$) 8.79 (s, 2H), 7.48 (d, J = 8.8 Hz, 2H), 7.03 (d, J = 8.8 Hz, 2H), 4.01 (t, J = 6.6 Hz, 2H), 1.75-1.85 (m, 2H), 1.42-1.53 (m, 2H), 1.26-1.41 (m, 10H), 0.89 (t, J = 6.9 Hz, 3H); ^{13}C NMR δ (101 MHz, $CDCl_3$) 160.2, 159.3, 156.8, 132.7, 128.0, 124.8, 115.5, 68.2, 31.8, 29.4, 29.3, 29.2, 29.1, 25.9, 22.6, 14.0; LRMS (EI) *m/z* 332 (M^+, 32), 206 (100); HRMS (EI) *m/z* calcd for $C_{19}H_{25}ClN_2O$ 332.1655, found 332.1662.

General procedure for the synthesis of QL17-*n*. The procedure described for the synthesis of 5-butyloxy-2-[4-(12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecyloxy)-phenyl]pyrimidine (**QL17-4**) is representative: To a suspension of NaH in mineral oil (60% w/w, (61 mg, 1.52 mmol)) in dry THF (10 mL) was added 12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecan-1-ol (220 mg, 0.57 mmol) and the mixture was stirred at room temperature for 30 min under nitrogen. The mixture was cooled to 0 ºC and a solution of **6(4)** (210 mg, 0.38 mmol) in dry THF (10 mL) was added dropwise. The mixture was allowed to warm to room temperature and stirred for 12 h. The reaction was quenched with sat aq NH_4Cl (5 mL) before adding water (40 mL). The crude product was extracted with ethyl acetate (3×20 mL) and the combined extracts were washed with 2M aq HCl (2×30 mL), water (40 mL), brine (40 mL), dried ($MgSO_4$) and concentrated. Purification by silica gel column chromatography (hexane/ethyl acetate 7:1) gave **QL17-4** (0.13g, 57%) as a white solid. The product was further purified by two recrystallizations, first from hexanes and then from EtOH: ^{1}H NMR δ (400 MHz, $CDCl_3$) 8.66 (s, 2H), 7.43 (d, J = 8.8 Hz, 2H), 7.00 (d, J = 8.8 Hz, 2H), 4.38 (t, J 6.7 Hz, 2H), 4.01 (t, J = 6.6 Hz, 2H), 1.75-1.86 (m, 4H), 1.44-1.56 (m, 4H), 1.24-1.41 (m, 14H), 0.95 (t, J = 7.5 Hz, 3H), 0.48-0.50 (m, 2H), 0.05 (s, 6H), 0.03 (s, 9H), 0.00 (s, 6H), -0.25 (s, 2H), -0.28 (s, 2H); ^{13}C NMR δ (101 MHz, $CDCl_3$) 164.4, 159.3, 156.8, 127.8, 127.5, 126.6, 115.2, 67.8, 67.8, 33.7, 31.2, 29.6, 29.59, 29.57, 29.3, 28.9, 25.9, 23.9, 19.2, 18.0, 13.8, 5.7, 4.0, 2.4, 1.4, -0.4; LRMS (EI) *m/z* 614 (M^+, 100), 599 (55), 217 (37), 129 (48), 73 (35) HRMS (EI) *m/z* calcd for $C_{34}H_{62}N_2O_2Si_3$ 614.4199, found 614.4139.

Anal. calcd for $C_{34}H_{62}N_2O_2Si_3$: C, 66.39; H, 10.16; N, 4.55, Found C, 66.11; H, 10.11; N, 4.51.

2-[4-(12,12,14,14,16,16-Hexamethyl-12,14,16-trisilaheptadecyloxy)phenyl]-5-pentyloxy-pyrimidine (QL17-5). Yield of 86%, white solid: ^{1}H NMR δ (400 MHz, $CDCl_3$) 8.66 (s, 2H), 7.43 (d, J = 8.8 Hz, 2H), 7.00 (d, J = 8.8 Hz, 2H), 4.38 (t, J = 6.7 Hz, 2H), 4.00 (t, J = 6.6 Hz, 2H), 1.76-1.86 (m, 4H), 1.28-1.51 (m, 16H), 0.95 (t, J = 7.2 Hz, 3H), 0.48-0.50 (m, 2H), 0.05 (s, 6H), 0.03 (s, 9H), 0.00 (s, 6H), -0.25 (s, 2H), -0.28 (s, 2H); ^{13}C NMR δ (101 MHz) 164.4, 159.3, 156.8, 127.8, 127.5, 126.6, 115.2, 68.1, 67.8, 33.7, 29.6, 29.59, 29.57, 29.39, 29.38, 29.2, 28.5, 28.1, 25.9, 23.9, 19.4, 18.0, 13.9, 5.7, 4.0, 2.4, 1.4, -0.4; LRMS (EI) *m/z* 628 (M^+, 100), 613 (43), 387 (42), 259 (41), 129 (31), 73 (20); HRMS (EI) *m/z* calcd for $C_{35}H_{64}N_2O_3Si_3$ 628.4276, found 628.4301.

Anal. calcd for $C_{35}H_{64}N_2O_2Si_3$: C, 66.82; H, 10.25; N, 4.45, Found C, 66.84; H, 10.36; N, 4.44.

2-[4-(12,12,14,14,16,16-Hexamethyl-12,14,16-trisilaheptadecyloxy)phenyl]-5-hexyloxy-pyrimidine (QL17-6). Yield of 91%, white solid: ^{1}H NMR δ (400 MHz, $CDCl_3$) 8.66 (s, 2H), 7.43 (d, J = 8.8 Hz, 2H), 7.00 (d, J = 8.8 Hz, 2H), 4.39 (t, J = 6.7 Hz, 2H), 4.00 (t, J = 6.6 Hz, 2H), 1.74-1.86 (m, 4H), 1.37-1.47 (m, 4H), 1.26-1.37 (m, 18H), 0.91 (t, J = 6.8 Hz, 3H), 0.48-0.50 (m, 2H), 0.05 (s, 6H), 0.03 (s, 9H), 0.00 (s, 6H), -0.25 (s, 2H), -0.28 (s, 2H); ^{13}C NMR δ (101 MHz, $CDCl_3$) 164.4, 159.3, 156.8, 127.8, 127.5, 126.7, 115.2, 68.1, 67.8, 33.7, 31.5, 29.63, 29.60, 29.5, 29.3, 29.1, 28.9, 25.9, 25.7, 23.9, 22.5, 18.0, 14.0, 5.7, 4.0, 2.4, 1.4, -0.4; LRMS (EI) *m/z* 642 (M^+, 100), 627 (46), 401 (41), 273 (54), 129 (69), 73 (64); HRMS (EI) *m/z* calcd for $C_{36}H_{66}N_2O_2Si_3$ 642.4432, found 642.4451.

Anal. Calcd for $C_{36}H_{66}N_2O_2Si_3$: C, 67.23; H, 10.34; N, 4.36. found C, 66.89; H, 10.35; N, 4.26.

5-Heptyloxy-2-[4-(12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecyloxy)phenyl]-pyrimidine (QL17-7). Yield of 90%, white solid: ^{1}H NMR δ (400 MHz, $CDCl_3$) 8.66 (s, 2H), 7.43 (d, J = 8.6 Hz, 2H), 7.00 (d, J = 8.6 Hz, 2H), 4.39 (t, J = 6.7 Hz, 2H), 4.00 (t, J = 6.6 Hz, 2H), 1.75-1.87 (m, 4H), 1.35-1.47 (m, 4H), 1.24-1.41 (m, 20H), 0.90 (t, J = 6.9 Hz, 3H), 0.48-0.50 (m, 2H), 0.05 (s, 6H), 0.03 (s, 9H), 0.00 (s, 6H), -0.25 (s, 2H), -0.28 (s, 2H); ^{13}C NMR δ (101 MHz, $CDCl_3$) 164.4, 159.3, 156.8, 127.8, 127.5, 126.7, 115.3, 68.1, 67.8, 33.7, 31.7, 29.64, 29.60, 29.5, 29.3, 29.2, 29.0, 28.9, 25.9, 23.9, 22.5, 18.0, 14.0, 5.8, 4.0, 2.4, 1.4, -0.4; LRMS (EI) *m/z* 656 (M^+, 100), 641 (38), 415 (41), 287 (70), 129 (96), 73 (81); HRMS (EI) *m/z* calcd for $C_{37}H_{68}N_2O_2Si_3$ 656.4589, found 656.4601.

Anal. calcd for $C_{37}H_{68}N_2O_2Si_3$: C, 67.62; H, 10.43; N, 4.26. Found C, 67.82; H, 10.37; N, 4.25.

2-[4-(12,12,14,14,16,16-Hexamethyl-12,14,16-trisilaheptadecyloxy)phenyl]-5-octyloxy-pyrimidine (QL17-8). Yield of 90%, white solid: ^{1}H NMR δ (400 MHz, $CDCl_3$) 8.66 (s, 2H), 7.43 (d, J = 8.8 Hz, 2H), 7.00 (d, J = 8.8 Hz, 2H), 4.38 (t, J = 6.7 Hz, 2H), 4.00 (t, J = 6.6 Hz, 2H), 1.76-1.78 (m, 4H), 1.39-1.52 (m, 4H), 1.27-1.39 (m, 22H), 0.90 (t, J = 7.2 Hz, 3H), 0.48-0.50 (m, 2H), 0.05 (s, 6H), 0.03 (s, 9H), 0.00 (s, 6H), -0.25 (s, 2H), -0.28 (s, 2H); ^{13}C NMR δ (101 MHz, $CDCl_3$) 164.4, 159.3, 156.8, 127.9, 127.5, 126.7, 115.3, 68.2, 67.8, 33.7, 31.8, 29.64, 29.61, 29.5, 29.39, 29.35, 29.2, 28.9, 26.0, 25.9, 23.9, 22.6, 18.0, 14.0, 5.8, 4.0, 2.4, 1.4, -0.4; LRMS (EI) *m/z* 670 (M^+, 100), 655 (37), 429 (36), 301 (37), 129 (41), 73 (34); HRMS (EI) *m/z* calcd for $C_{38}H_{70}N_2O_2Si_3$ 670.4745, found 670.4722.

Anal. calcd for $C_{38}H_{70}N_2O_2Si_3$: C, 68.00; H, 10.51; N, 4.17. Found C, 68.03; H, 10.45; N, 4.08.

2-[4-(12,12,14,14,16,16-Hexamethyl-12,14,16-trisilaheptadecyloxy)phenyl]-5-nonyloxy-pyrimidine (QL17-9). Yield of 88%, white solid: ^{1}H NMR δ (400 MHz, $CDCl_3$) 8.66 (s, 2H), 7.43 (d, J = 8.8 Hz, 2H), 7.00 (d, J = 8.8 Hz, 2H), 4.39 (t, J = 6.7 Hz, 2H), 4.00 (d, J = 6.4 Hz, 2H), 1.77-1.89 (m, 4H), 1.40-1.52 (m, 4H), 1.24-1.42 (m, 24H), 0.89 (,t, J = 6.9 Hz, 3H), 0.48-0.50 (m, 2H), 0.05 (s, 6H), 0.03 (s, 9H), 0.00 (s, 6H), -0.25 (s, 2H), -0.27 (s, 2H); ^{13}C NMR δ (101 MHz, $CDCl_3$) 164.4, 159.3, 156.8, 127.8, 127.5, 126.7, 115.3, 68.1, 67.8, 33.7, 31.8, 29.63, 29.60, 29.57, 29.52, 29.3, 29.25, 29.22, 28.9, 26.0, 25.9, 23.9, 22.6, 18.0, 14.0, 5.8, 4.0, 2.4, 1.4, -0.4; LRMS (EI) *m/z* 684 (M^+, 100), 669 (39), 443 (34), 315 (38), 129 (40), 73 (34); HRMS (EI) *m/z* calcd for $C_{39}H_{72}N_2O_2Si_3$ 684.4902, found 684.4877.

Anal. calcd for $C_{39}H_{72}N_2O_2Si_3$: C, 68.36; H, 10.59; N, 4.09, Found C, 68.59; H, 10.69; N, 4.08.

2,2,4-Trimethyl-2,4-disilapentane (7). A modification of the procedure reported by Reddy et al. was used.[4] Under a nitrogen atmosphere, a solution of chloromethyltrimethylsilane (9.2 g, 74.9 mmol) in dry THF (20 mL) was added to a suspension of Mg turnings (2.0 g, 82.8 mmol) in dry THF (60 mL) at such a rate as to initiate and maintain reflux. The mixture was heated at reflux for 6 h and then cooled to room temperature. Chlorodimethylsilane (7.1 g, 75 mmol) was then added dropwise and the mixture heated to reflux for 20 h. After cooling, the mixture was carefully quenched with water (150 mL) before adding hexane (75 mL). The organic layer was separated and the aqueous layer extracted with hexane (3×30 mL). The combined organic layers were dried (Na_2SO_4) and concentrated. Purification by vacuum distillation gave **7** (4.38 g, 40%) as a colorless oil: ^{1}H NMR δ (400 MHz, $CDCl_3$) ^{1}H NMR □ (400 MHz, $CDCl_3$) 3.97 (sept, J = 3.5 Hz, 1H), 0.10 (d, J = 3.5 Hz, 6H), 0.04 (s, 9H), -0.22 (d, J = 3.5 Hz, 2H).

1-Bromo-12,12,14,14-tetramethyl-12,14-disilapentadecane (8). To a solution of 11-bromoundecene (4.36 g, 18.7 mmol) in dry toluene (20 mL) was added **7** (3.28 g, 22.4 mmol). Karstedt's catalyst (~2 mol%, 0.1 mL) was then added and the mixture was stirred at room temperature for 20 h. The mixture was then concentrated and the residue purified by silica gel column chromatography (hexane) to give **8** (4.49 g, 63%) as a colorless oil: ^{1}H NMR δ (400 MHz, $CDCl_3$) 3.42 (t, J = 6.8 Hz, 2H), 1.83-1.90 (m, 2H), 1.40-1.47 (m, 2H), 1.23-1.36 (m, 14H), 0.46-0.50 (m, 2H), 0.03 (s, 6H), 0.00 (s, 9H), -0.29 (s, 2H).

2-Chloro-5-[4-(12,12,14,14-tetramethyl-12,14-disilapentadecyloxy)phenyl]pyrimidine (9). To a solution of **5** (300 mg, 1.45 mmol) and Cs_2CO_3 (1.53 g, 4.35 mmol) in acetone (20 mL) was added **8** (830 mg, 2.18 mmol) and the mixture was heated to reflux for 24 h. The mixture was cooled to room temperature and filtered. The filtrate was concentrated and the residue was dissolved in DCM (20 mL) and washed with 1M aq HCl (20 mL), brine (20 mL), dried ($MgSO_4$) and concentrated. Purification by silica gel column chromatography (hexane/ethyl acetate 7:1) gave **9** (630 mg, 86%) as a soft material: ^{1}H NMR δ (400 MHz, $CDCl_3$) 8.79 (s, 2H), 7.48 (d, J = 8.6 Hz, 2H), 7.03 (d, J = 8.6 Hz), 4.01 (t, J = 6.4 Hz, 2H), 1.79-1.86 (m, 2H), 1.44-1.52 (m, 2H), 1.29-1.37 (m, 14H), 0.46-0.50 (m, 2H), 0.02 (s, 9H), 0.00 (s, 6H), -0.29 (s, 2H); ^{13}C NMR δ (101 MHz, $CDCl_3$) 160.2, 159.3, 156.9, 132.7, 128.0, 124.8, 115.5, 68.2, 33.7, 29.6, 29.57, 29.55, 29.3, 29.1, 26.0, 23.9, 17.9, 2.5, 1.3, -0.5; LRMS (EI) *m/z* 504 (M^+, 23), 145 (100); HRMS (EI) *m/z* calcd for $C_{27}H_{45}ClN_2OSi_2$ 504.2759, found 504.2745.

2-Hexyloxy-5-[4-(12,12,14,14-tetramethyl-12,14-disilapentadecyloxy)phenyl]pyrimidine (QL24-6). To a suspension of NaH in mineral oil (60% w/w, 104 mg, 2.60 mmol) in dry THF (15 mL) was added 1-hexanol (270 mg, 2.60 mmol). The mixture was stirred at room temperature for 30 min, then cooled to 0 ºC and a solution of **9** (330 mg, 0.65 mmol) in dry THF (15 mL) was added dropwise. The mixture was allowed to warm to room temperature and stirred for 12 h. The reaction was quenched with sat aq NH_4Cl (5 mL) before adding water (20 mL). The crude product was extracted with ethyl acetate (3×20 mL) and the combined extracts were washed with brine (40 mL), dried ($MgSO_4$) and concentrated. Purification by silica gel column chromatography (hexane/ethyl acetate 7:1) gave **QL24-6** (350 mg, 95%) as a white solid. The product was further purified by two recrystallizations, first from hexanes and then from EtOH: ^{1}H NMR δ (400 MHz, $CDCl_3$) 8.66 (s, 2H), 7.43 (d, J = 8.6 Hz, 2H), 7.00 (d, J = 8.6 Hz, 2H), 4.39 (t, J = 6.7 Hz, 2H), 4.00 (t, J = 6.6 Hz, 2H), 1.78-1.88 (m, 4H), 1.44-1.54 (m, 4H), 1.24-1.38 (m, 18H), 0.91 (t, J = 7.2 Hz, 3H), 0.46-0.50 (m, 2H), 0.02 (s, 9H), 0.00 (s, 6H), -0.29 (s, 2H); ^{13}C NMR δ (101 MHz, $CDCl_3$) 164.4, 159.3, 156.8, 127.8, 127.5, 126.7, 115.2, 68.1, 67.8, 33.7, 31.5, 29.6, 29.59, 29.57, 29.3, 29.2, 28.8, 26.0, 25.6, 23.9,

22.6, 17.9, 14.0, 2.5, 1.3, -0.5; LRMS (EI) *m/z* 570 (M^+, 100), 555 (23), 146 (25), 145 (93), 131 (22), 73 (26); HRMS (EI) *m/z* calcd for $C_{33}H_{58}N_2O_2Si_2$ 570.4037, found 570.4019.

Anal. calcd for $C_{33}H_{58}N_2O_2Si_2$: C, 69.41; H, 10.24; N, 4.94 Found C, 69.55; H, 10.43; N, 4.94.

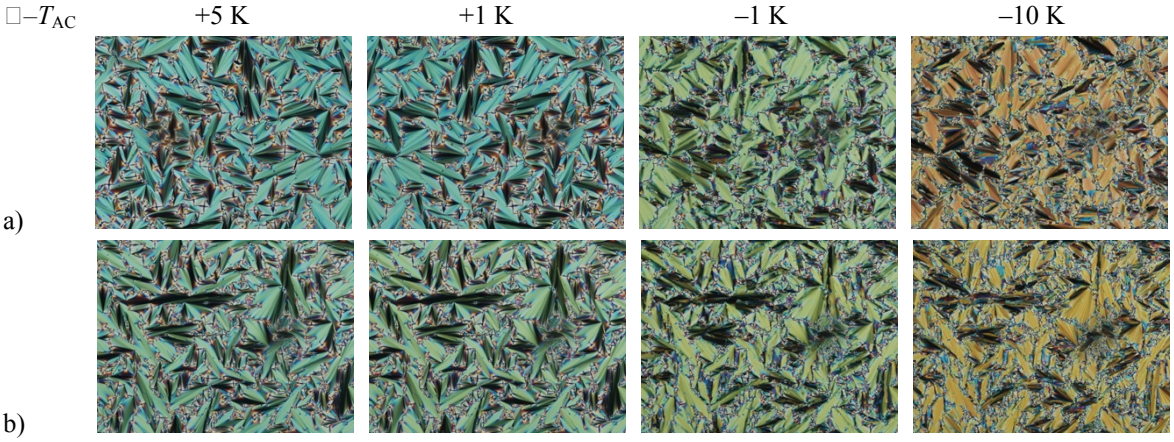


Fig. S1. Polarized photomicrographs of (a) **QL16-6** and (b) **QL17-6** as unaligned 10 m films in the SmA and SmC phases at four different reduced temperatures T–T_{AC}.

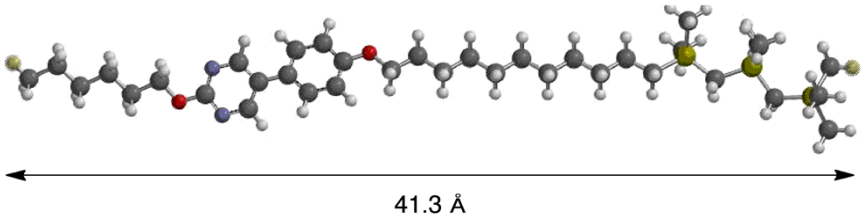


Fig. S2. Molecular model of **QL16-6** minimized at the B3LYP/6-31G* level (Spartan'14, Wavefunction, Inc.)

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