Electronic Supplementary Information for:

Siloxane-terminated phenylpyrimidine liquid crystal hosts

Li Li,[a] Christopher D. Jones,[b] Jakob Magolan,[a] and Robert P. Lemieux*[a]

[a] Chemistry Department, Queen's University, Kingston, Ontario, K7L 3N6, Canada
[b] Department of Physics, University of Colorado at Boulder, Boulder, CO, 80309, USA

Experimental

General

^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on Bruker Avance 400 and 500 spectrometers in deuterated chloroform. The chemical shifts are reported in δ (ppm) relative to tetramethylsilane as internal standard. Low- and high-resolution EI mass spectra were recorded on a Micromass GC-TOF mass spectrometer; low- and high-resolution ES spectra were recorded on an Applied Biosystems/MDS Sciex Q-TOF QSTAR XL mass spectrometer with electrospray ionization source. Peaks are reported as m/z (% intensity relative to the base peak) for low resolution mass spectra. Differential scanning calorimetry analyses were performed on a Perkin-Elmer DSC-7 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. Wide-angle powder X-ray diffraction analyses were performed at the Centre de Recherche en Sciences et Ingénierie des Macromolécules (CERSIM) of Université Laval using a Siemens/Bruker Kristalloflex 760 diffractometer (Cu-K_α radiation, λ=1.5418 Å) fitted with a Hi-Star bidimensional detector. Measurements of *d* spacings as a function of temperature were performed at the Liquid Crystal Materials Research Center of the University of Colorado (Boulder) using a Rigaku UltraX-18 rotating anode generator (Cu-K_α radiation, λ=1.5418 Å) and a Crismatec Scintiflex point detector mounted on a Huber four-circle goniometer. Temperature control of the powder samples was achieved using a Instec STC200 hot stage. The diffraction peaks, fit to a Gaussian, show an error in layer spacing of roughly $2x10^{-4}$ Å, and the machine resolution is q_{res}~$2.6x10^{-3}$ $Å^{-1}$ in the configuration used for the experiment. Molecular modeling calculations were performed at the semi-empirical AM1 level using Spartan '04, v. 1.0.3 (Wavefunction Inc.). Melting points were measured on a Fisher-Johns melting point apparatus and are uncorrected.

Materials

All reagents and chemicals were obtained from commercial sources and used without further purification unless otherwise noted. Tetrahydrofuran (THF) was distilled from sodium/benzophenone under argon; dimethylformamide (DMF) was passed through two columns containing activated alumina and copper using a PureSolv 400 solvent purification system (Innovative Technology Inc.). Flash chromatography was performed using 40–63 mm (230–400 mesh) silica gel (Silicycle Inc.). 11-(1,1,1,3,3,5,5-Heptamethyltrisiloxanyl)undecanol (**9a**),[1] 2-(4-hydroxyphenyl)-5-octyloxypyrimidine (**11b**),[2] and 2-(4-hydroxyphenyl)-5-decyloxypyrimidine (**11d**)[3] were prepared according to published procedures and shown to have the expected physical and spectral properties.

6-(1,1,1,3,3,5,5-Heptamethyltrisiloxanyl)hexanol (9b)
Under an argon atmosphere, a 3 wt% solution of platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in xylenes (264 μL, 0.026 mmol) was added to a solution of 5-hexen-1-ol (172 mg, 1.75 mmol), and 1,1,1,3,3,5,5-heptamethyltrisiloxane (584 mg, 2.63 mmol) in toluene (12 mL). The mixture was stirred at room temperature overnight, then concentrated, and the residue purified by flash chromatography on silica gel (EtOAC) to give **9b** (463 mg, 82%) as a clear liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.66 (t, *J* = 6.6 Hz, 2 H), 1.58 (m, 2 H), 1.46-1.35 (m, 8 H), 0.55 (t, *J* = 7.3 Hz, 2 H), 0.10 (s, 9 H), 0.08 (s, 6 H), 0.04 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 63.0, 33.2, 32.7, 25.5, 23.2, 18.2, 1.8, 1.2, 0.2; ^{29}Si NMR (99 MHz, $CDCl_3$) δ -20.9, 7.2, 7.6; MS (ES) m/z 323 ([M+H]$^+$, 27), 281(14), 233(98), 159(36), 149 (100); HRMS (ES) calcd for $C_{13}H_{35}O_3Si_3$ ([M+H]$^+$): 323.1894, found 323.1886.

2-(4-Hydroxyphenyl)-5-heptyloxypyrimidine (11a)
Under an argon atmosphere, 1-bromoheptane (263 mg, 1.46 mmol) was added to a solution of 2-(4-hydroxyphenyl)-5-pyrimidinol (331 mg, 1.76 mmol) and dry $CsCO_3$ (476 mg, 1.46 mmol) in dry DMF (40 mL). After the mixture was stirred at room temperature overnight, water was added and the mixture was extracted twice with ether. The combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated to a yellow oil. Purification by flash chromatography on silica gel (4:1 hexanes/EtOAc) gave **11a** (272 mg, 65%) as a white solid: mp 105-106 °C; ^{1}H NMR (400 MHz, CDCl3) δ 8.44 (s, 2H), 8.14 (d, *J*=8.3Hz, 2H), 6.86 (d, *J*=8.3Hz, 2H), 4.07 (t, *J*=6.6Hz, 2H), 1.82 (m, 2H), 1.47 (m, 2H), 1.32 (m, 6H), 0.91 (t, *J*=7.1Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 157.6, 151.2, 143.9, 129.4, 129.3, 115.7, 69.1, 31.7, 29.1, 29.0, 25.8, 22.6, 14.1; MS (EI) m/z 286 (M$^+$, 35), 188 (100), 119 (6); HRMS (EI) calcd for $C_{17}H_{22}N_2O_2$: 286.1681, found 286.1682.

2-(4-Hydroxyphenyl)-5-nonyloxypyrimidine (11c)
The procedure described for the synthesis of **11a** was repeated with 1-bromononane (378 mg, 1.83 mmol) and 2-(4-hydroxyphenyl)-5-pyrimidinol (416 mg, 2.21 mmol) to give **11c** (367mg, 62%) as a white solid: mp 114-115°C; ^{1}H NMR (400 MHz, CDCl3) δ 8.44 (s, 2H), 8.19 (d, J=8.6Hz, 2H), 6.89 (d, J=8.6Hz, 2H), 4.08 (t, J=6.6Hz, 2H), 1.83 (m, 2H), 1.48 (m, 2H), 1.30 (m, 10H), 0.90 (t, J=6.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 157.7, 151.2, 143.9, 129.4, 129.3, 115.7, 69.1, 31.9, 29.5, 29.3, 29.2, 29.1, 25.8, 22.7, 14.1; MS (EI) m/z 314 (M$^+$, 80), 188 (100), 159 (3), 132 (5), 119(14); HRMS (EI) calcd for $C_{19}H_{26}N_2O_2$: 314.1994, found 314.1985.

2-(4-Hydroxyphenyl)-5-dodecyloxypyrimidine (11e)
The procedure described for the synthesis of **11a** was repeated with 1-bromododecane (542 mg, 2.17 mmol) and 2-(4-hydroxyphenyl)-5-pyrimidinol (481 mg, 2.55 mmol) to give **11e** (490mg, 64%) as a white solid: mp 74-75°C; ^{1}H NMR (400 MHz, CDCl3) δ 8.43 (s, 2H), 8.21 (d, *J*=7.0Hz, 2H), 6.94 (d, *J*=7.0Hz, 2H), 4.08 (t, *J*=5.9Hz, 2H), 1.83 (m, 2H), 1.48 (m, 2H), 1.28 (m, 16H), 0.89 (t, *J*=5.8Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 158.5, 157.6, 151.1, 143.8, 129.3, 115.7, 69.0, 36.6, 31.9, 31.6, 29.6, 29.5, 29.3, 29.1, 25.9, 22.7, 14.1; MS (EI) m/z 356 (M$^+$, 39), 314 (3), 219 (4), 188 (100), 119 (7); HRMS (EI) calcd for $C_{22}H_{32}N_2O_2$: 356.2464, found 356.2468.

2-(4-(11-(1,1,1,3,3,5,5-Heptamethyltrisiloxanyl)undecyloxy)phenyl)-5-heptyloxypyrimidine (1a)
Under an argon atmosphere, diisopropylazodicarboxylate (103 mg, 0.50 mmol) was added dropwise to a stirred solution of **9a** (192 mg, 0.49 mmol), **11a** (117 mg, 0.41 mmol), and triphenylphosphine (130 mg, 0.50 mmol) in dry THF (10 mL). The mixture was stirred at room temperature for 24 h, and then concentrated to a yellow oil. Purification by flash chromatography on silica gel (30:1 hexanes/EtOAc)

gave **1a** (140 mg, 52%) as a white solid, which was further purified by recrystallization from EtOH after filtration through a 0.45mm PTFE filter: ^{1}H NMR (400 MHz, CDCl3) δ 8.44 (s, 2H), 8.29 (d, *J*=8.0Hz, 2H), 6.99 (d, *J*=8.0Hz, 2H), 4.10 (t, *J*=6.4Hz, 2H), 4.04 (t, *J*=6.6Hz, 2H), 1.84-1.30 (m, 28H), 0.92 (t, *J*=6.2Hz, 3H), 0.55 (t, *J*=7.3Hz, 2H), 0.11 (s, 9H), 0.08 (s, 6H), 0.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 157.6, 151.1, 143.8, 130.0, 129.0, 114.4, 69.0, 68.1, 33.5, 31.7, 30.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.1, 29.0, 26.1, 25.8, 23.2, 22.6, 18.3, 14.1, 1.8, 1.3, 0.2; MS (EI) m/z 660 (M_+, 53), 647 (29), 287 (27), 221 (100), 188(63); HRMS (EI) calcd for $C_{35}H_{64}N_2O_4Si_3$: 660.4174, found 660.4186.

2-(4-(11-(1,1,1,3,3,5,5-Heptamethyltrisiloxanyl)undecyloxy)phenyl)-5-octyloxypyrimidine (1b)
The procedure described for the synthesis of **1a** was repeated with **9a** (180 mg, 0.46 mmol) and **11b** (114 mg, 0.38 mmol) to give **1b** (125 mg, 49%) as a white solid, which was further purified by recrystallization from EtOH after filtration through a 0.45mm PTFE filter: ^{1}H NMR (400 MHz, CDCl3) δ 8.43 (s, 2H), 8.29 (d, *J*=8.5 Hz, 2H), 6.98 (d, *J*=8.5Hz, 2H), 4.09 (t, *J*=6.3Hz, 2H), 4.03 (t, *J*=6.4Hz, 2H), 1.90-1.31 (m, 30H), 0.91 (t, *J*=6.3Hz, 3H), 0.54 (t, *J*=7.6Hz, 2H), 0.10 (s, 9H), 0.07 (s, 6H), 0.03 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 157.7, 151.1, 143.8, 130.1, 129.0, 114.4, 68.9, 68.1, 33.5, 31.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 26.1, 25.9, 23.3, 22.7, 18.6, 18.3, 14.1, 1.8, 1.7, 1.3; MS (EI) m/z 674 (M_+, 100), 659 (25), 300 (13), 221 (49), 188(22); HRMS (EI) calcd for $C_{36}H_{66}N_2O_4Si_3$: 674.4330, found 674.4326.

2-(4-(11-(1,1,1,3,3,5,5-Heptamethyltrisiloxanyl)undecyloxy)phenyl)-5-nonyloxypyrimidine (1c)
The procedure described for the synthesis of **1a** was repeated with **9a** (169 mg, 0.43 mmol) and **11c** (113 mg, 0.36 mmol) to give **1c** (126 mg, 51%) as a white solid, which was further purified by recrystallization from EtOH after filtration through a 0.45mm PTFE filter: ^{1}H NMR (400 MHz, CDCl3) δ 8.44 (s, 2H), 8.29 (d, *J*=8.5Hz, 2H), 6.99 (d, *J*=8.5Hz, 2H), 4.10 (t, *J*=6.6Hz, 2H), 4.04 (t, *J*=6.6Hz, 2H), 1.83-1.30 (m, 32H), 0.91 (t, *J*=7.0Hz, 3H), 0.55 (t, *J*=7.0Hz, 2H), 0.11 (s, 9H), 0.08 (s, 6H), 0.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 157.6, 151.1, 143.8, 129.9, 129.0, 114.5, 69.0, 68.1, 33.5, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 26.1, 25.9, 23.2, 22.7, 18.3, 14.1, 1.8, 1.3, 0.2; MS (EI) m/z 688 (M_+, 16), 673 (6), 221 (100), 207 (64), 149(36); HRMS (EI) calcd for $C_{37}H_{68}N_2O_4Si_3$: 688.4487, found 688.4482.

2-(4-(11-(1,1,1,3,3,5,5-Heptamethyltrisiloxanyl)undecyloxy)phenyl)-5-decyloxypyrimidine (1d)
The procedure described for the synthesis of **1a** was repeated with **9a** (188 mg, 0.48 mmol) and **11d** (137 mg, 0.40 mmol) to give **1d** (134 mg, 48%) as a white solid, which was further purified by recrystallization from EtOH after filtration through a 0.45mm PTFE filter: ^{1}H NMR (400 MHz, CDCl3) δ 8.44 (s, 2H), 8.29 (d, *J*=8.6Hz, 2H), 6.99 (d, *J*=8.6Hz, 2H), 4.10 (t, *J*=6.4Hz, 2H), 4.04 (t, *J*=6.6Hz, 2H), 1.83-1.30 (m, 34H), 0.91 (t, *J*=6.2Hz, 3H), 0.55 (t, *J*=7.3Hz, 2H), 0.11 (s, 9H), 0.08 (s, 6H), 0.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ160.8, 157.5, 151.1, 143.8, 129.9, 129.0, 114.5, 69.0, 68.1, 33.5, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.1, 26.1, 25.9, 23.2, 22.7, 18.3, 14.1, 1.8, 1.3, 0.2; MS (EI) m/z 702 (M_+, 81), 687 (34), 221 (100), 188 (50); HRMS (EI) calcd for $C_{38}H_{70}N_2O_4Si_3$: 702.4643, found 702.4631.

2-(4-(11-(1,1,1,3,3,5,5-Heptamethyltrisiloxanyl)undecyloxy)phenyl)-5-dodecyloxypyrimidine (1e)
The procedure described for the synthesis of **1a** was repeated with **9a** (169 mg, 0.43 mmol) and **11e** (121 mg, 0.34 mmol) to give **1e** (117 mg, 47%) as a white solid, which was further purified by recrystallization from EtOH after filtration through a 0.45mm PTFE filter: ^{1}H NMR (400 MHz, CDCl3) δ 8.45 (s, 2H), 8.30 (d, *J*=8.6Hz, 2H), 6.99 (d, *J*=8.6Hz, 2H), 4.10 (t, *J*=6.6Hz, 2H), 4.03 (t, *J*=6.6Hz,

2H), 1.89 –1.20 (m, 38H), 0.90 (t, *J*=7.0Hz, 3H), 0.54 (t, *J*=7.6Hz, 2H), 0.10 (s, 9H), 0.07 (s, 6H), 0.03 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 157.6, 151.1, 143.8, 130.0, 129.0, 114.4, 69.0, 68.1, 33.5, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.1, 26.1, 25.9, 23.2, 22.7, 18.3, 14.1, 1.8, 1.3, 0.2; MS (EI) m/z 730 (M_+, 100), 715 (18), 221 (32); HRMS (EI) calcd for $C_{40}H_{74}N_2O_4Si_3$: 730.4949, found 730.4956.

2-(4-(6-(1,1,1,3,3,5,5-Heptamethyltrisiloxanyl)hexyloxy)phenyl)-5-heptyloxypyrimidine (2a)
The procedure described for the synthesis of **1a** was repeated with **9b** (155 mg, 0.48 mmol) and **11a** (114 mg, 0.40 mmol) to give **2a** (113 mg, 48%) as a white solid, which was further purified by recrystallization from EtOH after filtration through a 0.45mm PTFE filter: ^{1}H NMR (400 MHz, CDCl3) δ 8.36 (s, 2H), 8.29 (d, *J*=8.7Hz, 2H), 6.95 (d, *J*=8.7Hz, 2H), 3.97 (m, 4H), 1.80-1.30 (m, 18H), 0.90 (t, *J*=6.3Hz, 3H), 0.57 (t, *J*=7.7Hz, 2H), 0.11 (s, 9H), 0.09 (s, 6H), 0.05 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 157.5, 151.0, 143.6, 130.1, 129.0, 114.3, 68.8, 68.0, 33.2, 31.7, 29.2, 29.1, 29.0, 25.8, 23.2, 22.6, 18.2, 14.1, 1.8, 1.3, 0.2; MS (ES) m/z 591 ($[M+H]_+$, 100); HRMS (ES) calcd for $C_{30}H_{55}N_2O_4Si_3$ ([M+H]+): 591.3470, found 591.3453.

2-(4-(6-(1,1,1,3,3,5,5-Heptamethyltrisiloxanyl)hexyloxy)phenyl)-5-octyloxypyrimidine (2b)
The procedure described for the synthesis of **1a** was repeated with **9b** (141 mg, 0.44 mmol) and **11b** (111 mg, 0.37 mmol) to give **2b** (112 mg, 50%) as a white solid, which was further purified by recrystallization from EtOH after filtration through a 0.45mm PTFE filter: ^{1}H NMR (400 MHz, CDCl3) δ 8.43 (s, 2H), 8.29 (d, *J*=8.7Hz, 2H), 6.99 (d, *J*=8.7Hz, 2H), 4.09 (t, *J*=6.4Hz, 2H), 4.03 (t, *J*=6.6Hz, 2H), 1.83-1.32 (m, 20H), 0.91 (t, *J*=6.4Hz, 3H), 0.57 (t, *J*=7.6Hz, 2H), 0.11 (s, 9H), 0.09 (s, 6H), 0.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 157.6, 151.1, 143.8, 130.0, 129.0, 114.4, 69.0, 68.1, 33.2, 31.8, 29.3, 29.2, 29.1, 25.9, 25.8, 23.2, 22.7, 18.2, 14.1, 1.8, 1.3, 0.2; MS (ES) m/z 605 ($[M+H]_+$, 100); HRMS (ES) calcd for $C_{31}H_{57}N_2O_4Si_3$ ([M+H]+): 605.3626, found 605.3618.

2-(4-(6-(1,1,1,3,3,5,5-Heptamethyltrisiloxanyl)hexyloxy)phenyl)-5-nonyloxypyrimidine (2c)
The procedure described for the synthesis of **1a** was repeated with **9b** (145 mg, 0.45 mmol) and **11c** (119 mg, 0.38 mmol) to give **2c** (117 mg, 50%) as a white solid, which was further purified by recrystallization from EtOH after filtration through a 0.45mm PTFE filter: ^{1}H NMR (400 MHz, CDCl3) δ 8.45 (s, 2H), 8.30 (d, *J*=8.3Hz, 2H), 6.99 (d, *J*=8.3Hz, 2H), 4.10 (t, *J*=6.3Hz, 2H), 4.03 (t, *J*=6.3Hz, 2H), 1.85-1.27 (m, 22H), 0.90 (t, *J*=7.0Hz, 3H), 0.54 (t, *J*=7.6Hz, 2H), 0.10 (s, 9H), 0.07 (s, 6H), 0.03 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 157.6, 151.1, 143.8, 130.0, 129.0, 114.4, 68.9, 68.1, 33.2, 31.9, 29.7, 29.5, 29.3, 29.2, 29.1, 25.9, 25.8, 23.2, 22.7, 18.2, 14.1, 1.8, 1.3, 1.2; MS (ES) m/z 619 ($[M+H]_+$, 100); HRMS (ES) calcd for $C_{32}H_{59}N_2O_4Si_3$ ([M+H]+): 619.3783, found 619.3763.

2-(4-(6-(1,1,1,3,3,5,5-Heptamethyltrisiloxanyl)hexyloxy)phenyl)-5-decyloxypyrimidine (2d)
The procedure described for the synthesis of **1a** was repeated with **9b** (142 mg, 0.44 mmol) and **11d** (116 mg, 0.34 mmol) to give **2d** (112 mg, 52%) as a white solid, which was further purified by recrystallization from EtOH after filtration through a 0.45mm PTFE filter: ^{1}H NMR (400 MHz, CDCl3) δ 8.43 (s, 2H), 8.29 (d, *J*=8.9Hz, 2H), 6.99 (d, *J*=8.9Hz, 2H), 4.09 (t, *J*=6.4Hz, 2H), 4.04 (t, *J*=6.6Hz, 2H), 1.88 –1.30 (m, 24H), 0.91 (t, *J*=6.2Hz, 3H), 0.57 (t, *J*=7.2Hz, 2H), 0.11 (s, 9H), 0.09 (s, 6H), 0.05 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 157.7, 151.1, 143.8, 130.1, 129.0, 114.4, 68.9, 68.1, 33.2, 31.9, 29.5, 29.3, 29.2, 29.1, 25.8, 23.2, 22.7, 18.2, 14.1, 1.8, 1.3, 0.2; MS (EI) m/z 632 (M_+, 50), 533 (10), 221 (100), 207 (32), 188(9); HRMS (EI) calcd for $C_{33}H_{60}N_2O_4Si_3$: 632.3861, found 632.3850.

2-(4-(6-(1,1,1,3,3,5,5-Heptamethyltrisiloxanyl)hexyloxy)phenyl)-5-dodecyloxypyrimidine (2e)
The procedure described for the synthesis of **1a** was repeated with **9b** (122 mg, 0.38 mmol) and **11e** (112 mg, 0.31 mmol) to give **2e** (104 mg, 51%) as a white solid, which was further purified by recrystallization from EtOH after filtration through a 0.45mm PTFE filter: ^{1}H NMR (400 MHz, CDCl3) δ 8.43 (s, 2H), 8.29 (d, *J*=8.6Hz, 2H), 6.99 (d, *J*=8.6Hz, 2H), 4.10 (t, *J*=6.4Hz, 2H), 4.04 (t, *J*=6.4Hz, 2H), 1.83-1.29 (m, 28H), 0.90 (t, *J*=6.3Hz, 3H), 0.57 (t, *J*=7.5Hz, 2H), 0.11 (s, 9H), 0.09 (s, 6H), 0.05 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 157.6, 151.1, 143.8, 130.0, 129.0, 114.4, 69.0, 68.1, 33.2, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 25.9, 25.8, 23.2, 22.7, 18.2, 14.1, 1.8, 1.3, 0.2; MS (ES) m/z 661 ($[M+H]_+$, 100); HRMS (ES) calcd for $C_{35}H_{65}N_2O_4Si_3$ ([M+H]+): 661.4252, found 661.4255.

2-(4-Hydroxyphenyl)-5-(1-chlorooctyloxy)pyrimidine (12)
Under an Ar atmosphere, diisopropylazodicarboxylate (182 mg, 0.90 mmol) was added dropwise to a stirred solution of 8-chloro-1-octanol (141 mg, 0.86 mmol), 2-(4-hydroxyphenyl)-5-pyrimidinol (193 mg, 1.03 mmol), and triphenylphosphine (209 mg, 0.80 mmol) in dry THF (12 mL). The mixture was stirred at room temperature for 24 h, and then concentrated to a yellow oil. Purification by flash chromatography on silica gel (2:1 hexanes/EtOAc) and recrystallization from 1:15 hexane/acetonitrile gave **12** (107 mg, 54%) as a colorless solid: mp 109-110 °C; ^{1}H NMR (400 MHz, CDCl3) δ 8.43 (s, 2H), 8.13 (d, *J*=8.6Hz, 2H), 6.85 (d, *J*=8.6Hz, 2H), 4.06 (t, *J*=6.3Hz, 2H), 3.54 (t, *J*=6.7Hz, 2H), 1.84-1.36 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 157.7, 151.2, 143.9, 129.4, 129.2, 115.7, 69.0, 45.1, 32.6, 29.1, 28.8, 26.8, 25.7, 21.9; MS (EI) m/z 334 (M_+, 56), 188 (48), 119(22), 105(18), 86(100); HRMS (EI) calcd for $C_{18}H_{23}N_2O_2Cl$: 334.1448, found 334.1448.

2-(4-(11-(1,1,1,3,3,5,5-Heptamethyltrisiloxanyl)undecyloxy)phenyl)-5-(1-chlorooctyloxy)pyrimidine (3)
The procedure described for the synthesis of **1a** was repeated with **9a** (223 mg, 0.67 mmol) and **12** (193 mg, 0.66 mmol). Purification by flash chromatography on silica gel (9:1 hexanes/EtOAc) gave **3** (238 mg, 51%) as a white solid, which was further purified by recrystallization from EtOH after filtration through a 0.45mm PTFE filter: ^{1}H NMR (400 MHz, CDCl3) δ 8.43 (s, 2H), 8.28 (d, *J*=8.8Hz, 2H), 6.98 (d, *J*=8.8Hz, 2H), 4.09 (t, *J*=6.4Hz, 2H), 4.03 (t, *J*=6.6Hz, 2H), 3.56 (t, *J*=6.7Hz, 3H), 1.88 –1.29 (m, 30H), 0.54 (t, *J*=7.6Hz, 2H), 0.10 (s, 9H), 0.07 (s, 6H), 0.03 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 157.7, 151.1, 143.8, 130.0, 129.0, 114.5, 68.9, 68.1, 45.1, 33.5, 32.6, 29.7, 29.6, 29.4, 29.3, 29.2, 29.1, 28.8, 26.8, 25.8, 23.2, 18.3, 1.8, 1.3, 0.2; MS (EI) m/z 708 (M_+, 40), 693 (8), 672 (4), 334 (6), 221(100), 188(35); HRMS (EI) calcd for $C_{36}H_{65}N_2O_4Si_3Cl$: 708.3941, found 708.3973.

2-(4-(6-(1,1,1,3,3,5,5-Heptamethyltrisiloxanyl)hexyloxy)phenyl)-5-(1-chlorooctyloxy)pyrimidine (4)
The procedure described for the synthesis of **1a** was repeated with **9b** (122 mg, 0.38 mmol) and **13** (94 mg, 0.28 mmol). Purification by flash chromatography on silica gel (9:1 hexanes/EtOAc) gave **4** (84 mg, 47%) as a white solid, which was further purified by recrystallization from EtOH after filtration through a 0.45mm PTFE filter: ^{1}H NMR (400 MHz, CDCl3) δ 8.41 (s, 2H), 8.24 (d, *J*=8.9Hz, 2H), 6.97 (d, *J*=8.9Hz, 2H), 4.07 (t, *J*=6.4Hz, 2H), 4.01 (t, *J*=6.4Hz, 2H), 3.54 (t, *J*=6.7Hz, 2H), 2.20-1.38 (m, 20H), 0.55 (t, *J*=7.7Hz, 2H), 0.08 (s, 9H), 0.06 (s, 6H), 0.02 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 157.7, 151.0, 143.8, 132.2, 129.0, 114.4, 68.8, 68.1, 45.1, 33.2, 32.6, 29.2, 29.1, 28.8, 26.8, 25.8, 23.2, 18.2, 1.8, 1.3, 0.2; MS (EI) m/z 638 (M_+, 91), 539 (8), 334 (7), 221 (100), 188 (29), 149(23); HRMS (EI) calcd for $C_{31}H_{55}N_2O_4Si_3Cl$: 638.3158, found 638.3141.

2-(4-Hydroxyphenyl)-5-(11-(1,1,1,3,3,5,5-heptamethyltrisiloxanyl)undecyloxy)pyrimidine (13)
The procedure described for the synthesis of **12** was repeated with **9a** (416 mg, 1.06 mmol) and 2-(4-hydroxyphenyl)-5-pyrimidinol. Purification by flash chromatography on silica gel (5:1 hexanes/EtOAc) gave **13** (284 mg, 48 %) as a white solid: mp 50-51°C; ^{1}H NMR (400 MHz, CDCl3) δ 8.43 (s, 2H), 8.14 (d, *J*=8.7Hz, 2H), 6.85 (d, *J*=8.7Hz, 2H), 4.06 (t, *J*=6.2Hz, 2H), 1.82 (m, 2H), 1.83-1.29 (m, 16H), 0.54 (t, *J*=7.2Hz, 2H), 0.10 (s, 9H), 0.07 (s, 6H), 0.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 157.7, 151.2, 143.9, 129.4, 129.3, 115.7, 69.1, 33.5, 29.6, 29.5, 29.4, 29.3, 29.1, 25.9, 23.2, 18.3, 1.8, 1.3, 0.2; MS (EI) m/z 562 (M_+, 17), 547 (22), 472 (2), 398 (4), 221(100), 188(12); HRMS (EI) calcd for $C_{28}H_{50}N_2O_4Si_3$: 562.3078, found 562.3064.

2-(4-Hydroxyphenyl)-5-(11-(1,1,1,3,3,5,5-heptamethyltrisiloxanyl)hexyloxy)pyrimidine (14)
The procedure described for the synthesis of **12** was repeated with **9b** (889 mg, 2.76 mmol) and 2-(4-hydroxyphenyl)-5-pyrimidinol. Purification by flash chromatography on silica gel (5:1 hexanes/EtOAc) gave **14** (676 mg, 50 %) as a white solid: mp 75-76 °C; ^{1}H NMR (400 MHz, CDCl3) δ 8.41 (s, 2H), 8.12 (d, *J*=8.7Hz, 2H), 6.85 (d, *J*=8.7Hz, 2H), 4.02 (t, *J*=6.2Hz, 2H), 1.79 (m, 2H), 1.80-1.39 (m, 6H), 0.57 (t, *J*=7.3Hz, 2H), 0.11 (s, 9H), 0.09 (s, 6H), 0.05 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 157.7, 151.2, 143.8, 129.5, 128.9, 115.8, 69.0, 33.0, 29.0, 25.6, 23.1, 18.2, 1.8, 1.3, 0.2; MS (EI) m/z 492 (M_+, 39), 477 (15), 393 (17), 221 (100), 188(5); HRMS (EI) calcd for $C_{23}H_{40}N_2O_4Si_3$: 492.2296, found 492.2298.

2-(4-Octyloxyphenyl)-5-[11-(1,1,1,3,3,5,5-heptamethyltrisiloxanyl)undecyloxy]pyrimidine (5)
Under an Ar atmosphere, 1-bromooctane (57 mg, 0.30 mmol) was added to a solution of **13** (118 mg, 0.21 mmol) and dry $CsCO_3$ (85 mg, 0.26 mmol) in dry DMF (14 mL). After the mixture was stirred at room temperature overnight, water was added and the mixture was extracted twice with ether. The combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated to a white solid. Purification by flash chromatography on silica gel (13:1 hexanes/EtOAc) gave **5** (107mg, 76%) as a white solid, which was further purified by recrystallization from EtOH after filtration through a 0.45mm PTFE filter: ^{1}H NMR (400 MHz, CDCl3) δ 8.44 (s, 2H), 8.29 (d, *J*=8.2Hz, 2H), 6.99 (d, *J*=8.2Hz, 2H), 4.10 (t, *J*=5.8Hz, 2H), 4.04 (t, *J*=6.2Hz, 2H), 1.83-1.30 (m, 30H), 0.91 (t, *J*=5.5Hz, 3H), 0.55 (t, *J*=7.0Hz, 2H), 0.11 (s, 9H), 0.08 (s, 6H), 0.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ160.7, 157.6, 151.1, 143.8, 129.9, 129.0, 114.4, 69.0, 68.1, 33.5, 31.8, 29.6, 29.4, 29.3, 29.1, 26.1, 25.9, 23.2, 22.7, 18.3, 14.1, 1.8, 1.3, 0.2; MS (ES) m/z 675 ($[M+H]_+$, 100), 365 (12), 337 (7); HRMS (ES) calcd for $C_{36}H_{67}N_2O_4Si_3$ ([M+H]+): 675.4409, found 675.4396.

2-(4-Octyloxyphenyl)-5-(6-(1,1,1,3,3,5,5-heptamethyltrisiloxanyl)hexyloxy)pyrimidine (6)
The procedure described for the synthesis of **5** was repeated with **14** (113 mg, 0.23 mmol) to give **6** (108 mg, 78%) as a white solid, which was further purified by recrystallization from EtOH after filtration through a 0.45mm PTFE filter: ^{1}H NMR (400 MHz, CDCl3) δ 8.44 (s, 2H), 8.29 (d, *J*=8.6Hz, 2H), 6.99 (d, *J*=8.6Hz, 2H), 4.10 (t, *J*=6.4Hz, 2H), 4.04 (t, *J*=6.4Hz, 2H), 1.83-1.31 (m, 20H), 0.91 (t, *J*=6.0Hz, 3H), 0.57 (t, *J*=7.5Hz, 2H), 0.11 (s, 9H), 0.09 (s, 6H), 0.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 157.6, 151.1, 143.8, 129.9, 129.0, 114.5, 69.0, 68.1, 33.1, 31.8, 30.9, 29.4, 29.3, 29.1, 26.1, 25.6, 23.2, 22.7, 18.2, 14.1, 1.8, 1.3, 0.2; MS (EI) m/z 604 (M_+, 100), 589 (11), 221 (54), 188 (13); HRMS (EI) calcd for $C_{31}H_{56}N_2O_4Si_3$: 604.3548, found 604.3547.

2-(4-(1-Chlorooctyloxy)phenyl)-5-(11-(1,1,1,3,3,5,5-heptamethyltrisiloxanyl) undecyloxy)pyrimidine (7)

Under an argon atmosphere, diisopropylazodicarboxylate (73 mg, 0.36 mmol) was added dropwise to a stirred solution of 8-chloro-1-octanol (54 mg, 0.33 mmol), **13** (173 mg, 0.31 mmol), and triphenylphosphine (94 mg, 0.36 mmol) in dry THF (12 mL). The mixture was stirred at room temperature for 24 h, and then concentrated to a yellow oil. Purification by flash chromatography on silica gel (4:1 hexanes/EtOAc) gave **7** (103mg, 47%) as a white solid, which was further purified by recrystallization from EtOH after filtration through a 0.45mm PTFE filter: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 2H), 8.29 (d, J=8.6Hz, 2H), 6.98 (d, J=8.6Hz, 2H), 4.09 (t, J=6.4Hz, 2H), 4.03 (t, J=6.4Hz, 2H), 3.56 (t, J=6.7Hz, 2H), 1.88 –1.30 (m, 30H), 0.54 (t, J=7.4Hz, 2H), 0.10 (s, 9H), 0.08 (s, 6H), 0.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 157.6, 151.1, 143.8, 130.1, 129.0, 114.4, 69.0, 68.0, 45.2, 33.5, 32.6, 29.6, 29.4, 29.2, 29.1, 28.8, 26.8, 26.0, 23.2, 18.3, 1.8, 1.3, 0.2; MS (ES) m/z 709 ($[M+H]^+$, 84), 528 (96), 500 (44), 345 (96), 186 (100); HRMS (ES) calcd for $C_{36}H_{66}N_2O_4Si_3Cl$ ($[M+H]^+$): 709.4018, found 709.4053.

2-[4-(1-chlorooctyloxy)phenyl]-5-[6-(1,1,1,3,3,5,5-heptamethyltrisiloxanyl)hexyloxy]pyrimidine (8)

The procedure described for the synthesis of **7** was repeated with **14** (123 mg, 0.25 mmol) to give **8** (83 mg, 52%) as a white solid, which was further purified by recrystallization from EtOH after filtration through a 0.45mm PTFE filter:: ^{1}H NMR (400 MHz, CDCl3) δ 8.43 (s, 2H), 8.29 (d, *J*=8.7Hz, 2H), 6.98 (d, *J*=8.7Hz, 2H), 4.09 (t, *J*=6.3Hz, 2H), 4.03 (t, *J*=6.3Hz, 2H), 3.55 (t, *J*=6.7Hz, 2H), 1.58 –1.40 (m, 20H), 0.57 (t, *J*=7.5Hz, 2H), 0.10 (s, 9H), 0.08 (s, 6H), 0.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 157.6, 151.1, 143.8, 130.1, 129.0, 114.4, 68.9, 68.0, 45.1, 33.1, 32.6, 29.2, 29.1, 28.8, 26.8, 26.0, 25.6, 23.2, 18.2, 1.8, 1.3, 0.2; MS (EI) m/z 638 (M^+, 24), 602 (19), 221 (100), 188 (17); HRMS (EI) calcd for $C_{31}H_{55}N_2O_4Si_3Cl$: 638.3158, found 638.3143.

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Table S1. Transition temperatures (°C) and enthalpies of transitions (J g^{-1}, in parentheses) for compounds **1a-e** and **2a-e**.

Compound	Cr		Cr'		SmC		SmA		I
1a	•	47 (78)			•	84 (14)			•
1b	•	38	•	42 (69)[a]	•	92 (17)			•
1c	•	43	•	46 (54)[a]	•	89 (16)			•
1d	•	35	•	44 (47)[a]	•	93 (18)			•
1e	•	47	•	50 (33)[a]	•	94 (20)			•
2a	•	21	•	23 (23)[a]	•	71 (1.3)	•	74 (9)	•
2b	•	26 (23)			•	75 (1.6)	•	77 (9)	•
2c	•	18 (22)			•	72 (1.6)	•	74 (7)	•
2d	•	13	•	19 (16)[a]	•	71	•	73	•
2e	•	21	•	25 (46)[a]	•	70.7[b]	•	71 (10)	•

[a] ΔH derived from overlapping peaks for Cr-Cr' and Cr'-SmC transitions. [a] Measured by polarized microscopy on cooling.

Table S2. Transition temperatures (°C) and enthalpies of transitions (J g^{-1}, in parentheses) for compounds **3-8**.

Compound	Cr		Cr'		SmC		SmA		I
3	•	48 (64)			•	89 (0.3)	•	98 (15)	•
4	•	45 (80)			•	76 (0.9)	•	85 (12)	•
5	•	32	•	35 (31)[a]	•	82 (18)			•
6	•	37 (21)			•	49 (14)			•
7	•	56 (81)			•	83 (16)			•
8	•	34 (58)			•	61 (16)			•

[a] ΔH derived from overlapping peaks for Cr-Cr' and Cr'-SmC transitions. [a] Measured by polarized microscopy on cooling.

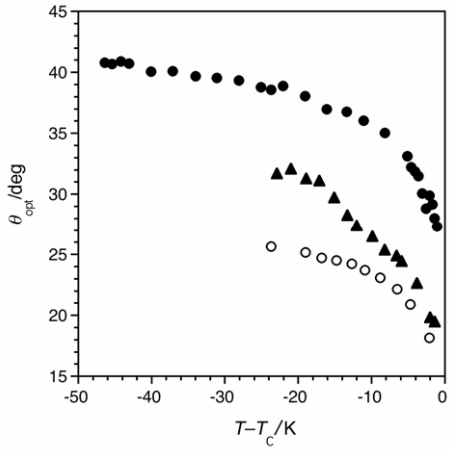

Fig. S1. Optical tilt angle θ_{opt} *vs.* reduced temperature $T–T_C$ for compounds **2b** (filled circles), **3** (open circles) and **4** (triangles).