Electronic Supplementary Information for:

Siloxane-terminated phenylpyrimidine liquid crystal hosts

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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 $\delta$ (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-$K_\alpha$ radiation, $\lambda$=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-$K_\alpha$ radiation, $\lambda$=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 an 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 $q_{\text{res}}$~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 ($9a$), 2-(4-hydroxyphenyl)-5-octyloxypyrimidine ($11b$), and 2-(4-hydroxyphenyl)-5-decyloxypyrimidine ($11d$) 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 xylene (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: 1H NMR (400 MHz, CDCl3) 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); 13C NMR (100 MHz, CDCl3) δ 63.0, 33.2, 32.7, 25.5, 23.2, 18.2, 1.8, 1.2, 0.2; 29Si NMR (99 MHz, CDCl3) 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 C13H35O3Si3 ([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 CsCO3 (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 (MgSO4) 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; 1H 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); 13C NMR (100 MHz, CDCl3) 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 (3), 132 (5), 119(14); HRMS (EI) calcd for C17H22N2O2: 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 (367 mg, 62%) as a white solid: mp 114-115°C; 1H 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); 13C NMR (100 MHz, CDCl3) δ 158.3, 157.6, 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 C19H26N2O2: 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 (490 mg, 64%) as a white solid: mp 74-75°C; 1H 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); 13C NMR (100 MHz, CDCl3) 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 C22H32N2O2: 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 0.45 mm PTFE filter: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.44 (s, 2H), 8.29 (d, $J$=8.0 Hz, 2H), 6.99 (d, $J$=8.0 Hz, 2H), 4.10 (t, $J$=6.4 Hz, 2H), 4.04 (t, $J$=6.6 Hz, 2H), 1.84-1.30 (m, 28H), 0.92 (t, $J$=6.2 Hz, 3H), 0.55 (t, $J$=7.3 Hz, 2H), 0.11 (s, 9H), 0.08 (s, 6H), 0.04 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 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) calcld for C$_{35}$H$_{64}$N$_2$O$_4$Si$_3$: 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 0.45 mm PTFE filter: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.43 (s, 2H), 8.29 (d, $J$=8.5 Hz, 2H), 6.98 (d, $J$=8.5 Hz, 2H), 4.09 (t, $J$=6.3 Hz, 2H), 4.03 (t, $J$=6.4 Hz, 2H), 1.90-1.31 (m, 30H), 0.91 (t, $J$=7.0 Hz, 3H), 0.54 (t, $J$=7.6 Hz, 2H), 0.10 (s, 9H), 0.07 (s, 6H), 0.03 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 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) calcld for C$_{36}$H$_{66}$N$_2$O$_4$Si$_3$: 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 0.45 mm PTFE filter: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.44 (s, 2H), 8.29 (d, $J$=8.5 Hz, 2H), 6.99 (d, $J$=8.5 Hz, 2H), 4.10 (t, $J$=6.6 Hz, 2H), 4.04 (t, $J$=6.6 Hz, 2H), 1.83-1.30 (m, 32H), 0.91 (t, $J$=7.0 Hz, 3H), 0.55 (t, $J$=7.0 Hz, 2H), 0.11 (s, 9H), 0.07 (s, 6H), 0.03 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 160.8, 157.6, 151.1, 143.8, 130.1, 129.0, 114.4, 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) calcld for C$_{37}$H$_{68}$N$_2$O$_4$Si$_3$: 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 0.45 mm PTFE filter: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.44 (s, 2H), 8.29 (d, $J$=8.6 Hz, 2H), 6.99 (d, $J$=8.6 Hz, 2H), 4.10 (t, $J$=6.4 Hz, 2H), 4.04 (t, $J$=6.6 Hz, 2H), 1.83-1.30 (m, 34H), 0.91 (t, $J$=6.2 Hz, 3H), 0.55 (t, $J$=7.3 Hz, 2H), 0.11 (s, 9H), 0.08 (s, 6H), 0.04 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 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 702 (M-, 81), 687 (34), 221 (100), 188 (50); HRMS (EI) calcld for C$_{38}$H$_{70}$N$_2$O$_4$Si$_3$: 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 0.45 mm PTFE filter: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.45 (s, 2H), 8.30 (d, $J$=8.6 Hz, 2H), 6.99 (d, $J$=8.6 Hz, 2H), 4.10 (t, $J$=6.6 Hz, 2H), 4.03 (t, $J$=6.6 Hz,
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: 1H 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); 13C NMR (100 MHz, CDCl3) 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, 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 C30H55N2O4Si3 ([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: 1H 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); 13C NMR (100 MHz, CDCl3) 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 C31H57N2O4Si3 ([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: 1H 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); 13C NMR (100 MHz, CDCl3) 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 C32H59N2O4Si3 ([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: 1H 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); 13C NMR (100 MHz, CDCl3) 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 C33H60N2O4Si3: 632.3861, found 632.3850.
2-(4-(6-(1,1,1,3,3,5,5-Heptamethyltrisiloxanyl)hexyloxy)phenyl)-5-dodecyloxy pyrimidine (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 0.45 mm PTFE filter: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.43 (s, 2H), 8.29 (d, \(J=8.6\) Hz, 2H), 6.99 (d, \(J=8.6\) Hz, 2H), 4.10 (t, \(J=6.4\) Hz, 2H), 4.04 (t, \(J=6.4\) Hz, 2H), 1.83-1.29 (m, 28H), 0.90 (t, \(J=6.3\) Hz, 3H), 0.57 (t, \(J=7.5\) Hz, 2H), 0.11 (s, 9H), 0.09 (s, 6H), 0.05 (s, 6H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 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, 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\(_2\)O\(_4\)Si\(_3\) ([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, CDCl\(_3\)) \(\delta\) 8.43 (s, 2H), 8.13 (d, \(J=8.6\) Hz, 2H), 6.85 (d, \(J=8.6\) Hz, 2H), 4.06 (t, \(J=6.3\) Hz, 2H), 3.54 (t, \(J=6.7\) Hz, 2H), 1.84-1.36 (m, 12H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 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\(_2\)O\(_2\)Cl: 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 0.45 mm PTFE filter: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.43 (s, 2H), 8.28 (d, \(J=8.8\) Hz, 2H), 6.98 (d, \(J=8.8\) Hz, 2H), 4.09 (t, \(J=6.4\) Hz, 2H), 4.03 (t, \(J=6.4\) Hz, 2H), 3.54 (t, \(J=6.7\) Hz, 2H), 1.84-1.36 (m, 28H), 0.54 (t, \(J=7.6\) Hz, 2H), 0.10 (s, 9H), 0.07 (s, 6H), 0.03 (s, 6H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 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\(_2\)O\(_4\)Si\(_3\)Cl: 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 0.45 mm PTFE filter: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.41 (s, 2H), 8.24 (d, \(J=8.9\) Hz, 2H), 6.97 (d, \(J=8.9\) Hz, 2H), 4.07 (t, \(J=6.4\) Hz, 2H), 4.01 (t, \(J=6.4\) Hz, 2H), 3.54 (t, \(J=6.7\) Hz, 2H), 2.20-1.38 (m, 20H), 0.55 (t, \(J=7.7\) Hz, 2H), 0.08 (s, 9H), 0.06 (s, 6H), 0.02 (s, 6H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 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\(_2\)O\(_4\)Si\(_3\)Cl: 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) $\delta$ 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, CDCl3) $\delta$ 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$_2$O$_4$Si$_3$: 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) $\delta$ 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, CDCl3) $\delta$ 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$_2$O$_4$Si$_3$: 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) $\delta$ 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, CDCl3) $\delta$ 160.7, 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]+), 365 (12), 337 (7); HRMS (ES) calcd for C$_{36}$H$_{67}$N$_2$O$_4$Si$_3$ ([M+H]+): 675.4409, found 675.4396.

2-(4-Octyloxyphenyl)-5-[11-(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) $\delta$ 8.44 (s, 2H), 8.29 (d, $J$=8.2Hz, 2H), 6.99
(d, $J$=8.6Hz, 2H), 4.10 (t, $J$=6.4Hz, 2H), 4.04 (t, $J$=6.4Hz, 2H), 1.83-1.30 (m, 30H), 0.91 (t, $J$=6.0Hz,
3H), 0.57 (t, $J$=7.5Hz, 2H), 0.11 (s, 9H), 0.08 (s, 6H), 0.04 (s, 6H); $^{13}$C NMR (100 MHz, CDCl3) $\delta$
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, 25.9, 23.2,
22.7, 18.2, 14.1, 1.8, 1.3, 0.2; MS (ES) m/z 604 (M+, 100), 589 (11), 221 (54), 188 (13); HRMS (ES) calcd for
C$_{31}$H$_{56}$N$_2$O$_4$Si$_3$: 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: 1H NMR (400 MHz, CDCl3) 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); 13C NMR (100 MHz, CDCl3) 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 C36H66N2O4Si3Cl ([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: 1H 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); 13C NMR (100 MHz, CDCl3) 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 C31H55N2O4Si3Cl: 638.3158, found 638.3143.

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

<table>
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<th>Compound</th>
<th>Cr</th>
<th>Cr'</th>
<th>SmC</th>
<th>SmA</th>
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<tr>
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<td>47 (78)</td>
<td>•</td>
<td>84 (14)</td>
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<tr>
<td>1b</td>
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<td>•</td>
<td>46 (54)ᵃ</td>
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<td>•</td>
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<tr>
<td>1e</td>
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<td>47</td>
<td>•</td>
<td>50 (33)ᵃ</td>
<td>94 (20)</td>
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<tr>
<td>2a</td>
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<tr>
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<td>72 (1.6)</td>
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<td>19 (16)ᵃ</td>
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<tr>
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<td>21</td>
<td>•</td>
<td>25 (46)ᵃ</td>
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ᵃ ΔH derived from overlapping peaks for Cr-Cr' and Cr'-SmC transitions. ᵇ Measured by polarized microscopy on cooling.

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

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<th>Cr'</th>
<th>SmC</th>
<th>SmA</th>
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<tr>
<td>3</td>
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<td>48 (64)</td>
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<td>89 (0.3)</td>
<td>98 (15)</td>
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<tr>
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<td>85 (12)</td>
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<td>5</td>
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<td>32</td>
<td>•</td>
<td>35 (31)ᵃ</td>
<td>82 (18)</td>
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<td>49 (14)</td>
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ᵃ ΔH derived from overlapping peaks for Cr-Cr' and Cr'-SmC transitions. ᵇ Measured by polarized microscopy on cooling.

**Fig. S1.** Optical tilt angle θopt vs. reduced temperature $T-T_C$ for compounds 2b (filled circles), 3 (open circles) and 4 (triangles).