Electronic Supplementary Information for:

Design of liquid crystals with 'de Vries-like' properties: structural variants of carbosilane-terminated 5-phenylpyrimidine mesogens.

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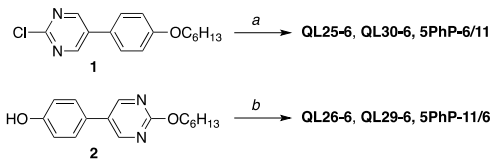
EXPERIMENTAL

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 LV100N-CH 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. 2,2,4,4,6-Pentamethyl-2,4,6-trisilaheptane, 2,2,4-trimethyl-2,4-disilapentane, 2-chloro-5-(4-hexyloxyphenyl)pyrimidine (**1**) and 4-(2-hexyloxypyrimid-5-yl)phenol (**2**) and, were prepared according to literature procedures and shown to have the expected physical and spectral properties.[1, 2]

Conformational analyses. Conformational analyses were performed using DFT at the B3LYP/6-31G* level on 2,2,4,4,6,6-hexamethyl-2,4,6-trisiladecane to using the Spartan '16 software package (Wavefunction Inc.). For each structure, a restricted hybrid HF-DFT SCF

calculation was performed using Pulay DIIS + Geometric Direct Minimization. Comformational energy profiles were obtained by constraining a particular torsional angle and minimizing the structure, repeating the process every 10 degrees over a 180 degree rotation.



Scheme. *Reagents and conditions*: (a) (i) 12,12,14,14-Tetramethyl-12,14-disilapentadecan-1-ol (**QL25-6**) or 12,14,14-trimethyl-12-(trimethylsilylmethyl)-12,14-disilapentadecan-1-ol (**QL30-6**) or 1-undecanol (**5PhP-6/11)**, NaH, THF, (ii) H_3O^+; (b) (11-bromoundecyl)trimethylsilane (**QL26-6**) or 1-bromo-12,14,14-trimethyl-12-(trimethylsilylmethyl)-12,14-disilapentadecane (**QL29-6**) or 1-bromoundecane (**5PhP-11/6**), Cs_2CO_3, acetone.

2,2,4,6,6-pentamethyl-2,4,6-trisilaheptasilane. A modification of the procedure by Zhang et al. was used.[1] Under a nitrogen atmosphere, a solution of chloromethyltrimethylsilane (10.2 g, 82.9 mmol) in dry THF (20 mL) was added to a suspension of Mg turnings (2.2 g, 91.2 mmol) in dry THF (60 mL) at such a rate as to initiate and maintain reflux. The mixture was heated to reflux for 6 h and then cooled to room temperature. Dichloromethylsilane (5.3 g, 45.6 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 2,2,4,6,6-pentamethyl-2,4,6-trisilaheptasilane (3.25 g, 33%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.02 (sex, J = 7.2, 3.5 Hz, 1H), 0.16 (d, J = 2.8 Hz, 3H) 0.11 (d, J = 3.5 Hz, 4H), 0.04 (s, 18H).

12,12,14,14-Tetramethyl-12,14-disilapentadecan-1-ol (3). To a mixture of 11-undecen-1-ol (1.99 g, 11.67 mmol) and 2,2,4-trimethyl-2,4-disilapentane (2.05 g, 14.00 mmol) heated to 40 °C was added Karstedt's catalyst (~2 mol%, 0.1 mL). The mixture was stirred at 40 °C for 2 h. Purification by flash chromatography on silica gel (4:1 hexane/EtOAc) gave **3** (1.64 g, 44%) as a colourless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.65 (m, 2H), 1.54-1.61 (m, 2H), 1.24-1.40 (m, 16H), 0.46-0.50 (m, 2H), 0.02 (s, 9H), 0.00 (s, 6H), –0.29 (s, 2H).

1-Bromo-12,14,14-trimethyl-12-(trimethylsilylmethyl)-12,14-disilapentadecane (4). The procedure described for the synthesis of **3** was repeated with 11-bromoundecene (4.56 g, 20.85 mmol) and 2,2,4,6,6-pentamethyl-2,4,6-trisilaheptasilane (4.05 g, 17.4 mmol) to give **4** (2.3 g, 25%) as a colourless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.42 (t, J = 6.8 Hz, 2H), 1.83-1.90 (m, 2H), 1.40-1.48 (m, 2H), 1.23-1.36 (m, 14H), 0.47-0.51 (m, 2H), 0.04 (s, 3H), 0.03 (s, 18H), –0.27 (s, 4H).

12,14,14-Trimethyl-12-(trimethylsilylmethyl)-12,14-disilapentadecan-1-ol (5). The procedure described for the synthesis of **3** was repeated with 11-undecen-1-ol (2.1 g, 12.4 mmol) and 2,2,4,6,6-pentamethyl-2,4,6-trisilaheptasilane (3.25 g, 14.9 mmol) to give **5** (1.26 g, 26%) as a colourless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.58 (t, J = 6.6 Hz, 2H), 1.34-1.62 (m, 4H), 1.19-1.39 (m, 15H), 0.47-0.51 (m, 2H), 0.05 (s, 3H), 0.03 (s, 18H), –0.27 (s, 4H).

(11-Bromoundecyl)trimethylsilane (6). To a mixture of 11-bromo-1-undecene (3.1 g, 13.34 mmol) and chlorodimethylsilane (1.5 g, 16.0 mmol) heated to 40 °C was added Karstedt's

catalyst (~2 mol%, 0.1 mL) and the mixture was stirred at 40 °C for 2 h. The mixture was diluted with dry THF (20 mL) under argon and methylmagnesium bromide (3M solution in THF, 14.6 mmol, 5 mL) was added dropwise. The mixture was stirred at room temperature for 2 h and then heated to reflux for 2 h. The mixture was quenched with water (100 mL) before adding hexane (50 mL). The layers were separated and the aqueous layer extracted with hexane (3 × 15 mL). The combined organic layers were dried ($MgSO_4$), concentrated and the residue purified by flash chromatography on silica gel (hexane) to give **6** (3.24 g, 79%) as a colourless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.41 (t, J = 6.9 Hz, 2H), 1.83-1.90 (m, 2H), 1.40-1.47 (m, 2H), 1.25-1.35 (m, 14H), 0.46-0.50 (m, 2H), –0.02 (s, 9H).

5-(4-Hexyloxyphenyl)-2-(12,12,14,14-tetramethyl-12,14-disilapentadecyloxy)-pyrimidine (QL25-6). To a suspension of NaH (60% suspension in mineral oil, 88 mg, 2.2 mmol) in dry THF (10 mL) kept under argon was added **3** (0.26 g, 0.83 mmol). The mixture was stirred at room temperature for 30 min, then cooled to 0 °C and a solution of **1** (0.16 g, 0.55 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), water (20 mL) and the mixture was extracted with ethyl acetate (3 × 15 mL). The combined extracts were washed with brine (40 mL), dried ($MgSO_4$), concentrated, and the residue purified by flash chromatography on silica gel (7:1 hexane/EtOAc) to give **QL25-6** (0.27 g, 90%) as a white solid which was further purified by recrystallization from ethanol, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (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), 1.45-1.53 (m, 4H), 1.24-1.42 (m, 18H), 0.92 (t, J = 7.2 Hz, 3H), 0.46-0.52 (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, 29.63, 29.60, 29.5, 29.3, 29.1, 28.9, 25.9, 25.7, 23.9, 22.5, 17.9, 14.0, 2.5, 1.4, –0.5; LRMS (EI) *m/z* 570 (M^+, 100), 272 (31); HRMS (EI) *m/z* calcd for $C_{33}H_{58}N_2O_2Si_2$ 570.4037, found 570.4029.

Anal. calcd for $C_{33}H_{58}N_2O_2Si_2$: C, 69.41; H, 10.24; N, 4.91. Found: C, 69.04; H, 9.91; N, 5.00.

2-Hexyloxy-5-(4-(11-(trimethylsilyl)undecyloxy)phenyl)pyrimidine (QL26-6). To a solution of **2** (0.20 g, 0.73 mmol) and Cs_2CO_3 (1.02 g, 2.90 mmol) in acetone (20 mL) was added **6** (0.89 g, 2.90 mmol). The reaction mixture was heated to reflux for 24 h, then cooled to room temperature, filtered and concentrated. The residue was dissolved in DCM (20 mL), washed with 1M aq HCl (20 mL), brine (20 mL), dried (MgSO4) and concentrated. Purification by flash chromatography on silica gel (8:1 hexane/EtOAc) gave **QL26-6** (0.32 g, 87%) as a white solid which was further purified by recrystallization from ethanol; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 2H), 7.43 (d, J = 8.6 Hz, 2H), 7.02 (d, J = 8.6 Hz, 2H), 4.45 (t, J = 6.7 Hz, 2H), 4.05 (t, J = 6.6 Hz, 2H), 1.82-1.95 (m, 4H), 1.49-1.51 (m, 4H), 1.24-1.45 (m, 18H), 0.92 (t, J = 7.3 Hz, 3H), 0.49-0.51 (m, 2H), 0.00 (s, 9H); ^{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, 31.5, 29.6, 29.58, 29.55, 29.3, 29.2, 28.8, 26.0, 25.6, 23.9, 22.6, 16.6, 14.0, -1.6; LRMS (EI) *m/z* 498 (M^+, 62), 188 (16), 73 (100); HRMS (EI) *m/z* calcd for $C_{30}H_{50}N_2O_2Si$ 498.3642, found 498.3658.

Anal. calcd for $C_{30}H_{50}N_2O_2Si$: C, 72.24; H, 10.10; N, 5.62. Found: C, 72.52; H, 10.34; N, 5.72.

2-Hexyloxy-5-(4-(12-(trimethylsilylmethyl)-12,14,14-trimethyl-12,14-disilapentadecyl-oxy)phenyl)pyrimidine (QL29-6). The procedure described for the synthesis of **QL26-6** was repeated with **2** (0.21 g, 0.77 mmol) and **4** (0.52 g, 1.16 mmol). The reaction mixture was heated

to reflux for 24 h, then cooled to room temperature and filtered. Purification by flash chromatography on silica gel (10:1 hexane/EtOAc) gave **QL29-6** (0.32 g, 64%) as a white solid which was further purified by recrystallization from ethanol: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (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), 1.78-1.88 (m, 4H), 1.44-1.54 (m, 4H), 1.24-1.39 (m, 22H), 0.91 (t, J = 6.7 Hz, 3H), 0.48-0.52 (m, 2H), 0.05 (s, 3H) 0.03 (s, 18H) –0.27 (s, 4H); ^{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, 33.8, 31.5, 29.59, 29.56, 29.3, 29.2, 28.8, 26.0, 25.6, 24.0, 22.6, 18.7, 14.0, 3.6, 1.5, 0.4; LRMS (EI) *m/z* 642 (M^+, 46), 498 (63), 217 (78), 129 (76), 73 (100); HRMS (EI) *m/z* calcd for $C_{36}H_{66}N_2O_2Si_3$ 642.4432, found 642.4456.

Anal. calcd for $C_{36}H_{66}N_2O_2Si_3$: C, 67.23; H, 10.34; N, 4.36. Found: C, 67.14; H, 10.61; N, 4.38.

5-(4-Hexyloxyphenyl)-2-(12-(trimethylsilylmethyl)-12,14,14-trimethyl-12,14-disilapentadecyloxy)pyrimidine (QL30-6). The procedure described for the synthesis of **QL25-6** was repeated with **5** (0.11 g, 0.28 mmol) and **1** (0.051 g, 0.19 mmol) to give **QL30-6** (0.53 g, 92%) as a white solid which was further purified by recrystallization from ethanol; ^{1}H NMR δ (400 MHz, $CDCl_3$) ^{1}H NMR δ (400 MHz, $CDCl_3$) 8.67 (2H, s), 7.43 (2H, d, J 8.8), 7.00 (2H, d, J 8.8), 4.39 (2H, t, J 6.6), 4.01 (2H, t, J 6.4), 1.82 (4H, m), 1.48 (4H, m), 1.26-1.37 (18H, m), 0.91 (3H, t, J 6.8), 0.48 (2H, m), 0.05 (6H, s), 0.00-0.03 (22H, m), -0.28 (3H, s); ^{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, 33.8, 31.5, 29.6, 29.5, 29.3, 29.1, 28.9, 25.9, 25.6, 24.0, 22.5, 18.7, 14.0, 3.6, 1.5, 0.4; HRMS (EI) *m/z* calcd for $C_{36}H_{66}N_2O_2Si_3$ 642.4432, found 642.4433.

Anal. calcd for $C_{36}H_{64}N_2O_3Si_3$: C, 67.23; H, 10.34; N, 4.36. Found: C, 67.55; H, 10.44; N, 4.39.

2-Hexyloxy-5-(4-undecyloxyphenyl)pyrimidine (5PhP-11/6). To a solution of **2** (0.12 g, 0.44 mmol) and Cs_2CO_3 (0.43 g, 1.32 mmol) in acetone (15 mL) was added 1-bromoundecane (0.21 g, 0.88 mmol). The reaction mixture was heated to reflux for 24 h, then cooled to room temperature, filtered and concentrated. The residue was dissolved in DCM (20 mL), washed with 1M aq HCl (20 mL), brine (20 mL), dried ($MgSO_4$) and concentrated. Purification by flash chromatography on silica gel (4:1 hexane/EtOAc) gave **5PhP-11/6** (0.17 g, 89%) as a white solid which was further purified by recrystallization from ethanol; ^{1}H NMR δ (400 MHz, $CDCl_3$) 8.66 (s, 2H), 7.43 (d, J = 8.6 Hz, 2H), 7.05 (d, J = 8.6 Hz, 2H), 4.39 (t, J = 6.7 Hz, 2H), 4.00 (d, J = 6.6 Hz, 2H), 1.78-1.88 (m, 4H), 1.44-1.54 (m, 4H), 1.25-1.41 (m, 18H), 0.88-0.93 (m, 6H); **^{13}C NMR** δ (101 MHz, $CDCl_3$) 164.4, 159.3, 156.7, 127.8, 127.5, 126.6, 115.2, 68.1, 67.8, 31.8, 31.5, 29.56, 29.54, 29.36, 29.31, 29.1, 28.8, 25.9, 25.6, 22.6, 22.5, 14.08, 14.01; LRMS (EI) *m/z* 426 (M^+, 100), 342 (48), 188 (38); HRMS (EI) *m/z* calcd for $C_{27}H_{42}N_2O_2$ 426.3246, found 426.3241.

Anal. calcd for $C_{27}H_{42}N_2O_2$: C, 76.01; H, 9.92; N, 6.57. Found: C, 76.19; H, 10.10; N, 6.97.

5-(4-Hexyloxyphenyl)-2-undecyloxypyrimidine (5PhP-6/11). To a suspension of NaH (60% suspension in mineral oil, 88 mg, 2.2 mmol) in dry THF (10 mL) kept under argon was added 1-undecanol (0.38 g, 2.20 mmol). The mixture was stirred at room temperature for 30 min, then cooled to 0 °C and a solution of **1** (0.15 g, 0.55 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), water (20 mL) and the mixture was extracted with ethyl acetate (3 × 15 mL). The combined extracts were washed with brine (20 mL), dried ($MgSO_4$), concentrated, and the residue purified by flash chromatography on silica gel (4:1

hexane/EtOAc) to give **5PhP-6/11** (0.21 g, 91%) as a white solid which was further purified by recrystallization from ethanol; ^{1}H NMR δ (400 MHz, $CDCl_3$) 8.67 (s, 2H), 7.43 (d, J = 8.8 Hz, 2H), 7.01 (d, J = 8.8 Hz, 2H), 4.39 (t, J = 6.7 Hz, 2H), 4.01 (t, J = 6.6 Hz, 2H), 1.78-1.88 (m, 4H), 1.45-1.54 (m, 4H), 1.25-1.39 (m, 18H), 0.87-0.94 (m, 6H); ^{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, 31.8, 31.5, 29.59, 29.56, 29.36, 29.32, 29.18, 28.9, 25.9, 25.6, 22.6, 22.5, 14.09, 14.01; HRMS (EI) *m/z* calcd for $C_{27}H_{42}N_2O_2$ 426.3426, found 426.3424.

Anal. calcd for $C_{27}H_{42}N_2O_2$: C, 76.01; H, 9.92; N, 6.57. Found: C, 76.18; H, 10.11; N, 6.76.

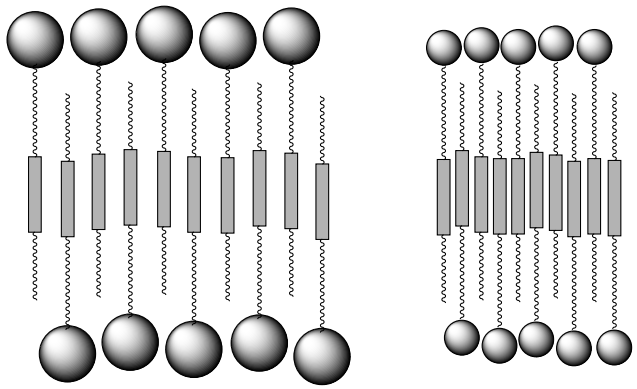


Figure S1. Schematic representation of partially intercalated bilayers formed by tricarbosilane-terminated mesogens (left) and monocarbosilane-terminated mesogens (right), illustrating the effect of end-group steric repulsion on free volume formation in the hydrocarbon sub-layer.

References

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