Electronic Supplementary Information for:

Tuning 'de Vries-like' properties in binary mixtures of liquid crystals with different molecular lengths

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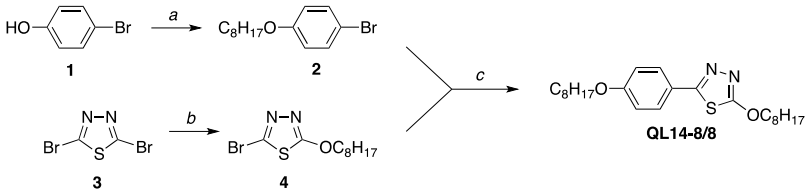
A. EXPERIMENTAL

General

^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance 400 spectrometer; chemical shifts (δ) are reported in parts per million (ppm) relative to TMS. Mass spectra were recorded using Waters/Micromass GC-TOF (low- and high-resolution) and Applied Biosystems/MDS Sciex QSTAR XL QTOF (low-resolution) instruments in electron ionization (EI) mode. Elemental analyses were performed on a Thermo Flash 2000 CHNS analyzer. Differential scanning calorimetry (DSC) analyses were performed using a TA Instruments Q2000 instrument with a scanning rate of 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. Small-angle X-ray scattering experiments were performed on a SAXSess system from Anton Paar GmbH. Unaligned samples (filled into Hilgenberg Mark capillary tubes of 0.7 mm diameter) were mounted in a temperature controlled sample holder unit (TSC 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. Chemicals were obtained from commercial sources unless otherwise noted. 2,2,4,4,6-Pentamethyl-2,4,6-trisilaheptane,[1] and 2,5-dibromo-1,3,4-thiadiazole (**3**)[2, 3] were prepared according to literature procedures and shown to have the expected physical and spectral properties.

Synthesis



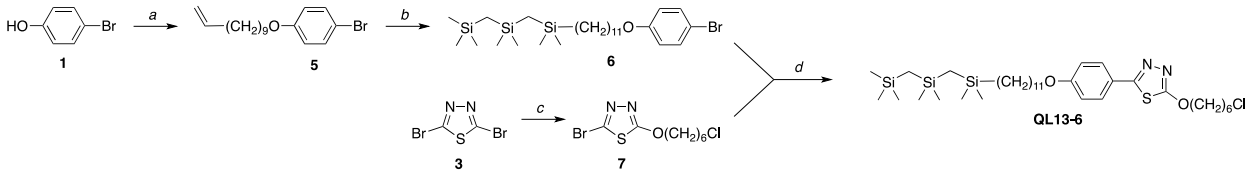
Scheme S1. *Reagents and conditions*: (a) $CH_3(CH_2)_7OH$, DIAD, Ph_3P, THF; (b) $CH_3(CH_2)_7OH$, NaH, CuO, KI, THF; (c) *n*-BuLi, $ZnCl_2$(TMEDA), $Pd(PPh_3)_4$, THF.

2-Bromo-5-octyloxy-1,3,4-thiadiazole (4). A mixture of 1-octanol (0.65 g, 5.0 mmol) and NaH (60% oil suspension, 0.20 g, 5.0 mmol) in dry THF (10 mL) was stirred for 1 h, and a

mixture of KI (8 mg, 0.048 mmol), CuO (0.14 g, 1.7 mmol) and **3** (1.22 g, 5.0 mmol) was added with dry THF (20 mL) to ensure complete transfer. The solution was refluxed for 72 h, then diluted with CH_2Cl_2, filtered through a pad of silica gel and washed with EtOAc. The filtrate was concentrated and the residue was purified by flash chromatography on silica gel (10% EtOAc/hexanes) to give **4** (0.59 g, 40%) as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.54 (t, J = 6.5 Hz, 2H), 1.76-1.94 (m, 2H), 1.17-1.54 (m, 10H), 0.89 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 130.5, 73.8, 31.7, 29.1, 28.6, 25.6, 22.6, 14.0; MS (ESI) *m/z* 295 ([(M+2)+H]$^+$, 21), 293 ([M+H]$^+$, 20); HRMS (ESI) *m/z* calcd for $C_{10}H_{18}N_2OS^{79}Br$ ([M+H]$^+$) 293.0318, found 293.0314.

2-Octyloxy-5-(4-octyloxyphenyl)-1,3,4-thiadiazole (QL14-8/8). A flame-dried 100 mL flask was charged with 1-bromo-4-octyloxybenzene (**2**) (0.43 g, 1.5 mmol) and dry THF (50 mL) under N_2 and cooled to –78 °C. A 1.6 M solution of *n*-BuLi in hexanes (1.05 mL, 1.68 mmol) was then added by syringe. After stirring for 1 h at –78 °C, $ZnCl_2$(TMEDA) (0.42 g, 1.55 mmol) was added and the reaction mixture was allowed to warm to room temperature. $Pd(PPh_3)_4$ (0.09 g, 0.75 mmol) and **4** (0.45 g, 1.55 mmol) were then added and the mixture was stirred and heated to reflux overnight. After cooling, the mixture was filtered through a pad of silica gel and washed with CH_2Cl_2. The filtrate was concentrated and the residue was purified by flash chromatography on silica gel (10% EtOAc/hexanes) to give **QL14-8/8** as white solid (0.25 g, 40%). Recrystallization from HPLC-grade ethanol (3×) gave a white solid with sharp phase transitions: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.6 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 4.54 (t, J = 6.6 Hz, 2H), 4.00 (t, J = 6.6 Hz, 2H), 1.74-1.91 (m, 4H), 1.21-1.53 (m, 20H), 0.89 (t, J = 6.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 162.1, 161.0, 128.5, 123.3, 114.8, 73.4, 68.2, 31.8, 29.3-29.1 (several overlapping peaks), 28.8, 26.0, 25.7, 22.6, 14.1; MS (EI) *m/z* 418 (M$^+$, 57), 307 (26), 306 (100), 194 (100), 137 (25), 134 (26), 120 (11), 57 (15), 55 (10); HRMS (EI) *m/z* calcd for $C_{24}H_{38}N_2O_2S$ 418.2654, found 418.2661.

Anal. Calcd for $C_{24}H_{38}N_2O_2S$: C, 68.86; H, 9.15; N, 6.69; S, 7.66. Found: C, 68.67; H, 9. 20; N, 6.79; S, 7.80.



Scheme S2. *Reagents and conditions*: (a) CH_2=$CH(CH_2)_9OH$, DIAD, Ph_3P, THF; (b) 2,2,4,4,6-pentamethyl-2,4,6-trisilaheptane, Karsted's catalyst, toluene; (c) $Cl(CH_2)_6OH$, NaH, CuO, KI, THF; (d) *n*-BuLi, $ZnCl_2$(TMEDA), $Pd(PPh_3)_4$, THF.

1-Bromo-4-(10-undecenyloxy)benzene (5). Under an N_2 atmosphere, DIAD (2.48 g, 2.40 mL, 12 mmol) was added to a solution of 10-undecenol (1.70 g, 10 mmol), 4-bromophenol (1.73 g, 10 mmol) and triphenylphosphine (3.41 g, 13 mmol) in dry THF (100 mL). The yellow solution was stirred overnight at room temperature, then concentrated and purified by flash chromatography on silica gel (hexanes) to give **5** (2.34 g, 72%) as clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.8 Hz, 2H), 6.78 (d, J = 8.8 Hz, 2H), 5.76-5.90 (m, 1H), 4.91-5.07 (m, 2H), 3.92 (t, J = 6.6 Hz, 2H), 2.06 (q, J = 6.8 Hz, 2H), 1.78 (dt, J = 6.8, 14.5 Hz, 2H), 1.21-1.52

(m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 139.2, 132.2, 116.3, 114.1, 112.5, 68.3, 33.8, 29.5-28.9 (several overlapping peaks), 26.0; MS (EI) *m/z* 326 ($[M+2]^+$, 26), 324 (M^+, 27), 174 (97), 172 (100), 86 (14), 84 (23), 69 (14), 67 (10), 55 (35); HRMS (EI) calcd for $C_{17}H_{25}O^{79}Br$ 324.1089, found 324.1077.

1-Bromo-4-(12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecyloxy)benzene (6). Under an Ar atmosphere, a 3 wt% solution of platinum(0)-1,3-divinyl-1,1,3,3-tetramethyl-disiloxane complex in xylenes (Karsted's catalyst, 0.5 mL, 0.5 mmol) was added to a solution of **5** (1.63 g, 5.0 mmol), and 2,2,4,4,6-pentamethyl-2,4,6-trisilaheptane (1.42 g, 6.5 mmol) in toluene (50 mL). The mixture was stirred at room temperature for 72 h, then concentrated and the residue purified by flash chromatography on silica gel (hexanes) to give **6** (1.77 g, 65%) as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.8 Hz, 2H), 6.78 (d, J = 8.8 Hz, 2H), 3.92 (t, J = 6.6 Hz, 2H), 1.71-1.84 (m, 2H), 1.40-1.51 (m, 2H), 1.22-1.40 (m, 14H), 0.49 (t, J = 8.6 Hz, 2H), 0.06 (s, 6H), 0.04 (s, 9H), 0.01 (s, 6H), –0.24 (s, 2H), –0.27 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 132.2, 116.3, 112.6, 68.3, 33.7, 29.6-29.2 (several overlapping peaks), 26.0, 24.0, 18.0, 5.8, 4.1, 2.5, 1.5, –0.4; MS (EI) *m/z* 544 ($[M+2]^+$, 8), 542 (M^+, 7), 376 (12), 375 (37), 374 (11), 373 (33), 303 (20), 301 (18), 219 (14), 218 (25), 217 (100), 174 (17), 172 (18), 145 (15), 131 (14), 130 (12), 129 (71), 73 (58), 59 (11); HRMS (EI) calcd for $C_{26}H_{51}O^{79}BrSi_3$ 542.2431, found 542.2449.

2-Bromo-5-(6-chlorohexyloxy)-1,3,4-thiadiazole (7). The procedure used for the preparation of **4** was repeated with **3** (1.22 g, 5 mmol) and 6-chloro-1-hexanol (0.68 g, 5 mmol). The crude product was purified by flash chromatography on silica gel (10% EtOAc/hexanes) to give **7** (0.64 g, 43%) as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.53 (t, J = 6.3 Hz, 2H), 3.54 (t, J = 6.6 Hz, 2H), 1.72-2.35 (m, 4H), 1.39-1.73 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 130.6, 73.4, 44.8, 32.3, 28.5, 26.4, 25.0; MS (ESI) *m/z* 303 ($[(M+4)+H]^+$, 5), 301 ($[(M+2)+H]^+$, 16), 299 ($[M+H]^+$, 13), 183 (100); HRMS (ESI) *m/z* calcd for $C_8H_{13}N_2OS^{35}Cl^{79}Br$ ($[M+H]^+$) 298.9615, found 298.9626.

2-(6-Chlorohexyloxy)-5-(4-(12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecyl-oxy)phenyl)-1,3,4-thiadiazole (QL13-6). The procedure used for the preparation of **QL14-8/8** was repeated with **6** (0.82g, 1.5 mmol) and **7** (0.51 g, 1.55 mmol). The crude product was purified by flash chromatography on silica gel (10% EtOAc/hexanes) to give **QL13-6** as a white solid (0.36 g, 35%). Recrystallization from HPLC-grade ethanol (3×) gave a white solid with sharp phase transitions: ^{1}H NMR (400 MHz $CDCl_3$) δ 7.75 (d, J = 8.8 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 4.56 (t, J = 6.6 Hz, 2H), 4.00 (t, J = 6.6 Hz, 2H), 3.56 (t, J = 6.6 Hz, 2H), 1.72-1.99 (m, 6H), 1.40-1.62 (m, 6H), 1.10-1.40 (m, 14H), 0.49 (t, J = 8.8 Hz, 2H), 0.05 (s, 6H), 0.03 (s, 9H), 0.00 (s, 6H), –0.25 (s, 2H), –0.27 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 162.2, 161.1, 128.5, 123.3, 114.9, 73.0, 68.2, 44.9, 33.7, 32.4, 29.6-29.5 (several overlapping peaks), 29.4, 29.1, 28.6, 26.5, 26.0, 25.1, 24.0, 18.0, 5.8, 4.0, 2.5, 1.5, –0.4; MS (EI) *m/z* 684 ($[M+2]^+$, 60), 682 (M^+, 100), 667 (73), 595 (34), 550 (44), 549 (98), 541 (47), 530 (35), 528 (67), 523 (40), 477 (39), 465 (35), 217 (78), 145 (45), 129 (86), 73 (57); HRMS (EI) calcd for $C_{34}H_{63}N_2O_2SSi_3{}^{35}Cl$ 682.3607, found 682.3633.

Anal. Calcd for $C_{34}H_{63}N_2O_2SSi_3Cl$: C, 59.73; H, 9.29; N, 4.10; S, 4.69. Found: C, 59.55; H, 9.32; N, 4.19; S, 4.51.

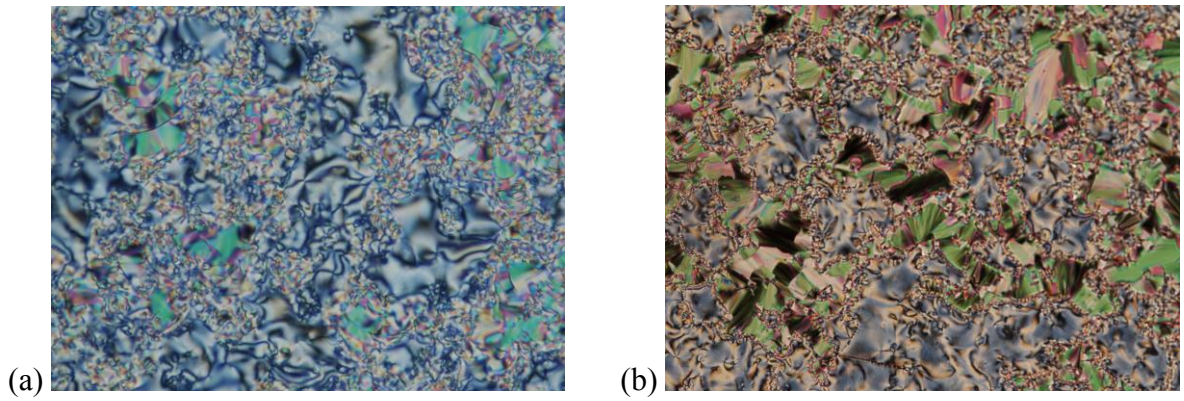


Fig. S1. Polarized photomicrographs of (a) **QL13-6** in the SmC phase at 78 °C and (b) **QL14-8/8** in the SmC phase at 94 °C on cooling from the isotropic liquid phase.

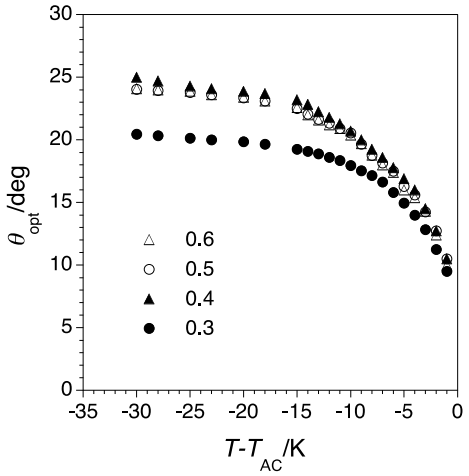


Fig. S2. Optical tilt angles $\theta_{\square\square\square}$ versus reduced temperature $T–T_{AC}$ for the binary mixtures **QL13-6/QL14-8/8** at different mole fractions $x_{\mathbf{13\text{-}6}}$.

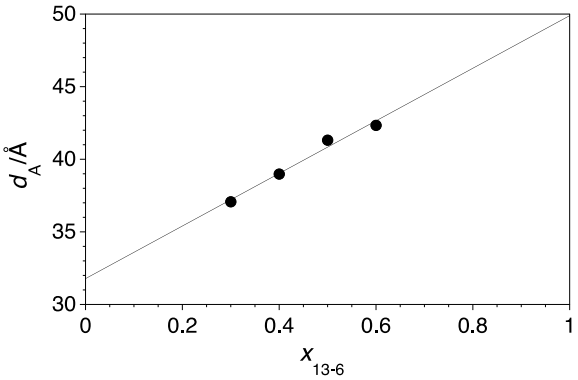


Fig. S3. Layer spacing d_A for the binary mixtures **QL13-6/QL14-8/8** in the SmA phase at 2K below the clearing point versus mole fraction $x_{\mathbf{13\text{-}6}}$; the solid line represents the least-squares fit ($R^2 = 0.9792$)

References

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