Electronic Supplementary Information for:

Electroclinic effect in a chiral carbosilane-terminated 5-phenylpyrimidine liquid crystal with 'de Vries-like' properties

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EXPERIMENTAL

General. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer; chemical shifts (δ) are reported in parts per million (ppm) relative to TMS. Low- and high-resolution mass spectra were recorded on a Waters/Micromass GC-TOF instrument in electron ionization (EI) or electrospray ionization (ESI) mode. Elemental analyses were performed on a Thermo Flash 2000 CHNS analyzer. Specific rotations were measured on a Atago AP300 automated polarimeter. The enantiomeric enrichment of compound **2** was measured by chiral phase HPLC on a Agilent 1260 Infinity instrument fitted with a Chiralpak AD column (250 mm × 4.6 mm i.d., 99:1 hexane/IPA, 1 mL min^{-1}). 1-Bromo-12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecane and 4-(2-chloropyrimidin-5-yl)phenol (**5**) were prepared according to literature procedures and shown to have the expected physical and spectral properties.[1] All other chemicals were obtained from commercial sources.

Differential scanning calorimetry (DSC) analyses were performed using a TA Instruments Q2000 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. Optical stripes analyses were performed using a Leica DM 2700 P polarized microscope fitted with an Instec HCS 302 hot stage; sample cells (ITO glass, homogeneous alignment, rubbed nylon coating, 3 μm cell gap, AWAT1, Poland) were filled by capillary action in the isotropic phase and slowly cooled (0.2 K min^{-1}) to the SmA* phase at T_{AC} and then slowly heated back up to T–T_{AC} = +0.2, +1 and +2 K; square wave 105 Hz ac fields up to 15 V μm^{-1} were applied using a HP 8116A waveform generator and a FLC Electronics F10A 10x voltage amplifier. 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. Induced optical tilt angles and birefringence were measured in a rotating analyzer setup previously described in the literature;[2] the linearly polarized light of a He-Ne Laser (λ = 633 nm, Linos Photonics, Göttingen) was circularly polarized with a Glan-Thompson prism and a quarter-wave plate and sent through the sample cells (ITO glass, homogeneous alignment, rubbed nylon coating, 3 μm cell gap, AWAT1, Poland), which were filled by capillary action in the isotropic phase; the sample temperature was controlled in a brass block with a Julabo FH-

25HP thermostat; the analyzer was a second Glan-Thompson prism rotated at a frequency of 3-4 Hz with an Owis HeDL-5540 A02 motor fitted with Hall probes to detect the angular position of the analyzer; the transmitted light intensity was recorded using a Linos Photonics/Spindler & Hoyer photodiode linked to a digital oscilloscope (Tektronix TDS460); unlike the setup described in literature, dc fields up to 20 V μm^{-1} were applied with alternating sign using a Kontron Elektronik 8021 waveform generator and a FLC Electronics F10A 10x voltage amplifier to slowly switch the sample between opposite tilt orientations, and to detect the optical signals separately for the two switching states; the setup was controlled and the data collected using a customized LabView 8.2 (National Instruments) program; the two optical signals were fitted according to the equations described by Langhoff *et al.,*[2] and the tilt angle and birefringence were extracted simultaneously.

[(2*R*,3*R*)-3-propyloxiran-2-yl]methanol. A 1-L three-neck flask with a suspension of 4 Å molecular sieves in dry DCM (500 mL) was purged with argon and cooled to –25 °C. Two separate solutions of (–)-diethyl *D*-tartrate (5.51 g, 26.7 mmol) in dry DCM (20 mL) and $Ti(OiPr)_4$ (6.08 g, 21.4 mmol) in dry DCM (20 mL) were stirred for 30 min over 4 Å molecular sieves under argon. The two solutions were transferred to the reaction flask and a solution of *t*-butylhydroperoxide in decane (5.5 M, 49.0 mL) was added. The reaction mixture was stirred at –25 ºC for 1 h. A solution of freshly distilled *E*-2-hexen-1-ol (**1**, 10.71 g, 106.9 mmol) in dry DCM (20 mL) was stirred for 30 min over 4 Å molecular sieves under argon and then transferred to the reaction vessel. The reaction mixture was stirred for 3 h at –25 °C before warming to 0 °C. Water (100 mL) was then added and the mixture was stirred for 1 h. A 30% aqueous solution of NaOH saturated with NaCl (15 mL) was added and the mixture was stirred for 30 min. The layers were separated and the aqueous layer extracted with DCM (2 × 200 mL). The combined organic layers were washed with brine (300 mL), dried ($MgSO_4$) and the solvent removed under reduced pressure. Purification by flash chromatography on silica gel (hexane, then 5:1 hexane/EtOAc) gave [(2*R*,3*R*)-3-propyloxiran-2-yl]methanol (19.57 g, 79%) as a colorless oil: $[\alpha]_D$ = +45.8° (*c* 1.04, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.91 (br d, *J* = 12.6 Hz, 1H), 3.63 (br d, *J* = 12.6 Hz, 1H), 2.98 (td, *J* = 5.5, 2.4 Hz, 1H), 2.93 (td, *J* = 4.4, 2.3 Hz, 1H), 1.85 (br s, 1H), 1.43-1.59 (m, 4H), 0.96 (t, *J* = 7.6 Hz, 3H).

[(2*R*,3*R*)-3-Propoxiran-2-yl]methyl *p*-toluenesulfonate (2). Pyridine (10.18 g, 128.7 mmol) was added dropwise to a solution of [(2*R*,3*R*)-3-propyloxiran-2-yl]methanol (5.98 g, 51.5 mmol) and *p*-toluenesulfonyl chloride (10.43 g, 52.5 mmol) in dry THF (15 mL) kept at 0 °C under argon. The reaction mixture was stirred at 0 °C for 1 h and then cooled to –20 °C and stirred for 16 h. A 30% aqueous solution of NH_4OH (5 mL) was added and the mixture was stirred for 30 min. A 5% aqueous solution of HCl (30 mL) was then added and the mixture was extracted with 1:1 EtOAC/hexane (2 × 50 mL). The combined organic layers were washed with 1M aq HCl (3 × 30 mL), brine (50 mL), dried ($MgSO_4$) and the solvent removed under reduced pressure. Purification by flash chromatography on silica gel (3:1 hexane/EtOAc) gave **2** (11.04 g, 79%) as a white crystalline solid with an enantiomeric enrichment of 95% ee: mp 49-50 °C; $[\alpha]_D$ = +36.7° (*c* 1.04, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 4.18 (dd, *J* = 11.4, 3.8 Hz, 1H), 3.99 (dd, *J* = 11.4, 5.8 Hz, 1H), 2.96 (ddd, *J* = 5.9, 3.9, 2.1 Hz, 1H), 2.80 (td, *J* = 5.4, 2.0 Hz, 1H), 2.46 (s, 3H), 1.40-1.54 (m, 4H), 0.94 (t, *J* = 7.6 Hz, 3H); LRMS (EI) *m/z* 270 (M+, 2), 227 (53), 198 (2), 155 (100), 98 (10), 91 (18); HRMS (EI) *m/z* calcd for $C_{13}H_{18}O_4S$ 270.0926, found 270.0921.

[(2*R*,3*S*)-3-Fluoro-2-hydroxyhexyl] *p*-toluenesulfonate (3). To a solution of **2** (2.48 g, 9.17 mmol) in dry DCM (30 mL) kept at 0 °C under argon in a PFA round bottom flask equipped with a Teflon stir bar was added a 70% solution of HF•pyridine (91.7 mmol, 2.4 mL). The mixture was stirred at 0 ºC for 16 h, then poured into a rapidly stirred solution of NaOH (3.0 g, 75.0 mmol) and Na_3PO_4 (1.2 g, 7.3 mmol) in ice/water (30 mL). The product was extracted with DCM (3 × 20 mL) and the combined extracts were washed with 1 M aq HCl (50 mL), brine (30 ml), dried ($MgSO_4$) and the solvent removed under reduced pressure. Purification by flash chromatography on silica gel (3:1 hexane/EtOAc) gave **3** (1.99 g, 75%) as a pale yellow oil which was used in the next step without further purification.

[(2*S*,3*S*)-2,3-Difluorohexyl] *p*-toluenesulfonate. To a solution of triethylamine trihydrofluoride (2.14 g, 13.30 mmol) and triethylamine (0.67 g, 6.65 mmol) in dry DCM (15 mL) kept at –78 °C under argon were successively added XtalFluor-E (2.28 g, 9.97 mmol) and a solution of **3** (1.93 g, 6.65 mmol) in dry DCM (5 mL). The mixture was stirred for 30 min at –78 °C and then allowed to warm to room temperature and stirred until TLC analysis showed no remaining starting material. The mixture was quenched at room temperature with a 5% aq $NaHCO_3$ solution and stirred for 15 min. The product was extracted with DCM (2 × 20 mL) and the combined extracts were dried ($MgSO_4$) and filtered through a pad of silica gel. Purification by flash chromatography on silica gel (4:1 hexane/EtOAc) gave [(2*S*,3*S*)-2,3-difluorohexyl] *p*-toluenesulfonate (0.79 g, 41%) as a white crystalline solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 4.45-4.75 (m, 2H), 4.28-4.30 (m, 1H), 4.23-4.25 (m, 1H), 2.47 (s, 3H), 1.75-1.84 (m, 1H), 1.38-1.55 (m, 3H), 0.96 (t, J = 7.3 Hz, 3H).

(2*S*,3*S*)-2,3-Difluorohexan-1-ol (4). To a 0.1 M solution of SmI_2 in THF (100 mL) kept under argon at room temperature was added [(2*S*,3*S*)-2,3-difluorohexyl] *p*-toluenesulfonate (0.49 g, 1.67 mmol). The mixture was stirred for 5 min before adding water (0.54 g, 30.1 mmol) and pyrrolidine (1.43 g, 20.0 mmol) sequentially with vigorous stirring. The mixture was diluted with ether (70 mL) and 0.5 M aq HCl (70 mL) was added. The layers were separated and the aqueous layer extracted with ether (2 × 25 mL). The combined extracts were dried ($MgSO_4$) and the solvent removed under reduced pressure. Purification by flash chromatography on silica gel (99:1 DCM/MeOH) gave **4** (0.12 g, 52%) as colorless needles: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.44-4.75 (m, 2H), 3.83-3.96 (m, 2H), 1.77-1.88 (m, 2H), 1.43-1.71 (m, 2H), 1.26 (br s, 1H), 0.99 (t, J = 7.3 Hz, 3H).

5-[4-(12,12,14,14,16,16-Hexamethyl-12,14,16-trisilaheptadecyloxy)phenyl-2-chloropyrimidine (6). To a solution of **5** (0.25 g, 1.21 mmol) and Cs_2CO_3 (1.28 g, 3.63 mmol) in acetone (25 mL) was added 1-bromo-12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecane (1.09 g, 2.42 mmol). The reaction mixture was heated to reflux for 24 h, then cooled to room temperature and filtered. The solvent was removed under reduced pressure and the crude product dissolved in DCM (20 mL). The organic phase was washed with 1 M aq HCl (20 mL), brine (20 mL), dried ($MgSO_4$) and the solvent removed under reduced pressure. Purification by flash chromatography on silica gel (7:1 hexane/EtOAc) gave **6** (0.68 g, 97%) as a mesomorphic material: Cr 18 SmA 48 I; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 2H), 7.46 (d, J = 8.6 Hz, 2H), 7.01 (d, J = 8.6 Hz, 2H), 4.00 (t, J = 6.6 Hz, 2H), 1.78-1.85 (m, 2H), 1.44-1.51 (m, 2H), 1.24-1.40 (m, 12H), 0.46-0.50 (m, 2H), 0.05 (s, 6H), 0.02 (s, 9H), 0.00 (s, 6H), –0.25 (s, 2H), –0.28 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 159.3, 156.8, 132.6, 127.9, 124.7,

115.5, 68.1, 33.6, 29.58, 29.54, 29.52, 29.3, 29.1, 25.9, 23.9, 18.0, 5.7, 3.9, 2.4, 1.4, –0.4; LRMS (EI) *m/z* 576 (M+, 38), 561 (63), 217 (100), 129 (34); HRMS (EI) *m/z* calcd for $C_{30}H_{53}ClN_2OSi_3$ 576.3154, found 576.3133.

2-[(2*S*,3*S*)-2,3-difluorohexyloxy]-5-[4-(12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecyloxy)phenyl]pyrimidine (QL32-6). To a suspension of NaH (60% suspension in mineral oil, 0.091 g, 2.28 mmol) in dry THF (10 mL) kept under argon was added **4** (0.12 g, 0.86 mmol). The mixture was stirred at room temperature for 30 min, then cooled to 0 ºC and a solution of **6** (0.33 g, 0.57 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) and then water (20 mL). The mixture was extracted with EtOAc (3 × 15 mL) and the combined extracts were washed with brine (40 mL), dried ($MgSO_4$) and the solvent removed under reduced pressure. Purification by flash chromatography on silica gel (8:1 hexane/EtOAc) gave **QL32-6** (0.35 g, 91%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 2H), 7.44 (d, J = 8.6 Hz, 2H), 7.01 (d, J = 8.6 Hz, 2H), 4.75-4.99 (m, 2H), 4.72 (br d, J = 5.3 Hz, 1H), 4.67 (dd, J = 4.2, 1.4 Hz, 1H), 4.00 (t, J = 6.6 Hz, 2H), 1.24-1.99 (m, 22H), 1.00 (t, J = 7.2 Hz, 3H), 0.46-0.51 (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 (100 MHz, $CDCl_3$) δ 163.6, 159.5, 156.9, 128.8, 127.6, 126.2, 115.3, 91.77 (dd, $^1J_{FC}$ = 216 Hz, $^2J_{FC}$ = 20 Hz), 90.0 (dd, $^1J_{FC}$ = 216 Hz, $^2J_{FC}$ = 19 Hz), 68.2, 65.6 (dd, $^2J_{FC}$ = 106 Hz, $^3J_{FC}$ = 7 Hz), 33.7, 32.2 (dd, $^2J_{FC}$ = 84 Hz, $^3J_{FC}$ = 5 Hz), 29.63, 29.60, 29.5, 29.39, 29.38, 29.2, 18.2 (d, $^3J_{FC}$ = 5 Hz), 18.0, 13.7, 5.7, 4.0, 2.4, 1.4, –0.4; LRMS (EI) *m/z* 679 (M+, 100), 515 (38), 495 (25); HRMS (EI) *m/z* calcd for $C_{36}H_{64}F_2N_2O_2Si_3$ 679.4332, found 679.4341

Anal. calcd for $C_{36}H_{64}F_2N_2O_2Si_3$: C, 63.66; H, 9.50; N, 4.12. Found: C, 63.81; H, 9.56; N, 4.23.

Fig. S1. Polarized photomicrographs of (a) a homeotropic domain formed by **QL32-6** in the SmA* phase at 63 °C, and developing Schlieren texture in the same domain upon transition to the SmC* phase at (b) 61 °C and (c) 51 °C.

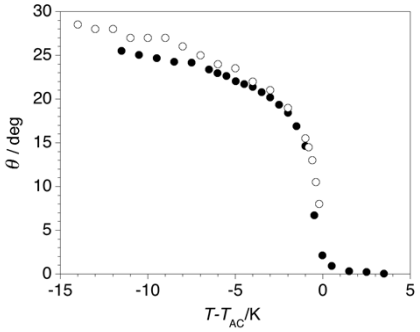

Fig. S2. Optical tilt angle θ *vs.* reduced temperature $T–T_{AC}$ for **QL32-6** (ஜ, measured with an electric field E = 0.5 V μm^{-1}) and **QL16-6** (ஐ, measured at zero-field, from ref. 1).

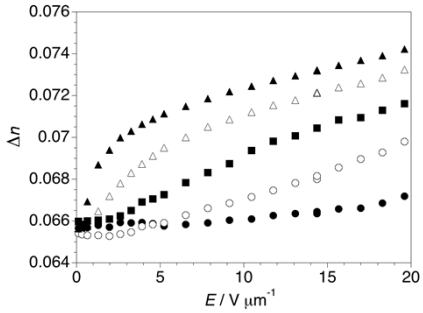

Fig. S3. Birefringence Δ*n vs.* electric field *E* measured in the SmA* phase formed by **QL32-6** at $T–T_{AC}$ = +0.2 K (□), +0.8 K (❐), +2 K (○), +3 K (◌) and +5 K (◌).

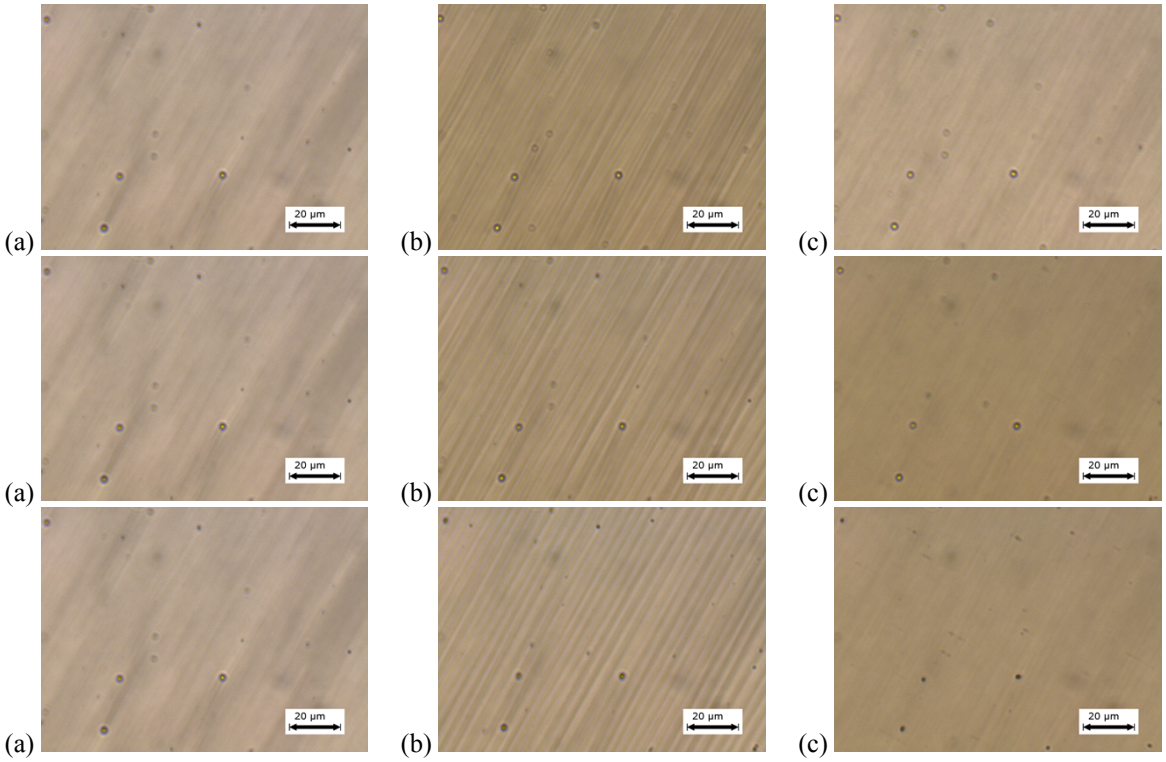

Fig. S4. Polarized photomicrographs of **QL32-6** in a 3 μm ITO glass cell with a rubbed nylon alignment substrate at $T–T_{AC}$ = +0.2 K (top), $T–T_{AC}$ = +1 K (middle) and $T–T_{AC}$ = +2 K (bottom): (a) at E = 0, (b) at E = 7.3 V μm^{-1}, and (c) at E = 15 V μm^{-1}, (105 Hz square wave ac field).

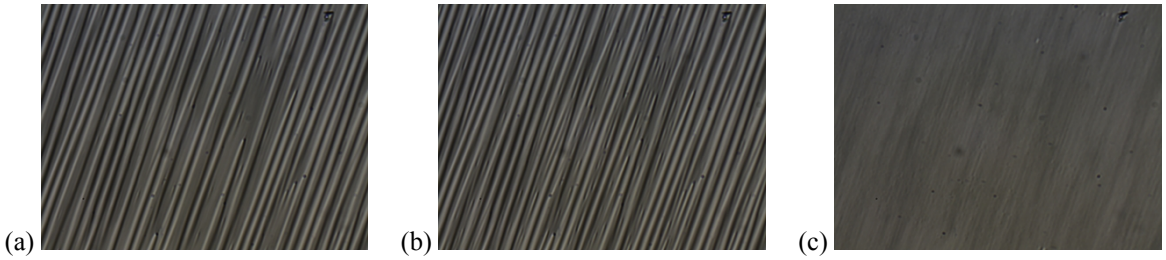

Fig. S5. Polarized photomicrographs of **QL32-6** in a 3 μm ITO glass cell with a rubbed nylon alignment substrate at $T–T_{AC}$ = +10 K: (a) at E = 0, (b) at E = 7.3 V μm^{-1}, and (c) at E = 15 V μm^{-1}, (105 Hz square wave ac field).

References

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2. A. Langhoff and F. Giesselmann, *ChemPhysChem*, 2002, **3**, 424-432.