Supporting Information for:

Directed Metalation-Cross Couping Route to Ferroelectric Liquid Crystals with a Chiral Fluorenol Core: The Effect of Intermolecular Hydrogen Bonding on Polar Order

J. Adam McCubbin,[†] Xia Tong,[‡] Yue Zhao,[‡] Victor Snieckus,[†] and Robert P. Lemieux*,[†]*

Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6, and Département de Chimie, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1

[†] Queen's University
[‡] Université de Sherbrooke

Experimental Section

General Methods. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on Bruker AV-400 instruments in $CDCl_3$ (unless otherwise indicated). The chemical shifts are reported in δ (ppm) relative to tetramethylsilane or $CDCl_3$ as internal standard. Low resolution mass spectra were recorded on a Micromass VG Quattro triple quadrupole mass spectrometer; peaks are reported as *m/z* (percent intensity relative to the base peak). High resolution mass spectra were recorded on a Micromass 70-250S double focusing mass spectrometer. Infrared spectra were recorded on a Bomem MB-100 FT-IR spectrometer as KBr pellets or neat on NaCl plates. Variable temperature infrared spectra were recorded as thin films on CaF_2 windows using a Bomem MB-200 FT-IR spectrometer fitted with a thermostated hot stage. Each spectrum was obtained by averaging 600 scans at a resolution of 4 cm^{-1}. Melting points were obtained using a Fisher Scientific hot stage apparatus and are uncorrected. Elemental analyses were performed by Canadian Microanalytical Service Ltd. (Delta, BC). Differential scanning calorimetry analyses were performed on a Perkin-Elmer DSC-7 instrument with a scanning rate of 5 K/min. 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. Spontaneous polarizations (P_S) were measured as a function of temperature by the triangular wave method[1] (10-15 V/μm, 80-100 Hz) using a Displaytech APT-III polarization testbed in conjunction with the Linkam hot stage. Rubbed polyimide-coated ITO glass cells with a 4 μm spacing (Displaytech Inc.) were used for all measurements. Alignment of the SmC* phase was achieved by slow cooling (0.1 K/min) from the isotropic phase while applying an AC field (4 Hz, 5 V/μm) across the film. Tilt angles (θ) were measured by polarized microscopy as half the rotation between two extinction positions corresponding to opposite signs of the applied field. The sign of P_S along the polar axis was assigned from the relative configuration of the electric field and the switching position of the sample according to the established convention.[2] Semiempirical molecular modeling calculations were carried out at the AM1 level using MOPAC97 as implemented on Chem3D Pro (version 4.0, CambridgeSoft). Modeling of the fluorenol dimers was carried out using the MMFF force field as implemented on Spartan '04 for Macintosh (version 1.0, Wavefunction Inc, Irvine, CA).

Materials. All starting materials were obtained from commercial sources unless otherwise noted. 1-(4-Undecyloxybenzoyl)benzotriazole, *N,N*-diethyl-4'-bromo-4-hydroxybiphenyl-2-carboxamide (**4**), 5-(4-butoxyphenyl)-2-octyloxypyrimidine (**16**) and 6-(4-butoxyphenyl)-3-octyloxypyridazine (**17**) were synthesized according to previously published procedures.[3,4]

***N,N*-Diethyl 4'-bromo-4-(1-octyloxy)biphenyl-2-carboxamide (5)**. Under an Ar atmosphere, 1-bromooctane (3.01g, 1.1 equiv) was added to a solution of **4** (4.93g, 14.2 mmol) and K_2CO_3 (5.87g, 3.0 equiv) in CH_3CN (150 mL) at room temperature. The mixture was heated to reflux for 4h, then concentrated in *vacuo* and dissolved in EtOAc. The solution was washed twice with saturated aq NH_4Cl, twice with water and with brine. The organic layer was dried ($MgSO_4$) and concentrated to a yellow oil. Purification by flash chromatography on silica gel (10% EtOAc/hexanes) gave 6.22g (96%) of **5** as a colorless solid: mp 47-48 °C (CH_2Cl_2/hexanes); IR (KBr) 1630 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J=8.6Hz, 2H), 7.32 (d, J=8.6Hz, 1H), 7.25 (d, J=8.6Hz, 1H), 6.95 (dd, ^3J=8.6Hz, ^4J=2.6Hz, 1H), 6.87 (d, J=2.6Hz, 1H), 3.97 (m, 2H), 3.71 (m, 1H), 3.00 (m, 2H), 2.69 (m, 1H), 1.79 (m, 2H), 1.36 (m, 10H), 0.95 (t, J=7.1Hz, 3H), 0.88 (m, 3H), 0.77 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 159.1, 138.8, 137.5, 131.6, 130.7, 130.6, 129.5, 121.5, 115.9, 112.9, 68.5, 42.6, 38.7, 32.0, 29.5, 29.4, 26.2, 22.9, 14.3, 13.7, 12.3; MS (EI) m/z 460 (M^+, 24), 461 ($(M+1)^+$, 13), 308 (19), 196 (100); HRMS (EI) calcd for $C_{25}H_{34}BrNO_2$: 459.1773, found 459.1778.

***N,N*-Diethyl 4'-hydroxy-4-(1-octyloxy)biphenyl-2-carboxamide (6)**. Under an Ar atmosphere, a 2.63 M solution of *n*-BuLi in hexanes (10.2 mL, 2.2 equiv) was added dropwise to a solution of **5** (5.57g, 12.2 mmol) in THF (130 mL) cooled to –78 °C. After the solution was stirred for 5 min at –78 °C, neat $(i\text{-PrO})_3B$ (6.17 mL, 2.2 equiv) was added dropwise and the mixture allowed to warm to room temperature over 30 min. The mixture was cooled to 0 °C and 35% (w/w) aq H_2O_2 (5.91 mL, 5.0 equiv) was added. After allowing the mixture to warm to room temperature over 15 min, it was diluted with saturated aq NH_4Cl, concentrated and extracted twice with CH_2Cl_2. The combined organic extracts were washed with brine, dried ($MgSO_4$) and concentrated to a yellow oil. Purification by flash chromatography on silica gel (33% EtOAc/hexanes) gave 4.00g (83%) of **6** as a colorless solid: mp 110-111°C (CH_2Cl_2/hexanes); IR (KBr) 3260, 1606 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J=8.6Hz, 1H), 7.21 (d, J=8.3Hz, 2H), 6.94 (dd, ^3J=8.6Hz, ^4J=2.8Hz, 1H), 6.84 (d, J=2.8Hz, 1H), 6.75 (d, J=8.3Hz, 2H), 3.95 (m, 2H), 3.70 (m, 1H), 3.06 (m, 2H), 2.77 (m, 1H), 1.78 (m, 2H), 1.34 (m, 10H), 0.94 (t, J=7.0Hz, 3H), 0.89 (m, 3H), 0.83 (t, J=7.0Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 158.1, 156.0, 136.6, 131.3, 130.9, 130.8, 129.8, 115.7, 115.4, 112.4, 68.3, 42.6, 38.7, 31.8, 29.4, 29.3, 29.2, 26.0, 22.7, 14.1, 13.5, 12.1; MS (EI) m/z 397 (M^+, 36), 325 (22), 284 (17), 213 (100); HRMS (EI) calcd for $C_{25}H_{35}NO_3$: 397.2617, found 397.2613.

***N,N*-Diethyl 4'-Methoxymethoxy-4-(1-octyloxy)biphenyl-2-carboxamide (7)**. Under an Ar atmosphere, MOMCl (1.06 mL, 2.0 equiv) was added dropwise to a solution of **6** (2.35g, 5.91 mmol) and $i\text{-Pr}_2NEt$ (2.13mL, 2.0 equiv) in dry CH_2Cl_2 (60 mL) cooled to 0 °C. The mixture was stirred for 4 hours at room temperature and extracted twice with CH_2Cl_2. The combined organic extracts were dried ($MgSO_4$) and concentrated to a yellow oil. Purification by flash chromatography on silica gel (20% EtOAc/hexanes) gave 2.15g (82%) of **7** as a colorless oil: IR (NaCl) 1629 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J=8.6Hz, 2H), 7.26 (d, J=8.6Hz, 1H), 7.01 (d, J=8.6Hz, 2H), 6.94 (dd, ^3J=8.6Hz, ^4J=2.8Hz, 1H), 6.87 (d, J=2.8Hz, 1H), 3.97 (m, 2H),

3,74 (m, 1H), 3.47 (s, 3H), 3.01 (m, 2H), 2.68 (m, 1H), 1.79 (m, 2H), 1.38 (m, 10H), 0.90 (m, 6H), 0.76 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 158.7, 156.8, 137.4, 133.7, 130.8, 130.6, 130.2, 116.4, 116.0, 112.8, 94.8, 68.6, 56.2, 42.6, 38.7, 32.1, 29.6, 29.5, 26.3, 23.0, 14.4, 13.7, 12.3; MS (EI) m/z 441 (M^+, 100), 337 (29), 309 (23), 196 (64); HRMS (EI) calcd for $C_{27}H_{39}NO_4$: 441.2879, found 441.2881.

2-Methoxymethoxy-7-(1-octyloxy)fluoren-9-one (8). Under an Ar atmosphere, a freshly prepared 1.0 M solution of LDA in THF (22.1 mL, 5.0 equiv) was added dropwise to a solution of **7** (1.95g, 4.42 mmol) in THF (250 mL) cooled to 0 °C. After the mixture was stirred at room temperature for 12 h, saturated aq NH_4Cl solution was added and the mixture was extracted twice with Et_2O. The combined organic extracts were washed with brine, dried ($MgSO_4$) and concentrated to a red oil. Purification by flash chromatography on silica gel (10% EtOAc/hexanes) gave 1.08g (67%) of **8** as a red solid: mp 69-70 °C (CH_2Cl_2/hexanes); IR (KBr) 1712 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J=8.1Hz, 1H), 7.26 (d, J=8.1Hz, 1H), 7.24 (d, J=2.5Hz, 1H), 7.12 (d, J=2.3Hz, 1H), 7.04 (dd, ^{3}J=8.1Hz, ^{4}J=2.3Hz, 1H), 6.90 (dd, ^{3}J=8.1Hz, ^{4}J=2.5Hz, 1H), 5.16 (s, 2H), 3.95 (t, J=6.6Hz, 2H), 3.48 (s, 3H), 1.75 (m, 2H), 1.36 (m, 10H), 0.89 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.9, 160.0, 157.8, 138.9, 137.3, 136.3, 136.2, 122.4, 121.2, 120.9, 120.7, 113.0, 110.4, 94.9, 68.9, 56.4, 32.1, 29.6, 29.5, 29.4, 26.3, 23.0, 14.4; MS (EI) m/z 368 (M^+, 51), 256 (15), 226 (100), 211 (67); HRMS (EI) calcd for $C_{23}H_{28}O_4$: 368.1988, found 368.1998.

2-Hydroxy-7-(1-octyloxy)fluoren-9-one (9). To a solution of **8** (943 mg, 2.56 mmol) in *i*-PrOH (30 mL) was added 6 M aq HCl (0.85 mL, 2.0 equiv). After the mixture was stirred for 4 h at room temperature, it was concentrated in *vacuo*, diluted with water and extracted twice with CH_2Cl_2. The combined extracts were washed with brine, dried ($MgSO_4$) and concentrated to a red solid. Purification by flash chromatography on silica gel (10% EtOAc/hexanes) gave 832 mg (96%) of **9** as a dark red solid: mp 114-115 °C (CH_2Cl_2/hexanes); IR (KBr) 3214, 1695 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J=8.1Hz, 1H), 7.23 (d, J=8.1Hz, 1H), 7.13 (d, J=2.5Hz, 1H), 7.11 (d, J=2.3Hz, 1H), 6.92 (dd, ^{3}J=8.1Hz, ^{4}J=2.5Hz, 1H), 6.89 (dd, ^{3}J=8.1Hz, ^{4}J=2.3Hz, 1H), 5.75 (s, 1H), 3.97 (t, J=6.6Hz, 2H), 1.76 (m, 2H), 1.36 (m, 10H), 0.89 (t, J=6.6Hz, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 194.1, 159.6, 156.1, 137.6, 137.4, 136.2, 135.8, 121.1, 121.0, 120.7, 120.5, 112.0, 110.3, 68.6, 31.8, 29.3, 29.2, 29.1, 26.0, 22.7, 14.1; MS (EI) m/z 324 (M^+, 10), 212 (100), 183 (8), 155 (17); HRMS (EI) calcd for $C_{21}H_{24}NO_3$: 324.1725, found 324.1728.

7-(1-octyloxy)-2-((4-undecyloxybenzoyl)oxy)fluoren-9-one (11). A solution of **9** (200 mg, 0.62 mmol), 4-undecyloxybenzoic acid (216 mg, 1.2 equiv), DCC (153 mg, 1.2 equiv) and DMAP (8 mg, 0.1 equiv) in CH_2Cl_2 (10 mL) was stirred for 4h at room temperature. The solution was diluted with water and extracted twice with CH_2Cl_2. The combined organic extracts were dried ($MgSO_4$) and concentrated to a yellow solid. Purification by flash chromatography on silica gel (10% EtOAc/hexanes) gave 314g (85%) of **11** as a yellow solid: IR (KBr) 1741, 1719 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J=8.8Hz, 2H), 7.43 (m, 2H), 7.39 (d, J=8.1Hz, 1H), 7.37 (d, 8.1Hz, 1H), 7.25 (dd, ^{3}J=8.1Hz, ^{4}J=2.1Hz, 1H), 7.18 (d, J=2.5Hz, 1H), 6.97 (d, J=8.8Hz, 2H), 4.04 (t, J=6.6Hz, 2H), 3.99 (t, J=6.6Hz, 2H), 1.79 (m, 4H), 1.48 (m, 4H), 1.27 (m, 22H), 0.89 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 165.1, 164.1, 160.6, 151.3, 142.6, 136.7, 136.5, 136.1, 132.7, 128.0, 121.6, 121.4, 121.3, 120.5, 118.7, 114.7, 110.5, 68.9, 68.7, 32.2, 32.1,

29.9, 29.7, 29.6, 29.5, 29.4, 26.3, 23.0, 14.4; MS (EI) m/z 598.4 (M^+, 1), 324 (4), 275 (94), 212 (32); HRMS (EI) calcd for $C_{39}H_{50}O_5$: 598.3658, found 598.3656.

(*RS*)-7-(1-octyloxy)-2-((4-undecyloxybenzoyl)oxy)fluoren-9-ol ((*RS*)-3). To a solution of **11** (103 mg, 0.17 mmol) in 1:1 Et_2O/MeOH (5 mL) was added solid $NaBH_4$ (7 mg, 1.0 equiv). The yellow solution was stirred for 5 min at room temperature, then diluted with saturated aq NH_4Cl and extracted twice with CH_2Cl_2. The combined organic extracts were dried ($MgSO_4$) and concentrated to a colorless solid. Purification by flash chromatography on silica gel (10% EtOAc/hexanes) gave 101 mg (98%) of (*RS*)-**3** as a colorless solid: IR (KBr) 3362, 1729 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J=9.1Hz, 2H), 7.54 (d, J=8.1Hz, 1H), 7.50 (d, J=8.4Hz, 1H), 7.43 (d, J=2.0Hz, 1H), 7.18 (d, J=2.3Hz, 1H), 7.16 (dd, ^{3}J=8.1Hz, ^{4}J=2.0Hz, 1H), 6.97 (d, J=9.0Hz, 2H), 6.91 (dd, ^{3}J=8.4Hz, ^{4}J=2.3Hz, 1H), 5.51 (s, 1H), 4.04 (t, J=6.6Hz, 2H), 4.00 (t, J=6.8Hz, 2H), 1.81 (m, 4H), 1.46 (m, 4H), 1.28 (m, 22H), 0.89 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 163.6, 159.5, 150.0, 147.7, 146.7, 137.8, 132.3, 131.9, 122.5, 121.5, 120.7, 119.6, 119.0, 115.7, 114.3, 111.3, 75.0, 68.4, 68.3, 31.9, 31.8, 29.6, 29.4, 29.3, 29.2, 29.1, 26.1, 26.0, 22.7, 14.0; MS (EI) m/z 600 (M^+, 2), 275 (100), 212 (26), 121 (99).

Anal. Calcd for $C_{39}H_{52}O_5$: C, 77.96; H, 8.72. Found: C, 77.64; H, 8.34.

(*R*)- and (*S*)-2-Hydroxy-7-(octyloxy)fluoren-9-ol ((*R*)-10 and (*S*)-10). To a solution of **9** (101 mg, 0.31 mmol) in 1:1 Et_2O/MeOH (5 mL) was added solid $NaBH_4$ (24 mg, 2.0 equiv). The red solution was stirred for 5 min at room temperature, then diluted with saturated aq NH_4Cl and extracted twice with CH_2Cl_2. The combined extracts were dried ($MgSO_4$) and concentrated to a colorless solid. Purification by flash chromatography on silica gel (30% EtOAc/hexanes) gave 101 mg (99%) of (*RS*)-**10** as a colorless solid: mp >300 °C (EtOAc/hexanes); IR (KBr) 3362 cm^{-1}; ^1H NMR (400 MHz, MeOD-d_4) δ 7.39 (d, J=8.3Hz, 1H), 7.37 (d, J=8.3Hz, 1H), 7.11 (d, J=2.3Hz, 1H), 7.01 (d, J=2.3Hz, 1H), 6.85 (dd, ^{3}J=8.3Hz, ^{4}J=2.3Hz, 1H), 6.75 (dd, ^{3}J=8.3Hz, ^{4}J=2.3Hz, 1H), 5.37 (s, 1H), 4.57 (s, 1H), 3.99 (t, J=6.6Hz, 2H), 1.75 (m, 2H), 1.34 (m, 10H), 0.88 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ159.9, 157.9, 148.9, 148.6, 134.5, 133.3, 120.5, 120.2, 116.5, 116.0, 113.4, 112.6, 75.3, 69.4, 33.1, 30.8, 30.5, 30.4, 27.3, 23.7, 14.5; MS (EI) m/z 326 (M^+, 27), 214 (100), 197 (62); HRMS calcd for $C_{21}H_{26}O_3$: 326.1881, found 326.1876. Resolution of the two enantiomers by semi-prep HPLC on a Chiralpak AS column (20% *i*-PrOH/hexanes, 3.0 mL/min) gave (*R*)-**10** (first eluted, >99% ee) and (*S*)-**10** (second eluted, >99% ee).

(*R*)-7-(1-octyloxy)-2-((4-undecyloxybenzoyl)oxy)fluoren-9-ol ((*R*)-3). To a solution of (*S*)-**10** (51 mg, 0.16 mmol) in 0.5 M aq NaOH (1.55 mL, 5 equiv) was added dropwise a solution of 1-(4-undecyloxybenzoyl)benzotriazole (307 mg, 5 equiv) in THF (2.0 mL) at room temperature. The solution was stirred for 30 min, then diluted with saturated aq NH_4Cl and extracted twice with CH_2Cl_2. The combined extracts were dried ($MgSO_4$) and concentrated to give a colorless solid. Purification by flash chromatography on silica gel (10% EtOAc/hexanes) gave 53 mg (56%) of (*R*)-**3** as a colorless solid, which was recrystallized from hexanes/Et_2O, and showed the same spectral properties as (*RS*)-**3** (vide supra).

4-Hydroxy-4'-Octyloxybiphenyl (14). Under an Ar atmosphere, 1-bromooctane (2.07g, 1.0 equiv) was added to a solution of 4,4'-biphenol (**12**, 2.00g, 10.7 mmol) and K_2CO_3 (4.45g, 3.0 equiv) in CH_3CN (100 mL) at room temperature. The mixture was heated to reflux for 4h,

then concentrated in *vacuo* and dissolved in EtOAc. The solution was washed twice with saturated aq NH_4Cl, twice with water and with brine . The organic layer was dried ($MgSO_4$) and concentrated to a yellow oil. Purification by flash chromatography on silica gel (20% EtOAc/hexanes) gave 1.43g (45%) of **14** as a colorless solid: mp > 300 °C (EtOAc/hexanes), (lit. 420 °C (EtOH))[5]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (m, 4H), 6.94 (d, J=8.8Hz, 2H), 6.88 (d, J=8.6Hz, 2H), 4.80 (s, 1H), 3.98 (t, J=6.6Hz, 2H), 1.80 (m, 2H), 1.48 (m, 2H), 1.29 (m, 8H), 0.90 (m, 3H).

4-Octyloxy-4'-((4-undecyloxybenzoyl)oxy)biphenyl (BPh). A solution of **14** (299 mg, 1.00 mmol), 4-undecyloxybenzoic acid (322 mg, 1.1 equiv), DCC (206 mg, 1.1 equiv) and DMAP (12 mg, 0.1 equiv) in CH_2Cl_2 (10 mL) was stirred for 4h at room temperature. The solution was diluted with water and extracted twice with CH_2Cl_2. The combined organic extracts were dried ($MgSO_4$) and concentrated to a colourless solid. Purification by flash chromatography on silica gel (10% EtOAc/hexanes) gave 476 mg (83%) of **BPh** as a colourless solid: IR (KBr) 1725 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J=8.8Hz, 2H), 7.57 (d, J=8.6Hz, 2H), 7.50 (d, J=8.8Hz, 2H), 7.24 (d, J=8.8Hz, 2H), 6.97 (d, J=8.8Hz, 2H), 6.93 (d, J=8.6Hz, 2H), 4.05 (t, J=6.6Hz, 2H), 3.98 (m, 2H), 1.81 (m, 4H), 1.32 (m, 26H), 0.89 (m, 6H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 165.4, 163.9, 159.1, 150.4, 138.9, 133.2, 132.6, 128.5, 128.0, 122.3, 121.9, 115.1, 114.7, 68.7, 68.5, 34.1, 32.3, 32.2, 30.0, 29.9, 29.7, 29.6, 29.5, 26.4, 26.3, 25.9, 25.2, 23.0, 14.4; MS (EI) m/z (M^+, 4), 410 (12), 298 (7), 275 (100), 186 (35), 121 (99); HRMS (EI) calcd for $C_{38}H_{52}O_4$: 572.3851, found 572.3866.

2-(4-Hydroxyphenyl)-5-octyloxypyrimidine (15). Under an Ar atmosphere, 1-bromooctane (412 mg, 1.0 equiv) was added to a solution of 2-(4-hydroxyphenyl)-5-pyrimidinol (**13**, 402 mg, 2.14 mmol) and K_2CO_3 (886 mg, 3.0 equiv) in CH_3CN (25 mL) at room temperature. The mixture was heated to reflux for 4h, then concentrated in *vacuo* and dissolved in EtOAc. The solution was washed twice with saturated aq NH_4Cl, twice with water and with brine . The organic layer was dried ($MgSO_4$) and concentrated to a yellow oil. Purification by flash chromatography on silica gel (20% EtOAc/hexanes) gave 328 mg (51%) of **15** as a colorless solid: mp 127-128 °C (CH_2Cl_2/hexanes); IR (KBr) 3356 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6) δ 8.46 (s, 2H), 8.21 (d, J=8.8Hz, 2H), 6.90 (d, J=8.8Hz, 2H), 4.14 (t, J=6.6Hz, 2H), 1.80 (m, 2H), 1.48 (m, 2H), 1.31 (m, 8H), 0.90 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.6, 163.2, 161.3, 155.3, 147.7, 132.9, 119.0, 72.7, 35.6, 33.0, 32.9, 29.6, 26.4, 17.3; MS (EI) m/z 300 (M^+, 47), 188 (100), 160 (6), 119 (19); HRMS (EI) calcd for $C_{18}H_{24}N_2O_2$: 300.1838, found 300.1843.

2-((4-Undecyloxybenzoyl)oxy)-5-octyloxypyrimidine (2-PPy). A solution of **15** (198 mg, 0.661 mmol), 4-undecyloxybenzoic acid (232 mg, 1.2 equiv), DCC (164 mg, 1.2 equiv) and DMAP (8 mg, 0.1 equiv) in CH_2Cl_2 (10 mL) was stirred for 4h at room temperature. The solution was diluted with water and extracted twice with CH_2Cl_2. The combined organic extracts were dried ($MgSO_4$) and concentrated to a colourless solid. Purification by flash chromatography on silica gel (10% EtOAc/hexanes) gave 309 mg (81%) of **2-PPy** as a colourless solid: IR (KBr) 1727 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 2H), 8.42 (d, J=8.8Hz, 2H), 8.15 (d, J=9.1Hz, 2H), 7.31 (d, J=8.8Hz, 2H), 6.96 (d, J=9.1Hz, 2H), 4.08 (t, J=6.6Hz, 2H), 4.03 (t, J=6.6Hz, 2H), 1.82 (m, 4H), 1.46 (m, 4H), 1.28 (m, 22H), 0.89 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 163.6, 156.9, 152.5, 151.6, 143.8, 135.0, 132.3, 128.8, 121.8, 121.5, 114.3, 68.9, 68.3, 31.9, 31.8,

29.6, 29.4, 29.3, 29.2, 29.1, 26.0, 25.9, 22.7, 22.6, 14.1; MS (EI) m/z 275 (M^+, 100), 121 (52); HRMS (EI) calcd for $C_{38}H_{52}O_4$: 574.3771, found 574.3758.

5-(4-Hydroxyphenyl)-2-octyloxypyrimidine (18). To a solution of **16** (1.00g, 2.81 mmol) in CH_2Cl_2 (50 mL) cooled to –78 °C under argon was added dropwise a freshly prepared 1 M solution of BBr_3 in CH_2Cl_2 (14.0 mL, 5.0 equiv). The mixture was stirred for 30 min at –78 °C, then allowed to warm to room temperature over 30 min. The reaction mixture was cooled to 0 °C, neutralized with saturated aq Na_2CO_3, diluted with water and extracted twice with CH_2Cl_2. The combined organic extracts were dried ($MgSO_4$) and concentrated to a colorless solid. Purification by flash chromatography on silica gel (20% EtOAc/hexanes) gave 646 mg (77%) of **18** as a colourless solid: mp 90-91 °C (CH_2Cl_2/hexanes); IR (KBr) 3371 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.41 (s, br, 1H), 8.69 (s, 2H), 7.37 (d, J=8.1Hz, 2H), 7.09 (d, 8.1Hz, 2H), 4.43 (m, 2H), 1.82 (m, 2H), 1.46 (m, 2H), 1.25 (m, 8H), 0.85 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 157.7, 156.8, 127.8, 125.6, 116.9, 68.4, 31.9, 29.5, 29.4, 29.0, 26.1, 22.8, 14.2; MS (EI) m/z 300 (M^+, 52), 188 (100), 146 (67); HRMS (EI) calcd for $C_{18}H_{24}N_2O_2$: 300.1838, found 300.1842.

5-((4-Undecyloxybenzoyl)oxy)-2-octyloxypyrimidine (5-PPy). A solution of **18** (540 mg, 1.80 mmol), 4-undecyloxybenzoic acid (632 mg, 1.2 equiv), DCC (446 mg, 1.2 equiv) and DMAP (22 mg, 0.1 equiv) in CH_2Cl_2 (20 mL) was stirred for 4h at room temperature. The solution was diluted with water and extracted twice with CH_2Cl_2. The combined organic extracts were dried ($MgSO_4$) and concentrated to a colourless solid. Purification by flash chromatography on silica gel (10% EtOAc/hexanes) gave 818 mg (79%) of **5-PPy** as a colourless solid: IR (KBr) 1719 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 2H), 8.16 (d, J=9.1Hz, 2H), 7.56 (d, J=8.3Hz, 2H), 7.32 (d, J=8.3Hz, 2H), 6.98 (d, J=9.1Hz, 2H), 4.41 (t, J=6.6Hz, 2H), 4.05 (t, J=6.6Hz, 2H), 1.83 (m, 4H), 1.49 (m, 4H), 1,28 (m, 22H), 0.89 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 164.0, 157.6, 151.5, 151.5, 132.7, 132.5, 128.0, 127.8, 123.1, 121.6, 114.7, 68.7, 68.4, 32.3, 32.2, 30.0, 29.9, 29.7, 29.6, 29.4, 29.2, 26.3, 23.0, 14.5, 14.4; MS (EI) m/z 575 (M^+, 3), 463 (2), 275 (100), 187 (9), 121 (57); HRMS (EI) calcd for $C_{36}H_{50}N_2O_4$: 574.3771, found 574.3799.

6-(4-Hydroxyphenyl)-3-octyloxypyridazine (19). To a solution of **17** (872 mg, 2.45 mmol) in CH_2Cl_2 (25 mL) cooled to –78 °C under argon was added dropwise a freshly prepared 1M solution of BBr_3 in CH_2Cl_2 (12.2 mL, 5.0 equiv). The mixture was stirred for 30 min at –78 °C, then allowed to warm to room temperature over 30 min. The reaction mixture was cooled to 0 °C, neutralized with saturated aq Na_2CO_3, diluted with water and extracted twice with CH_2Cl_2. The combined organic extracts were dried ($MgSO_4$) and concentrated to a colorless solid. Purification by flash chromatography on silica gel (20% EtOAc/hexanes) gave 558 mg (76%) of **19** as a colourless solid: mp 105-106 °C (CH_2Cl_2/hexanes); IR (KBr) 3150 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J=8.6Hz, 2H), 7.48 (d, J=9.1Hz, 1H), 6.77 (d, J=9.1Hz, 1H), 6.66 (d, J=8.6Hz, 2H), 4.39 (s, br, 1H), 4.18 (t, J=6.8Hz, 2H), 1.54 (m, 2H), 1.19 (m, 2H), 1.00 (m, 8H), 0.60 (3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 158.6, 155.1, 127.8, 127.5, 127.1, 118.4, 115.7, 31.6, 29.1, 29.0, 28.7, 25.8, 22.4, 13.6; MS (EI) m/z 300 (M^+, 35), 243 (10), 188 (100), 146 (45); HRMS (EI) calcd for $C_{18}H_{24}N_2O_2$: 300.1838, found 300.1846.

6-((4-Undecyloxybenzoyl)oxy)-3-octyloxypyridazine (PPz). A solution of **19** (369 mg, 1.23 mmol), 4-undecyloxybenzoic acid (430 mg, 1.2 equiv), DCC (304 mg, 1.2 equiv) and

DMAP (15 mg, 0.1 equiv) in CH_2Cl_2 (15 mL) was stirred for 4h at room temperature. The solution was diluted with water and extracted twice with CH_2Cl_2. The combined organic extracts were dried ($MgSO_4$) and concentrated to a colourless solid. Purification by flash chromatography on silica gel (10% EtOAc/hexanes) gave 571 mg (81%) of **PPz** as a colourless solid: IR (KBr) 1719 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J=8.9Hz, 2H), 8.07 (d, J=8.7Hz, 2H), 7.78 (d, J=9.2Hz, 1H), 7.34 (d, J=8.7Hz, 2H), 7.03 (d, J=9.2Hz, 1H), 6.98 (d, J=8.9Hz, 2H), 4.57 (m, 2H), 4.05 (m, 2H), 1.26 (m, 32H), 0.89 (m, 6H); MS (EI) m/z 575 (M^+, 1), 275 (100), 244 (11), 188 (28), 121 (54); HRMS (EI) calcd for $C_{36}H_{50}N_2O_4$: 574.3771, found 574.3741.

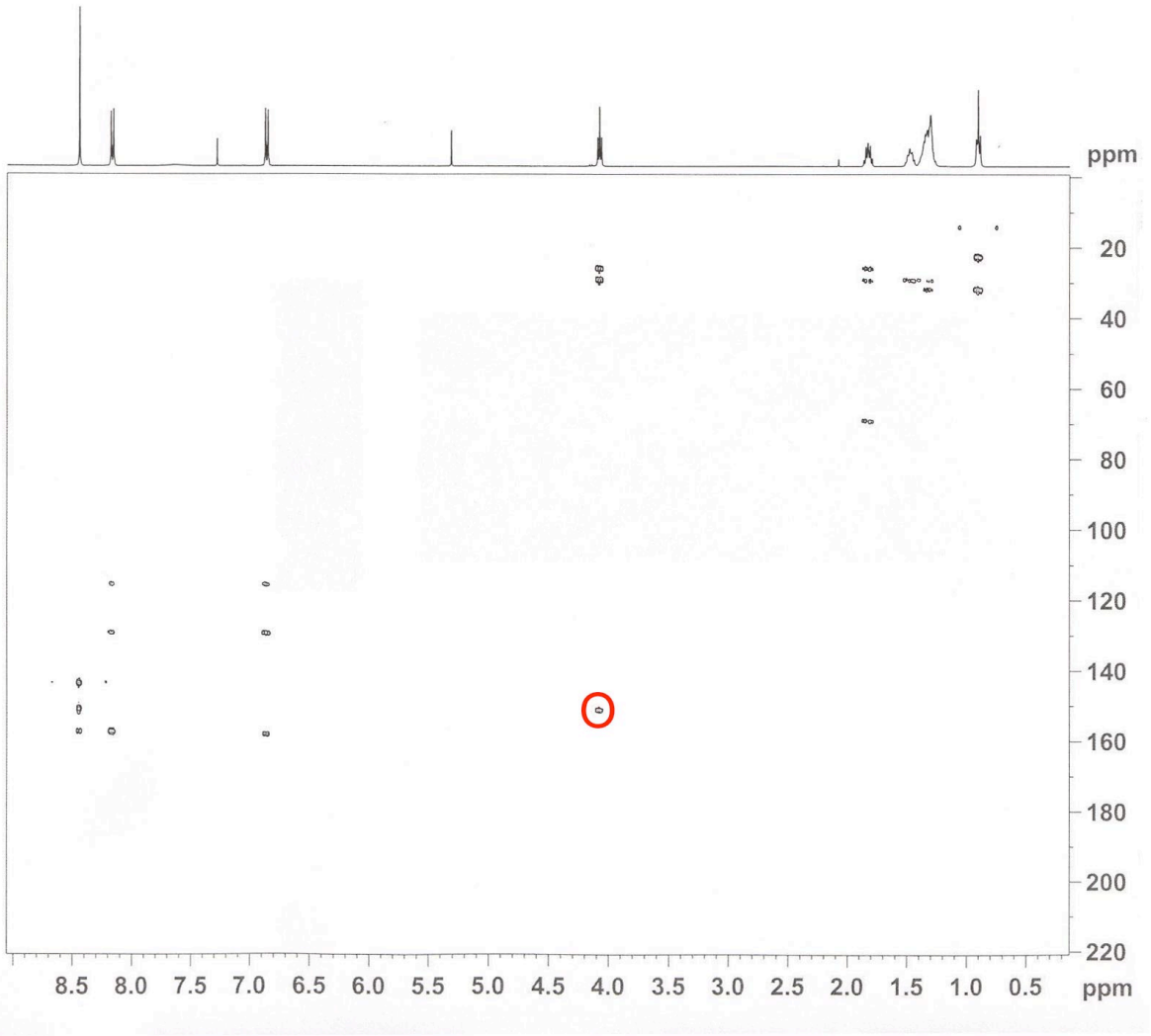

Figure 1. HMBC NMR spectrum of **15**. The cross-peak indicated by the circle corresponds to a correlation between the $–CH_2O–$ protons and C-5 of the pyrimidine ring.

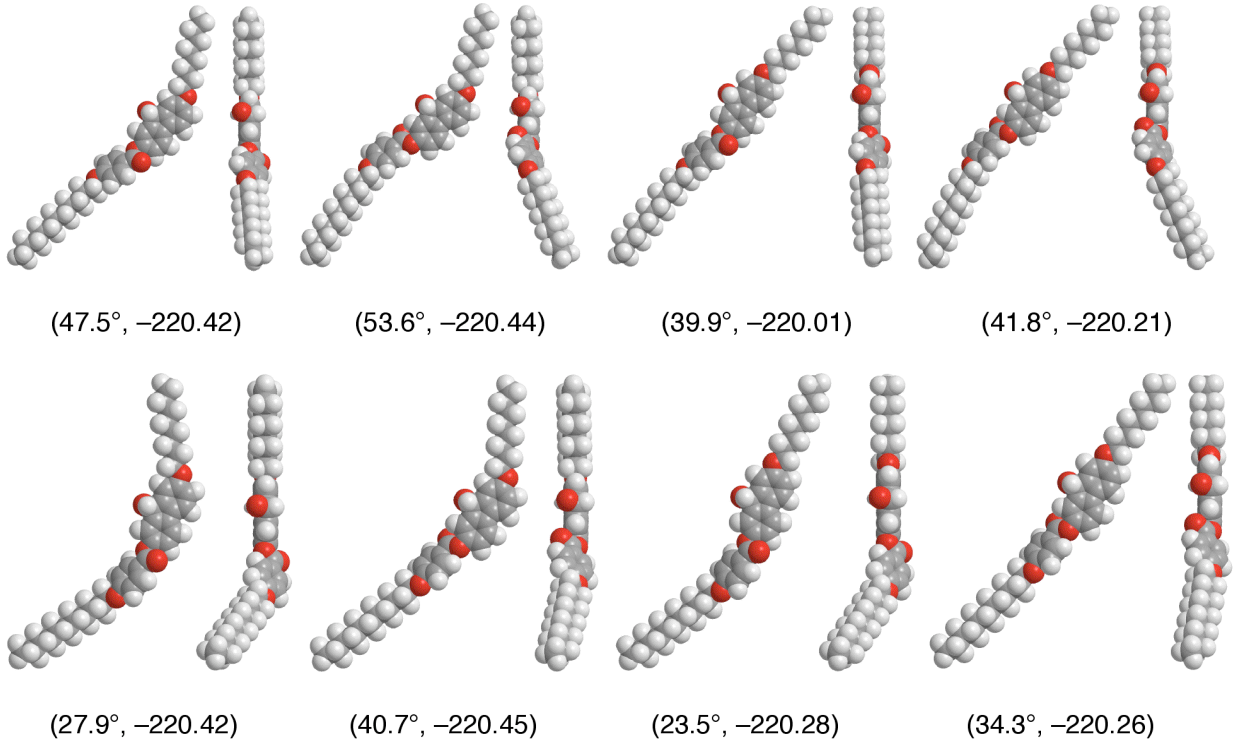

Figure 2. Molecular models (AM1) with negative P_S as side-on (left) and end-on views. Calculated optical tilt angles θ_{opt} and heats of formation in kcal/mol are given in parentheses.

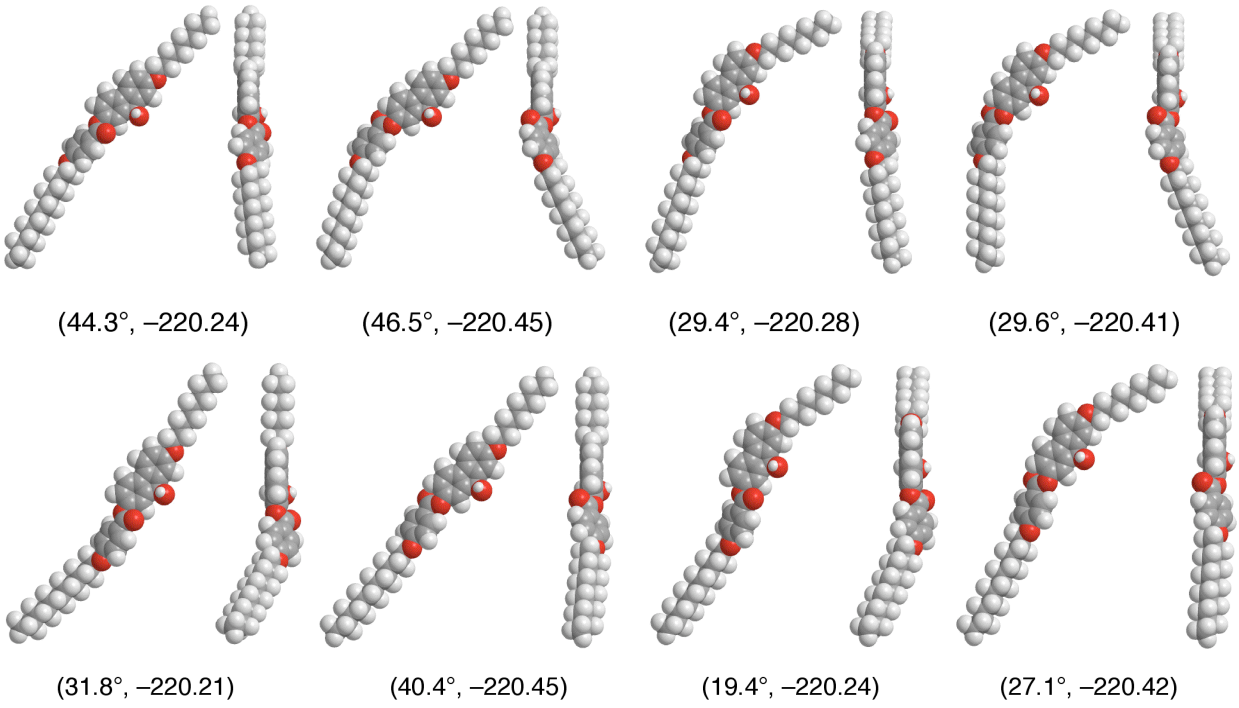

Figure 3. Molecular models (AM1) with positive P_S as side-on (left) and end-on views. Calculated optical tilt angles θ_{opt} and heats of formation in kcal/mol are given in parentheses.

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