Electronic Supplementary Information for:

Elucidating the SmA-promoting effect of halogen end-groups in calamitic liquid crystals

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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 123). 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 (KAF 2084x2083 SCX) and processed and analysed using the SAXSquant 3.5 software. Chemicals were obtained from commercial sources unless otherwise noted.

General procedure for the synthesis of mesogens QL8-*m/n* and QL10-X. Under a N_2 atmosphere, 2-(4-hydroxyphenyl)pyrimidin-5-ol (0.10 g, 0.53 mmol) was combined with 1.0 equivalent of halogen-terminated alkan-1-ol and triphenylphosphine (0.28 g, 1.06 mmol) in dry THF (5 mL). After stirring the colourless solution for 15 min, DIAD (0.21 g, 0.21 mL, 1.06 mmol) was added dropwise over 15 min. The mixture was stirred at room temperature overnight, and then concentrated and purified by flash chromatography on silica gel (10% EtOAc/Hexane) to give the halogen-terminated 5-alkoxy-2-(4-hydroxyphenyl)pyrimidine (40-70% yield) as a yellow solid. The product was recrystallized from acetonitrile and hexanes to give a white solid. The reaction was then repeated with the halogen-terminated 5-alkoxy-2-(4-hydroxyphenyl)pyrimidine and 1.0 equivalent of alkan-1-ol. Purification by flash chromatography on silica gel (10% EtOAc/Hexane) gave the halogen-terminated **QL8-*m/n*** or **QL10-X** (40-60% yield) as a yellow solid. The final product was recrystallized from acetonitrile and hexanes to give a white solid. The mesogens **QL9-*m/n*** were synthesized using the same procedure except that the alkan-ol was used in the first reaction and the chloro-terminated alkan-1-ol was used in the second reaction.

5-(11-Chloroundecyloxy)-2-(4-pentyloxyphenyl)pyrimidine (QL8-5/11): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 2H), 8.28 (d, J = 8.97 Hz, 2H), 6.98 (d, J = 8.97 Hz, 2H), 4.09 (t, J = 6.51 Hz, 2H), 4.03 (t, J = 6.57 Hz, 2H), 3.54 (t, J = 6.76 Hz, 2H), 1.67-1.94 (m, 6H), 1.13-1.54 (m, 18H), 0.93 (t, J = 6.85 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.5, 25.9, 26.9, 28.2, 28.9, 29.0, 29.1, 29.3, 29.4, 29.5, 32.6, 45.2, 68.1, 68.9, 114.4, 129.0, 130.0, 143.8, 151.1, 157.7, 160.7; LRMS (EI) *m/z* 448 (M+2, 35), 446 (M+, 100), 378 (4), 376 (17), 188 (96); HRMS (EI) calcd for $C_{26}H_{39}N_2O_2Cl$ 446.2700, found 446.2715.

Anal. Calcd for $C_{26}H_{39}N_2O_2Cl$: C, 69.85; H, 8.79; N, 6.27. Found: C, 69.44; H, 8.35; N, 5.95.

5-(10-Chlorodecyloxy)-2-(4-hexyloxyphenyl)pyrimidine (QL8-6/10): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 2H), 8.28 (d, J = 8.84 Hz, 2H), 6.98 (d, J = 8.84 Hz, 2H), 4.09 (t, J = 6.51 Hz, 2H), 4.03 (t, J = 6.57 Hz, 2H), 3.54 (t, J = 6.76 Hz, 2H), 1.81 (m, 6H), 1.26-1.55 (m, 18H), 0.92 (t, J = 6.84 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.03, 22.6, 25.7, 25.8, 26.9, 28.9, 29.1, 29.2, 29.3, 29.4, 29.4, 31.6, 32.6, 45.2, 68.1, 68.9, 114.4, 128.9, 130.1, 143.8, 151.0, 157.7, 160.7; LRMS (EI) *m/z* 448 (M+2, 37), 446 (M+, 100), 364 (8), 362 (22), 188 (90); HRMS (EI) calcd for $C_{26}H_{39}N_2O_2Cl$ 446.2700, found 446.2712.

Anal. Calcd for $C_{26}H_{39}N_2O_2Cl$: C, 69.85; H, 8.79; N, 6.27. Found: C, 69.35; H, 8.61; N, 6.30.

5-(9-Chlorononyloxy)-2-(4-heptyloxyphenyl)pyrimidine (QL8-7/9): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 2H), 8.28 (d, J = 8.72 Hz, 2H), 6.98 (d, J = 8.84 Hz, 2H), 4.08 (t, J = 6.44 Hz, 2H), 4.02 (t, J = 6.57 Hz, 2H), 3.55 (t, J = 6.76 Hz, 2H), 1.72-1.91 (m, 6H), 1.55-1.24 (m, 18H), 0.91 (t, J = 6.83 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 157.7, 151.0, 143.8, 130.0, 128.9, 114.4, 68.9, 68.1, 45.1, 32.6, 31.8, 29.3, 29.3, 29.2, 29.1, 29.1, 28.8, 26.8, 26.0, 25.8, 22.6, 14.1; LRMS (EI) *m/z* 448 (M+2, 39), 446 (M+, 100), 350(11), 348 (30), 188 (85); HRMS (EI) calcd for $C_{26}H_{39}N_2O_2Cl$ 446.2700, found 446.2712.

Anal. Calcd for $C_{26}H_{39}N_2O_2Cl$: C, 69.85; H, 8.79; N, 6.27. Found: C, 69.56; H, 8.44; N, 6.20.

5-(8-Chlorooctyloxy)-2-(4-octyloxyphenyl)pyrimidine (QL8-8/8): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 2H), 8.28 (d, J = 8.97 Hz, 2H), 6.98 (d, J = 8.97 Hz, 2H), 4.08 (t, J = 6.44 Hz, 2H), 4.02 (t, J = 6.57 Hz, 2H), 3.55 (t, J = 6.69 Hz, 2H), 1.69-1.96 (m, 6H), 1.20-1.58 (m, 18H), 0.91 (t, J = 6.86 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 157.7, 151.0, 143.8, 130.0, 128.9, 114.4, 68.8, 68.1, 45.1, 32.6, 31.8, 29.4, 29.3, 29.2, 29.1, 29.1, 28.8, 26.8, 26.0, 25.8, 22.7, 14.1; LRMS (EI) *m/z* 448 (M+2, 40), 446 (M+, 100), 336 (15), 334 (40), 188 (100); HRMS (EI) calcd for $C_{26}H_{39}N_2O_2Cl$ 446.2700, found 446.2721.

Anal. Calcd for $C_{26}H_{39}N_2O_2Cl$: C, 69.85; H, 8.79; N, 6.27. Found: C, 69.43; H, 8.79; N, 6.29.

5-(7-Chloroheptyloxy)-2-(4-nonyloxyphenyl)pyrimidine (QL8-9/7): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 2H), 8.28 (d, J = 8.97 Hz, 2H), 6.98 (d, J = 8.97 Hz, 2H), 4.09 (t, J = 6.38 Hz, 2H), 4.03 (t, J = 6.63 Hz, 2H), 3.56 (t, J = 6.63 Hz, 2H), 1.82 (m, 6H), 1.21-1.59 (m, 18H), 0.90 (t, J = 6.85 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 157.7, 151.0, 143.8, 129.0, 114.4, 68.8, 68.1, 45.0, 32.5, 31.9, 29.5, 29.4, 29.3, 29.0, 28.6, 26.8, 26.0, 25.8, 22.7, 14.1; LRMS (EI)

m/z 448 (M+2, 39), 446 (M+, 100), 322 (10), 320 (35), 188 (89); HRMS (EI) calcd for $C_{26}H_{39}N_2O_2Cl$ 446.2700, found 446.2689.

Anal. Calcd for $C_{26}H_{39}N_2O_2Cl$: C, 69.85; H, 8.79; N, 6.27. Found: C, 69.73; H, 8.61; N, 6.34.

5-(6-Chlorohexyloxy)-2-(4-decyloxyphenyl)pyrimidine (QL8-10/6): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 2H), 8.28 (d, J = 8.97 Hz, 2H), 6.98 (d, J = 8.84 Hz, 2H), 4.09 (t, J = 6.25 Hz, 2H), 4.02 (t, J = 6.57 Hz, 2H), 3.57 (t, J = 6.57 Hz, 2H), 1.73-1.94 (m, 6H), 1.18-1.63 (m, 18H), 0.90 (t, J = 6.86 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 157.7, 151.0, 143.8, 130.0, 128.9, 114.4, 68.6, 68.1, 44.9, 32.4, 31.9, 29.6, 29.5, 29.4, 29.3, 29.3, 29.0, 26.6, 26.0, 25.2, 22.7, 14.1; LRMS (EI) *m/z* 448 (M+2, 37), 446 (M+, 100), 308 (11), 306 (33), 188 (85); HRMS (EI) calcd for $C_{26}H_{39}N_2O_2Cl$ 446.2700, found 446.2717.

Anal. Calcd for $C_{26}H_{39}N_2O_2Cl$: C, 69.85; H, 8.79; N, 6.27. Found: C, 69.65; H, 8.73; N, 6.36.

5-(5-Chloropentyloxy)-2-(4-undecyloxyphenyl)pyrimidine (QL8-11/5): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 2H), 8.28 (d, J = 8.97 Hz, 2H), 6.98 (d, J = 8.97 Hz, 2H), 4.11 (t, J = 6.32 Hz, 2H), 4.02 (t, J = 6.63 Hz, 2H), 3.60 (t, J = 6.57 Hz, 2H), 1.96-1.56 (m, 6H), 1.19-1.55 (m, 18H), 0.90 (t, J = 6.84 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 157.8, 150.9, 143.8, 130.0, 129.0, 114.4, 68.5, 68.1, 44.7, 32.2, 31.9, 29.6, 29.6, 29.4, 29.3, 29.3, 28.5, 26.0, 23.4, 22.7, 14.1; LRMS (EI) *m/z* 448 (M+2, 39), 446 (M+, 100), 294 (15), 292 (41), 188 (75); HRMS (EI) calcd for $C_{26}H_{39}N_2O_2Cl$ 446.2700, found 446.2690.

Anal. Calcd for $C_{26}H_{39}N_2O_2Cl$: C, 69.85; H, 8.79; N, 6.27. Found: C, 69.29; H, 8.81; N, 6.31.

5-(4-Chlorobutyloxy)-2-(4-dodecyloxyphenyl)pyrimidine (QL8-12/4): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 2H), 8.28 (d, J=8.97 Hz, 2H), 6.98 (d, J=8.97 Hz, 2H), 4.10 (t, J = 6.32 Hz, 2H), 4.03 (t, J = 6.63 Hz, 2H), 3.65 (t, J = 6.57 Hz, 2H), 1.75-2.11 (m, 6H), 1.18-1.53 (m, 18H), 0.91 (t, J = 6.85 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 157.9, 150.8, 143.8, 130.0, 129.0, 114.4, 68.1, 67.9, 44.5, 31.9, 29.7, 29.6, 29.6, 29.6, 29.4, 29.3, 29.3, 29.0, 26.6, 26.0, 22.7, 14.1; LRMS (EI) *m/z* 448 (M+2, 40), 446 (M+, 100), 280 (11), 278 (35), 188 (47); HRMS (EI) calcd for $C_{26}H_{39}N_2O_2Cl$ 446.2700, found 446.2711.

Anal. Calcd for $C_{26}H_{39}N_2O_2Cl$: C, 69.85; H, 8.79; N, 6.27. Found: C, 69.92; H, 8.68; N, 6.36.

2-[4-(11-Chloroundecyloxy)phenyl]-5-pentyloxypyrimidine (QL9-5/11). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 2H), 8.28 (d, J = 8.72 Hz, 2H), 6.98 (d, J = 8.72 Hz, 2H), 4.09 (t, J = 6.51 Hz, 2H), 4.03 (t, J = 6.51 Hz, 2H), 3.54 (t, J = 6.76 Hz, 2H), 1.71-1.92 (m, 6H), 1.24-1.55 (m, 18H), 0.96 (t, J = 6.83 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 157.6, 151.1, 143.8, 130.1, 128.9, 114.4, 68.9, 68.0, 45.2, 32.6, 29.5, 29.4, 29.4, 29.2, 28.9, 28.8, 28.0, 26.9, 26.0, 22.4, 14.0; LRMS (EI) *m/z* 448 (M+2, 40), 446 (M+, 100), 258 (41), 188 (100); HRMS (EI) calcd for $C_{26}H_{39}N_2O_2Cl$ 446.2700, found 446.2689.

Anal. Calcd for $C_{26}H_{39}N_2O_2Cl$: C, 69.85; H, 8.79; N, 6.27. Found: C, 69.64; H, 8.69; N, 6.05.

2-[4-(10-Chlorodecyloxy)phenyl]-5-hexyloxypyrimidine (QL9-6/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 2H), 8.28 (d, J = 9.09 Hz, 2H), 6.98 (d, J = 8.97 Hz, 2H), 4.09 (t, J = 6.51 Hz, 2H), 4.03 (t, J = 6.57 Hz, 2H), 3.54 (t, J = 6.82 Hz, 2H), 1.66-1.97 (m, 6H), 1.26-1.55 (m, 18H), 0.94 (t, J = 6.85 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 157.6, 151.1, 143.8, 130.1, 128.9, 114.4, 68.9, 68.0, 45.2, 32.6, 31.5, 29.4, 29.4, 29.3, 29.2, 29.1, 28.9, 26.9, 26.0, 25.5, 22.6, 14.0; LRMS (EI) *m/z* 448 (M+2, 38), 446 (M+, 100), 272 (37), 188 (87); HRMS (EI) calcd for $C_{26}H_{39}N_2O_2Cl$ 446.2700, found 446.2687.

Anal. Calcd for $C_{26}H_{39}N_2O_2Cl$: C, 69.85; H, 8.79; N, 6.27. Found: C, 69.47; H, 8.87; N, 6.34.

2-[4-(9-Chlorononyloxy)phenyl]-5-heptyloxypyrimidine (QL9-7/9). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 2H), 8.28 (d, J = 8.84 Hz, 2H), 6.98 (d, J = 8.97 Hz, 2H), 4.08 (t, J = 6.51 Hz, 2H), 4.03 (t, J = 6.57 Hz, 2H), 3.54 (t, J = 6.76 Hz, 2H), 1.68-1.95 (m, 6H), 1.25-1.57 (m, 18H), 0.91 (t, J = 6.83 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 157.6, 151.1, 143.8, 130.1, 128.9, 114.4, 68.9, 68.0, 45.2, 32.6, 31.7, 29.4, 29.3, 29.2, 29.1, 29.0, 28.8, 26.9, 26.0, 25.8, 22.6, 14.1; LRMS (EI) *m/z* 448 (M+2, 38), 446 (M+, 100), 286 (34), 188 (89); HRMS (EI) calcd for $C_{26}H_{39}N_2O_2Cl$ 446.2700, found 446.2716.

Anal. Calcd for $C_{26}H_{39}N_2O_2Cl$: C, 69.85; H, 8.79; N, 6.27. Found: C, 69.63; H, 8.64; N, 6.31.

2-[4-(8-Chlorooctyloxy)phenyl]-5-octyloxypyrimidine (QL9-8/8). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 2H), 8.28 (d, J = 8.84 Hz, 2H), 6.97 (d, J = 8.84 Hz, 2H), 4.08 (t, J = 6.51 Hz, 2H), 4.03 (t, J = 6.51 Hz, 2H), 3.55 (t, J = 6.76 Hz, 2H), 1.72-1.94 (m, 6H), 1.14-1.59 (m, 18H), 0.91 (t, J = 6.86 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 157.6, 151.1, 143.8, 130.1, 128.9, 114.4, 68.9, 68.0, 45.1, 32.6, 31.8, 29.3, 29.2, 29.2, 29.1, 28.8, 26.8, 25.9, 25.9, 22.6, 14.1; LRMS (EI) *m/z* 448 (M+2, 38), 446 (M+, 99), 300 (31), 188 (100); HRMS (EI) calcd for $C_{26}H_{39}N_2O_2Cl$ 446.2700, found 446.2718.

Anal. Calcd for $C_{26}H_{39}N_2O_2Cl$: C, 69.85; H, 8.79; N, 6.27. Found: C, 69.46; H, 8.74; N, 6.41.

2-[4-(7-Chloroheptyloxy)phenyl]-5-nonyloxypyrimidine (QL9-9/7). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 2H), 8.28 (d, J = 8.97 Hz, 2H), 6.97 (d, J = 8.97 Hz, 2H), 4.09 (t, J = 6.51 Hz, 2H), 4.03 (t, J = 6.51 Hz, 2H), 3.55 (t, J = 6.69 Hz, 2H), 1.74-1.93 (m, 6H), 1.21-1.56 (m, 18H), 0.90 (t, J = 6.85 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 157.6, 151.1, 143.8, 130.1, 129.0, 114.4, 68.9, 67.9, 45.1, 32.5, 31.8, 29.5, 29.3, 29.2, 29.1, 29.1, 28.7, 26.8, 25.9, 25.9, 22.7, 14.1; LRMS (EI) *m/z* 448 (M+2, 38), 446 (M+, 100), 314 (22), 188 (86); HRMS (EI) calcd for $C_{26}H_{39}N_2O_2Cl$ 446.2700, found 446.2691.

Anal. Calcd for $C_{26}H_{39}N_2O_2Cl$: C, 69.85; H, 8.79; N, 6.27. Found: C, 69.21; H, 8.71; N, 6.31.

2-[4-(6-Chlorohexyloxy)phenyl]-5-decyloxypyrimidine (QL9-10/6). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 2H), 8.28 (d, J = 8.84 Hz, 2H), 6.97 (d, J = 8.84 Hz, 2H), 4.08 (t, J = 6.51 Hz, 2H), 4.03 (t, J = 6.44 Hz, 2H), 3.56 (t, J = 6.69 Hz, 2H), 1.42-1.93 (m, 6H), 1.19-1.41 (m, 18H), 0.89 (t, J = 6.86 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 157.6, 151.1, 143.8, 130.2, 129.0, 114.4, 68.9, 67.8, 45.0, 32.5, 31.9, 29.5, 29.3, 29.3, 29.1, 26.7, 25.9, 25.4, 22.7, 14.1;

LRMS (EI) *m/z* 448 (M+2, 36), 446 (M+, 100), 328 (12), 188 (74); HRMS (EI) calcd for $C_{26}H_{39}N_2O_2Cl$ 446.2700, found 446.2687.

Anal. Calcd for $C_{26}H_{39}N_2O_2Cl$: C, 69.85; H, 8.79; N, 6.27. Found: C, 69.47; H, 8.87; N, 6.34.

2-[4-(5-Chloropentyloxy)phenyl]-5-undecyloxypyrimidine (QL9-11/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 2H), 8.28 (d, J = 8.84 Hz, 2H), 6.97 (d, J = 8.84 Hz, 2H), 4.08 (t, J = 6.57 Hz, 2H), 4.05 (t, J = 6.38 Hz, 2H), 3.59 (t, J = 6.63 Hz, 2H), 1.47-1.96 (m, 6H), 1.15-1.42 (m, 18H), 0.89 (t, J = 6.82 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 157.6, 151.1, 143.8, 130.2, 129.0, 114.4, 68.9, 67.6, 44.9, 32.3, 31.9, 29.6, 29.6, 29.5, 29.3, 29.1, 28.5, 25.9, 23.6, 22.7, 14.1; LRMS (EI) *m/z* 448 (M+2, 38), 446 (M+, 100), 342 (8), 188 (65); HRMS (EI) calcd for $C_{26}H_{39}N_2O_2Cl$ 446.2700, found 446.2685.

Anal. Calcd for $C_{26}H_{39}N_2O_2Cl$: C, 69.85; H, 8.79; N, 6.27. Found: C, 69.62; H, 8.58; N, 5.97.

2-[4-(4-Chlorobutyloxy)phenyl]-5-dodecyloxypyrimidine (QL9-12/4): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 2H), 8.28 (d, J = 8.84 Hz, 2H), 6.97 (d, J = 8.84 Hz, 2H), 4.08 (t, J = 6.53 Hz, 2H), 4.02 (t, J = 6.34 Hz, 2H), 3.65 (t, J = 6.13 Hz, 2H), 1.76-2.11 (m, 6H), 1.19-1.66 (m, 18H), 0.82-0.98 (t, J = 6.84 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$-*d*) δ ppm 160.3, 157.5, 151.1, 143.8, 130.4, 129.0, 114.4, 68.9, 67.0, 44.7, 31.9, 29.6, 29.6, 29.6, 29.5, 29.3, 29.3, 29.1, 26.6, 25.8, 22.7, 14.1; LRMS (EI) *m/z* 448 (M+2, 38), 446 (M+, 100), 356 (3), 188 (53); HRMS (EI) calcd for $C_{26}H_{39}N_2O_2Cl$ 446.2700, found 446.2715.

Anal. Calcd for $C_{26}H_{39}N_2O_2Cl$: C, 69.85; H, 8.79; N, 6.27. Found: C, 70.06; H, 8.92; N, 6.52.

5-(8-Fluorooctyloxy)-2-(4-octyloxyphenyl)pyrimidine (QL10-F). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 2H), 8.28 (d, J = 8.84 Hz, 2H), 6.98 (d, J = 8.84 Hz, 2H), 4.51 (t, J = 6.13 Hz, 2H), 4.40 (t, J = 6.13 Hz, 2H), 4.08 (t, J = 6.44 Hz, 1H), 4.02 (t, J = 6.57 Hz, 1H), 1.58-1.91 (m, 6H), 1.21-1.57 (m, 18H), 0.89 (t, J = 6.86 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 157.7, 151.0, 143.8, 130.0, 128.9, 114.4, 84.9, 83.3, 68.8, 68.1, 31.8, 30.5, 30.3, 29.4, 29.3, 29.2, 29.2, 29.1, 29.1, 26.0, 25.8, 25.1, 25.1, 22.6, 14.1; LRMS (EI) *m/z* 431 (M+1, 28), 430 (M+, 100), 319 (7), 318 (31), 188 (77); HRMS (EI) calcd for $C_{26}H_{39}N_2O_2F$ 430.2996, found 430.2981.

Anal. Calcd for $C_{26}H_{39}N_2O_2F$: C, 72.52; H, 9.13; N, 6.51. Found: C, 72.46; H, 9.06; N, 6.49.

5-(8-Bromooctyloxy)-2-(4-octyloxyphenyl)pyrimidine (QL10-Br). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 2H), 8.28 (d, J = 8.59 Hz, 2H), 6.98 (d, J = 8.72 Hz, 2H), 4.09 (t, J = 6.44 Hz, 2H), 4.03 (t, J = 6.57 Hz, 2H), 3.43 (t, J = 6.82 Hz, 2H), 1.75-1.94 (m, 6H), 1.23-1.60 (m, 18H), 0.89 (t, J = 6.85 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 151.0, 143.8, 129.0, 114.4, 68.9, 68.1, 33.9, 32.8, 31.8, 29.4, 29.3, 29.2, 29.1, 29.1, 28.6, 28.1, 26.1, 25.8, 22.7, 14.1; LRMS (EI) *m/z* 492 (M+2, 80), 490 (M+, 78), 380 (25), 378 (25), 188 (100); HRMS (EI) calcd for $C_{26}H_{39}N_2O_2Br$ 492.2178, found 492.2213.

Anal. Calcd for $C_{26}H_{39}N_2O_2Br$: C, 63.54; H, 8.00; N, 5.70. Found: C, 62.88; H, 7.98; N, 5.59.

5-(8-Iodooctyloxy)-2-(4-octyloxyphenyl)pyrimidine (QL10-I). Under a N_2 atmosphere, **QL10-Br** (0.020 g, 0.05 mmol) was combined with sodium iodide (0.030 g, 0.19 mmol) in

acetone (3 mL) and the solution was stirred under reflux for 20 h. The reaction mixture was then diluted with water (10 mL) and extracted with dichloromethane (3 x 20 mL). The combined extracts were dried (Na_2SO_4), concentrated and the crude product was purified by preparative thin layer chromatography (1:15 EtOAc/hexanes) to give **QL10-I** (88%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 2H), 8.27 (d, J = 8.84 Hz, 2H), 6.97 (d, J = 8.84 Hz, 2H), 4.08 (t, J = 6.44 Hz, 2H), 4.02 (t, J = 6.57 Hz, 2H), 3.21 (t, J = 7.01 Hz, 2H), 1.74-1.91 (m, 6H), 1.16-1.57 (m, 18H), 0.87 (t, J = 6.85 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 157.7, 151.0, 143.8, 130.0, 129.0, 114.4, 68.8, 68.1, 33.4, 31.8, 30.4, 29.4, 29.3, 29.2, 29.1, 29.1, 28.4, 26.0, 25.8, 22.6, 14.1; LRMS (EI) *m/z* 539 (M+1, 16), 538 (M+, 51), 427(3), 426 (20), 188 (100); HRMS (EI) calcd for $C_{26}H_{39}N_2O_2I$ 538.2056, found 538.2037.

Anal. Calcd for $C_{26}H_{39}N_2O_2I$: C, 57.99; H, 7.30; N, 5.20. Found: C, 58.64; H, 7.45; N, 4.94.

2-(4-Dodecyloxyphenyl)-5-pentyloxypyrimidine (2PhP-12/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 2H), 8.28 (d, J = 8.97 Hz, 2H), 6.98 (d, J = 8.97 Hz, 2H), 4.09 (t, J = 6.51 Hz, 2H), 4.03 (t, J = 6.57 Hz, 2H), 1.83 (ddd, J = 6.44, 8.21, 12.76 Hz, 8H), 1.18-1.59 (m, 18H), 0.96 (t, J = 6.84 Hz, 3H), 0.89 (t, J = 6.85 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 157.7, 151.1, 143.8, 128.9, 114.4, 68.9, 31.9, 29.7, 29.6, 29.6, 29.6, 29.4, 29.3, 29.3, 28.8, 28.0, 26.0, 22.7, 22.4, 14.0; LRMS (EI) *m/z* 426 (M+, 100), 258 (38), 188 (67); HRMS (EI) calcd for $C_{27}H_{42}N_2O_2$ 426.3246, found 426.3235.

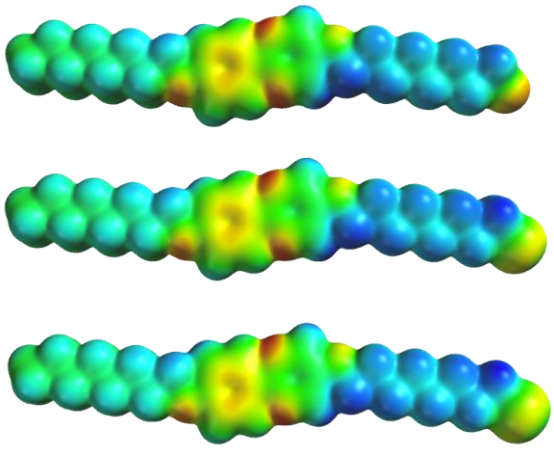

Fig. S1. Electrostatic potential isosurfaces calculated at the B3LYP/6-31G* level for **QL10-F** (top), **QL8-8/8** (middle) and **QL10-Br** (bottom). The color scale ranges from red (–155 kJ mol^{-1}) to blue (+105 kJ mol^{-1}).