### **Electronic Supplementary Material for:**

# Electroclinic Effect in Chiral SmA\* Liquid Crystals Induced by Atropisomeric Biphenyl Dopants: Amplification of the Electroclinic Coefficient Using Achiral Additives

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#### General

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker Avance 300 and 400 spectrometers; chemical shifts are reported in  $\delta$  (ppm) relative to tetramethylsilane. Low- and high-resolution EI mass spectra were recorded on a Waters/Micromass GC-TOF system; peaks are reported as m/z (% intensity relative to the base peak). Elemental analyses were performed by Canadian Microanalytical Service Ltd. (Delta, British Columbia). All reagents, chemicals, and solvents were obtained from commercial sources and used without further purification.

#### 5-(Hexyloxy)-2-(4-(hexyloxy)phenyl)pyrimidine (3a)

Under an argon atmosphere, a mixture of (4-hydroxyphenyl)-5-pyrimidinol (54 mg, 90% purity, 0.26 mmol), 1-bromohexane (131 mg, 0.79 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (189 mg, 0.58 mmol) in anhyd. DMF (3 mL) was stirred at room temperature overnight. The mixture was then partitioned between water and Et<sub>2</sub>O. The aqueous layer was extracted with ether (2×), and the combined organic layers washed with water, dried (MgSO<sub>4</sub>), and concentrated to a white solid. Purification by flash chromatography (9:1 hexanes:EtOAc) gave 87 mg (94%) of **3a** as a white solid. Prior to doping experiments the material was recrystallized from HPLC-grade hexanes with filtration through a 0.45 µm PTFE filter: Cr 69 SmC 74 SmA 77 N 100 I; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  0.91 (m, 6H), 1.34 (m, 8H), 1.47 (m, 4H), 1.80 (m, 4H), 4.00 (t, *J* = 6.6 Hz, 2H), 4.05 (t, *J* = 6.4 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 8.27 (d, *J* = 8.8 Hz, 2H), 8.40 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  14.1, 14.2, 22.7, 22.7, 25.6, 25.8, 29.2, 29.4, 31.6, 31.7, 68.2, 69.0, 114.5, 129.0, 130.1, 143.9, 151.2, 157.7, 160.8; MS (EI) *m/z* 356 (M<sup>+</sup>, 86), 272 (55), 188 (100); HRMS (EI) Calcd. for C<sub>22</sub>H<sub>32</sub>N<sub>2</sub>O<sub>2</sub>: 356.2464. Found: 356.2474.

### 5-(Octyloxy)-2-(4-(octyloxy)phenyl)pyrimidine (3b)

The procedure for the synthesis of **3a** was repeated using (4-hydroxyphenyl)-5-pyrimidinol (52 mg, 90% purity, 0.25 mmol) and 1-bromooctane (147 mg, 0.76 mmol). Purification by flash chromatography (9:1 hexanes:EtOAc) gave 99 mg (96%) of **3b** as a white solid. Prior to doping experiments the material was recrystallized from HPLC-grade hexanes with filtration through a 0.45  $\mu$ m PTFE filter: Cr 53 SmC 93 SmA 101 N 102 I; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  0.89 (m, 6H), 1.2-1.4 (m, 16H), 1.46 (m, 4H), 1.80 (m, 4H), 4.00 (t, *J* = 6.6 Hz, 2H), 4.05 (t, *J* = 6.4 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 8.27 (d, *J* = 8.8 Hz, 2H), 8.40 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  14.2, 22.8, 22.8, 26.0, 26.2, 29.2, 29.3, 29.4, 29.4, 29.4, 29.5, 31.9, 31.9, 68.2, 69.0,

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114.5, 129.1, 130.1, 143.9, 151.2, 157.7, 160.8; MS (EI) *m*/*z* 412 (M<sup>+</sup>, 100), 300 (31), 188 (92); HRMS (EI) Calcd. for C<sub>26</sub>H<sub>40</sub>N<sub>2</sub>O<sub>2</sub>: 412.3090. Found: 412.3102.

### 5-(Nonyloxy)-2-(4-(nonyloxy)phenyl)pyrimidine (3c)

The procedure for the synthesis of **3a** was repeated using (4-hydroxyphenyl)-5-pyrimidinol (51 mg, 90% purity, 0.24 mmol) and 1-bromononane (159 mg, 0.77 mmol). Purification by flash chromatography (9:1 hexanes:EtOAc) gave 93 mg (86%) of **3c** as a white solid. Prior to doping experiments the material was recrystallized from HPLC-grade hexanes with filtration through a 0.45  $\mu$ m PTFE filter: Cr 64 SmC 97 SmA 101 I; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  0.89 (m, 6H), 1.2-1.4 (m, 20H), 1.46 (m, 4H), 1.80 (m, 4H), 4.00 (t, *J* = 6.6 Hz, 2H), 4.05 (t, *J* = 6.4 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 8.27 (d, *J* = 8.8 Hz, 2H), 8.40 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  14.2, 22.8, 26.0, 26.2, 29.2, 29.4, 29.4, 29.5, 29.6, 29.6, 29.7, 32.0, 32.0, 68.2, 69.0, 114.5, 129.1, 130.2, 143.9, 151.2, 157.8, 160.8; MS (EI) *m/z* 440 (M<sup>+,</sup> 100), 314 (23), 188 (60); HRMS (EI) Calcd. for C<sub>28</sub>H<sub>44</sub>N<sub>2</sub>O<sub>2</sub>: 440.3403. Found: 440.3415.

#### 5-(Decyloxy)-2-(4-(decyloxy)phenyl)pyrimidine (3d)

The procedure for the synthesis of **3a** was repeated using (4-hydroxyphenyl)-5-pyrimidinol (50 mg, 90% purity, 0.24 mmol) and 1-bromodecane (166 mg, 0.75 mmol). Purification by flash chromatography (9:1 hexanes:EtOAc) gave 82 mg (73%) of **3d** as a white solid. Prior to doping experiments the material was recrystallized from HPLC-grade hexanes with filtration through a 0.45 µm PTFE filter: Cr 58 SmC 104 I; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  0.88 (m, 6H), 1.2-1.4 (m, 24H), 1.46 (m, 4H), 1.80 (m, 4H), 4.00 (t, *J* = 6.6 Hz, 2H), 4.05 (t, *J* = 6.6 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 8.27 (d, *J* = 8.5 Hz, 2H), 8.40 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  14.2, 22.8, 26.0, 26.2, 29.2, 29.4, 29.4, 29.4, 29.5, 29.7, 29.7, 29.7, 32.0, 32.0, 68.2, 69.0, 114.5, 129.1, 130.2, 143.9, 151.2, 157.7, 160.8; MS (EI) *m/z* 468 (M<sup>+</sup>, 100), 328 (17), 188 (55); HRMS (EI) Calcd. for C<sub>30</sub>H<sub>48</sub>N<sub>2</sub>O<sub>2</sub>: 468.3716. Found: 468.3735.

#### 5-(Undecyloxy)-2-(4-(undecyloxy)phenyl)pyrimidine (3e)

The procedure for the synthesis of **3a** was repeated using (4-hydroxyphenyl)-5-pyrimidinol (50 mg, 90% purity, 0.24 mmol) and 1-bromoundecane (172 mg, 0.73 mmol). Purification by flash chromatography (9:1 hexanes:EtOAc) followed by recrystallization from hexanes gave 109 mg (92%) of **3e** as a white solid. Prior to doping experiments the material was again recrystallized from HPLC-grade hexanes with filtration through a 0.45 µm PTFE filter: Cr 74 SmC 103 I; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  0.88 (t, *J* = 6.8 Hz, 6H), 1.2-1.4 (m, 28H), 1.46 (m, 4H), 1.80 (m, 4H), 4.00 (t, *J* = 6.6 Hz, 2H), 4.04 (t, *J* = 6.4 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 8.28 (d, *J* = 8.6 Hz, 2H), 8.40 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  14.2, 22.8, 26.0, 26.2, 29.2, 29.4, 29.5, 29.5, 29.7, 29.7, 32.0, 68.2, 69.0, 114.5, 129.0, 130.2, 143.9, 151.2, 157.7, 160.8; Anal. Calcd. for C<sub>32</sub>H<sub>52</sub>N<sub>2</sub>O<sub>2</sub>: C, 77.37; H, 10.55; N, 5.64. Found: C, 77.24; H, 10.82; N, 5.45.

#### 5-(Dodecyloxy)-2-(4-(dodecyloxy)phenyl)pyrimidine (3f)

The procedure for the synthesis of **3a** was repeated using (4-hydroxyphenyl)-5-pyrimidinol (47 mg, 90% purity, 0.23 mmol) and 1-bromododecane (183 mg, 0.73 mmol). Purification by flash chromatography (9:1 hexanes:EtOAc) followed by recrystallization from hexanes gave 100 mg (84%) of **3f** as a white solid. Prior to doping experiments the material was again recrystallized from HPLC-grade hexanes with filtration through a 0.45  $\mu$ m PTFE filter: Cr 66 SmC 105 I; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  0.88 (m, 6H), 1.2-1.4(m, 32H), 1.46 (m, 4H), 1.80 (m, 4H), 4.00 (t, *J* 

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= 6.6 Hz, 2H), 4.05 (t, J = 6.4 Hz, 2H), 6.96 (d, J = 8.6 Hz, 2H), 8.27 (d, J = 8.9 Hz, 2H), 8.40 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  14.2, 22.8, 26.0, 26.2, 29.2, 29.4, 29.5, 29.5, 29.6, 29.7, 29.7, 29.7, 29.8, 29.8, 32.0, 68.2, 69.0, 114.5, 129.1, 130.2, 143.9, 151.2, 157.8, 160.8; MS (EI) *m*/*z* 524 (M<sup>+</sup>, 100), 468 (12), 356 (12), 188 (54); HRMS (EI) Calcd. for C<sub>34</sub>H<sub>56</sub>N<sub>2</sub>O<sub>2</sub>: 524.4342. Found: 524.4352.

# 5-(Tetradecyloxy)-2-(4-(tetradecyloxy)phenyl)pyrimidine (3g)

The procedure for the synthesis of **3a** was repeated using (4-hydroxyphenyl)-5-pyrimidinol (50 mg, 90% purity, 0.24 mmol) and 1-bromotetradecane (206 mg, 0.74 mmol). Purification by flash chromatography (19:1 hexanes:EtOAc) followed by recrystallization from hexanes gave 101 mg (73%) of **3g** as a white solid. Prior to doping experiments the material was again recrystallized from HPLC-grade hexanes with filtration through a 0.45  $\mu$ m PTFE filter: Cr 77 SmC 104 I; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  0.88 (m, 6H), 1.2-1.4 (m, 40H), 1.47 (m, 4H), 1.81 (m, 4H), 4.01 (t, *J* = 6.4 Hz, 2H), 4.06 (t, *J* = 6.4 Hz, 2H), 6.96 (d, *J* = 8.6 Hz, 2H), 8.27 (d, *J* = 8.6 Hz, 2H), 8.41 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  14.2, 22.8, 26.0, 26.2, 29.3, 29.4, 29.5, 29.5, 29.6, 29.7, 29.7, 29.8, 29.8, 29.8, 32.1, 68.2, 69.1, 114.6, 129.1, 130.1, 143.9, 151.2, 157.8, 160.1; MS (EI) *m/z* 580 (M<sup>+</sup>, 40), 397 (19), 384 (20), 218 (21), 188 (100); HRMS (EI) Calcd. for C<sub>38</sub>H<sub>64</sub>N<sub>2</sub>O<sub>2</sub>: 580.4968. Found: 580.4952.

# 5-(Hexadecyloxy)-2-(4-(hexadecyloxy)phenyl)pyrimidine (3h)

The procedure for the synthesis of **3a** was repeated using (4-hydroxyphenyl)-5-pyrimidinol (50 mg, 90% purity, 0.24 mmol) and 1-bromohexadecane (232 mg, 0.76 mmol). Purification by flash chromatography (9:1 hexanes:EtOAc) followed by recrystallization from hexanes gave 120 mg (79%) of **3h** as a white solid. Prior to doping experiments the material was again recrystallized from HPLC-grade hexanes with filtration through a 0.45  $\mu$ m PTFE filter: Cr 85 SmX 86 SmC 102 I; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  0.88 (m, 6H), 1.2-1.4 (m, 48H), 1.47 (m, 4H), 1.81 (m, 4H), 4.01 (t, *J* = 6.6 Hz, 2H), 4.07 (t, *J* = 6.5 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 8.28 (d, *J* = 8.8 Hz, 2H), 8.41 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  14.3, 22.8, 26.0, 26.2, 29.3, 29.4, 29.5, 29.5, 29.6, 29.7, 29.7, 29.8, 29.8, 29.8, 29.8, 32.1, 68.2, 69.1, 114.6, 129.2, 130.1, 144.0, 151.2, 157.7, 160.9; MS (EI) *m*/*z* 637 (M<sup>+</sup>, 70), 425 (41), 412 (31), 188 (100); HRMS Calcd. for C<sub>42</sub>H<sub>72</sub>N<sub>2</sub>O<sub>2</sub>: 636.5594. Found: 636.5580.