

**Electronic Supplementary Information for:**

**Liquid crystals with axially chiral 3,3'-dinitro-2,2',6,6'-tetramethylbiphenyl cores: The lateral shielding effect of bicyclo[2.2.2]octane-1-carboxylate terminal chains**

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**Experimental**

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using Bruker Avance 300 and 400 spectrometers; chemical shifts ( $\delta$ ) are reported in parts per million (ppm) relative to TMS as internal standard. Mass spectra were recorded using Waters/Micromass GC-TOF (low- and high- resolution) and Applied Biosystems/MDS Sciex QSTAR XL QTOF (low-resolution) instruments. Elemental analyses were performed on a Thermo Flash 2000 combustion analyzer. Differential scanning calorimetry (DSC) analyses were performed using either a Perkin-Elmer DSC-7 or a TA Instruments Q2000 instrument with a scanning rate of 5 K min<sup>-1</sup>. 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. Racemic 4,4'-dihydroxy-2,2',6,6'-tetramethyl-3,3'-dinitrobiphenyl (*RS*)-**8** was obtained by demethylation of 4,4'-dimethoxy-2,2',6,6'-tetramethyl-3,3'-dinitrobiphenyl<sup>1</sup> with BBr<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> in 89% yield, and shown to have the expected physical and spectral properties.<sup>2</sup> Racemic (*RS*)-**8** was resolved on a 1-gram scale by preparative chiral phase HPLC using a Daicel Chiralpak AS column (50 cm  $\times$  5 cm i.d., 20% EtOH/hexanes, 50 mL min<sup>-1</sup>); the first eluant was identified as the (*R*) enantiomer by co-elution with an authentic sample.<sup>1</sup> Ethyl 4-hydroxybicyclo[2.2.2]octane-1-carboxylate was prepared according to a literature procedure and shown to have the expected physical and spectral properties.<sup>3</sup>

**(*R*)-2,2',6,6'-Tetramethyl-3,3'-dinitro-4,4'-bis-((4-pentylbicyclo[2.2.2]octan-1-oyl)oxy)biphenyl (4)**

Under an Ar atmosphere, solid DCC (35 mg, 0.17 mmol) was added to a solution of (*R*)-**8** (25 mg, 0.077 mmol), DMAP (21 mg, 0.17 mmol) and 4-pentylbicyclo[2.2.2]octane-1-carboxylic acid (38 mg, 0.17 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL). After stirring for 24 hours, the reaction mixture was filtered, diluted with EtOAc and washed with 10% aq. HCl (2 $\times$ ), H<sub>2</sub>O and brine. The organic layer was dried (MgSO<sub>4</sub>) and concentrated to a white solid, which was purified by flash chromatography on silica gel (toluene) to give 33 mg (55%) of **4** as a white solid. The compound was further purified by recrystallization from hexanes after passing through a 0.45  $\mu$ m PTFE filter: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.10 (s, 2H), 1.96 (s, 6H), 1.92 (s, 6H), 2.05-1.80 (m, 12H), 1.48-1.43 (m, 12H), 1.33-1.14 (m, 18H), 0.90 (t, *J* = 7.1 Hz, 6H); <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  14.4, 15.3, 20.6, 23.0, 23.7, 28.8, 30.5, 30.8, 33.1, 39.9, 41.5, 123.8, 129.9, 136.4, 140.2, 142.1, 143.6, 175.8.

Anal. Calcd for C<sub>44</sub>H<sub>60</sub>N<sub>2</sub>O<sub>8</sub>: C, 70.94; H, 8.12; N, 3.76. Found: C, 71.39; H, 8.19; N, 3.95.

**4-Butyloxybicyclo[2.2.2]octane-1-carboxylic acid (9(4))**

A flame-dried flask was charged with ethyl 4-hydroxy bicyclo[2.2.2]octane carboxylate (300 mg, 1.52 mmol), NaH (400 mg, 10 mmol) and THF (20 mL). After heating to 60-65  $^{\circ}$ C for 30 min, iodobutane (2 mL, 17.4 mmol) was added and the reaction mixture was refluxed overnight. After cooling, the mixture was quenched slowly with water (40 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (2  $\times$  20 mL) to remove excess iodobutane. The aqueous layer was acidified to pH 3 with 1M aq HCl and then extracted with CH<sub>2</sub>Cl<sub>2</sub> (3  $\times$  30 mL). The combined extracts were washed twice with brine, dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated to give 111 mg (32%) of **9(4)** as a white solid: mp 133-135  $^{\circ}$ C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  3.31 (t, *J* = 6.4 Hz, 2H), 1.96-1.88 (m, 6H), 1.73-1.66 (m, 6H), 1.49 (quintet, *J* = 8.0 Hz, 2H), 1.37-1.29 (m, 2H), 0.87 (t, *J* =

6.5 Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  183.7, 73.3, 61.3, 38.4, 32.9, 29.48, 29.44, 19.7, 14.2; LRMS (EI)  $m/z$  226 ( $\text{M}^+$ , 17), 181 (15), 171 (26), 124 (100), 111 (90), 71 (24); LRMS (EI)  $m/z$  226 ( $\text{M}^+$ , 22), 171 (31), 152 (20), 124 (100), 111 (90); HRMS (EI) calcd for  $\text{C}_{13}\text{H}_{22}\text{O}_3$  226.1569, found: 226.1560. Anal. Calcd for  $\text{C}_{13}\text{H}_{22}\text{O}_3$ : C, 68.99; H, 9.80. Found: C, 68.78; H, 9.85.

#### 4-Octyloxybicyclo[2.2.2]octane-1-carboxylic acid (9(8))

The procedure described for the synthesis of **9(4)** was repeated with 400 mg of ethyl 4-hydroxy bicyclo[2.2.2]octane carboxylate to give 225 mg (52%) of **9(8)** as a white solid: mp 138-140 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.30 (t,  $J$  = 7.2 Hz, 2H), 1.97-1.90 (m, 6H), 1.70-1.66 (m, 6H), 1.49 (quintet,  $J$  = 8.0 Hz, 2H), 1.26 (br s, 10H), 0.87 (t,  $J$  = 8.8, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  183.3, 73.2, 61.6, 38.3, 32.0, 30.8, 29.6, 29.5, 29.4, 29.3, 26.4, 22.9, 14.3; LRMS (EI)  $m/z$  282 ( $\text{M}^+$ , 8), 171 (48), 167 (66), 124 (100), 95 (26), 71 (23); HRMS (EI) calcd for  $\text{C}_{17}\text{H}_{30}\text{O}_3$  282.2195, found: 282.2171. Anal. Calcd for  $\text{C}_{17}\text{H}_{30}\text{O}_3$ : C, 72.30; H, 10.71. Found: C, 72.06; H, 10.60.

#### 4-Dodecyloxybicyclo[2.2.2]octane-1-carboxylic acid (9(12))

The procedure described for the synthesis of **9(4)** was repeated with 350 mg of ethyl 4-hydroxy bicyclo[2.2.2]octane carboxylate to give 236 mg (40 %) of **9(12)** as a white solid: mp 123-124 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.29 (t,  $J$  = 8.4 Hz, 2H), 1.94-1.90 (m, 6H), 1.70-1.66 (m, 6H), 1.48 (quintet,  $J$  = 8.8 Hz, 2H), 1.25 (br s, 18H), 0.87 (t,  $J$  = 8.8 Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  183.5, 73.2, 61.6, 38.3, 33.4, 32.1, 30.8, 29.9, 29.8, 29.7, 29.62, 29.56, 29.40, 29.35, 28.8, 26.4, 22.9, 14.3; LRMS (EI)  $m/z$  368 (100,  $\text{M}^+$ ), 229 (50), 223 (62), 211 (20), 171 (46), 125 (69), 97 (50), 83 (51), 57 (100); HRMS (EI) calcd for  $\text{C}_{21}\text{H}_{38}\text{O}_3$  338.2821, found 338.2838. Anal. Calcd for  $\text{C}_{21}\text{H}_{38}\text{O}_3$ : C, 74.51; H, 11.31. Found: C, 74.50; H, 11.62.

#### (R)-4,4'-Bis-((4-butyloxybicyclo[2.2.2]octan-1-oyl)oxy)-2,2',6,6'-tetramethyl-3,3'-dinitrophenyl (5(4))

Under an argon atmosphere, solid DCC (290 mg, 1.40 mmol) was added to a solution of (*R*)-**8** (90 mg, 0.27 mmol), **9(4)** (140 mg, 0.62 mmol) and DMAP (130 mg, 1.06 mmol) in  $\text{CH}_2\text{Cl}_2$  (4 mL). After stirring overnight at room temperature, the mixture was filtered, diluted with EtOAc and washed twice with 20% aq HCl and water. The organic layer was dried ( $\text{MgSO}_4$ ) and concentrated to a pale yellow solid which was purified by flash chromatography on silica gel (10% EtOAc/hexanes) to give 134 mg (64 %) of **5(4)** as a white solid. The compound was further purified by recrystallization from acetonitrile after passing through a 0.45  $\mu\text{m}$  PTFE filter:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.08 (s, 2H), 3.33 (t,  $J$  = 6.8 Hz, 4H), 2.08-2.00 (m, 12H), 1.94 (s, 6H), 1.90 (s, 6H), 1.79-1.70 (m, 12H), 1.50 (quintet,  $J$  = 6.8 Hz, 4H), 1.36 (quintet,  $J$  = 6.8 Hz, 4H), 0.90 (t,  $J$  = 7.6, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  174.9, 143.5, 141.9, 140.2, 136.4, 129.9, 123.6, 73.0, 61.3, 39.1, 32.8, 29.4, 29.3, 20.5, 19.6, 15.2, 14.1; HRMS (MALDI) calcd for  $\text{C}_{42}\text{H}_{56}\text{O}_{10}\text{N}_2\text{Na}$  771.3832, found 771.3858.

Anal. Calcd for  $\text{C}_{42}\text{H}_{56}\text{N}_2\text{O}_{10}$ : C, 67.36; H, 7.54; N, 3.74. Found: C, 66.97; H, 7.66; N, 3.72.

#### (R)-2,2',6,6'-Tetramethyl-3,3'-dinitro-4,4'-bis-((4-octyloxybicyclo[2.2.2]octan-1-oyl)oxy)biphenyl (5(8))

The procedure described for the synthesis of **5(4)** was repeated with 100 mg (0.30 mmol) of (*R*)-**8** and 180 mg (0.64 mmol) of **9(8)** to give 160 mg (60%) of **5(8)** as a white solid. The compound was further purified by recrystallization from hexane after passing through a 0.45  $\mu\text{m}$  PTFE filter:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.07 (s, 2H), 3.32 (t,  $J$  = 8.4 Hz, 4H), 2.09-2.03 (m, 12H), 1.94 (s, 6H), 1.90 (s, 6H), 1.77-1.73 (m, 12H), 1.50 (quintet,  $J$  = 8.8 Hz, 4H), 1.28 (br s, 20H), 0.88 (t,  $J$  = 8.8, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  174.9, 143.4, 141.9, 140.2, 136.4, 129.9, 123.6, 73.0, 61.6, 39.1, 32.1, 30.8, 29.7, 29.5, 29.40, 29.3, 26.4, 22.9, 20.5, 15.2, 14.3; HRMS (MALDI) calcd for  $\text{C}_{50}\text{H}_{72}\text{O}_{10}\text{N}_2\text{Na}$  883.5084, found 883.5037.

**(*R*)-4,4'-Bis-((4-dodecyloxybicyclo[2.2.2]octan-1-yl)oxy)-2,2',6,6'-tetramethyl-3,3'-dinitrobiphenyl (5(12))**

The procedure described for the synthesis of **5(4)** was repeated with 105 mg (0.31 mmol) of (*R*)-**8** and 210 mg (0.62 mmol) of **9(12)** to give 220 mg (73%) of **5(12)** as a white solid. The compound was further purified by recrystallization from acetonitrile after passing through a 0.45 µm PTFE filter: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.07 (s, 2H), 3.31 (t, *J* = 8.8 Hz, 4H), 2.05-2.01 (m, 12H), 1.94 (s, 6H), 1.90 (s, 6H), 1.76-1.72 (m, 12H), 1.50 (quintet, *J* = 8.8 Hz, 4H), 1.26 (br s, 36H), 0.88 (t, *J* = 8.4, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 174.9, 143.4, 141.9, 140.2, 136.4, 129.9, 123.6, 73.0, 61.7, 39.1, 32.1, 30.8, 29.8, 29.7, 29.6, 29.40, 29.36, 26.4, 22.9, 20.5, 15.2, 14.3; HRMS (MALDI) calcd for C<sub>58</sub>H<sub>88</sub>O<sub>10</sub>N<sub>2</sub>Na 995.6331, found 995.6243. Anal. Calcd for C<sub>58</sub>H<sub>88</sub>N<sub>2</sub>O<sub>10</sub>: C, 71.57; H, 9.11; N, 2.88. Found: C, 71.00; H, 9.23; N, 2.87.

**(*R*)-4-Hydroxy-2,2',6,6'-tetramethyl-3,3'-dinitro-4'-((4-pentylbicyclo[2.2.2]octan-1-yl)oxy)biphenyl (10)**

Under an Ar atmosphere, solid DCC (982 mg, 4.76 mmol) was added to a solution of (*R*)-**8** (781 mg, 2.35 mmol), 4-pentylbicyclo[2.2.2]octane-1-carboxylic acid (571 mg, 2.55 mmol) and DMAP (575 mg, 4.72 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL). After stirring for 20 h, the reaction mixture was filtered, diluted with EtOAc and washed with 10% aq HCl (2×), H<sub>2</sub>O and brine. The organic layer was dried (MgSO<sub>4</sub>) and concentrated to a yellow oil, which was purified by flash chromatography on silica gel (7:1 hexanes/EtOAc) to give 689 mg (54%) of **10** as a yellow solid: mp 59-61 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.86 (t, *J* = 7.2 Hz, 3H), 1.11-1.28 (m, 8H), 1.41-1.45 (m, 6H), 1.85-1.89 (m, 12H), 1.92 (s, 3H), 2.14 (s, 3H), 6.99 (s, 1H), 7.07 (s, 1H), 10.00 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 14.0, 15.0, 18.0, 20.2, 20.9, 22.6, 23.3, 28.4, 30.2, 30.4, 32.7, 39.5, 41.2, 118.7, 123.3, 129.8, 131.4, 133.9, 134.8, 136.7, 140.2, 141.6, 143.3, 145.2, 154.0, 175.5; MS (ESI) *m/z* 577 ([M + K]<sup>+</sup>, 64), 430 (65), 429 (100), 409 (75), 381 (67), 140 (53); HRMS (ESI) calcd for C<sub>30</sub>H<sub>38</sub>N<sub>2</sub>O<sub>7</sub>K 577.2316, found 577.2340.

**(*R*)-2,2',6,6'-Tetramethyl-3,3'-dinitro-4'-((4-octyloxybenzoyl)oxy)-4'-((4-pentylbicyclo[2.2.2]octan-1-yl)oxy)biphenyl (6(8))**

The procedure described for the synthesis of **4** was repeated with 30 mg (0.06 mmol) of **10** and 28 mg (0.11 mmol) of 4-octyloxybenzoic acid to give 23 mg (54 %) of **6(8)** as a white solid. The compound was further purified by recrystallization from isopropanol after passing through a 0.45 µm PTFE filter: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.86-0.89 (m, 6H), 1.11-1.34 (m, 16H), 1.42-1.45 (m, 8H), 1.79-1.83 (m, 2H), 1.86-1.88 (m, 6H), 1.94 (s, 6H), 1.97 (s, 6H), 4.03 (t, *J* = 6.5 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 7.10 (s, 1H), 7.31 (s, 1H), 8.06 (d, *J* = 8.9 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 14.1, 15.0, 20.3, 20.3, 22.6, 22.7, 23.3, 25.9, 28.5, 29.0, 29.2, 29.3, 29.7, 30.2, 30.4, 31.8, 32.8, 39.5, 41.2, 68.4, 114.5, 119.9, 123.5, 123.5, 129.7, 129.7, 132.7, 136.1, 139.9, 140.0, 141.8, 141.9, 143.3, 143.4, 163.6, 164.1, 175.5; MS (ESI) *m/z* 793 ([M + Na]<sup>+</sup>, 1), 577 (100), 413 (59), 123 (45); HRMS (ESI) calcd for C<sub>45</sub>H<sub>58</sub>N<sub>2</sub>O<sub>9</sub>Na 793.4040, found 793.4058.

**(*R*)-4-((4-Decyloxybenzoyl)oxy)-2,2',6,6'-tetramethyl-3,3'-dinitro-4'-((4-pentylbicyclo[2.2.2]octan-1-yl)oxy)biphenyl (6(10))**

The procedure described for the synthesis of **4** was repeated with 38 mg (0.07 mmol) of **10** and 39 mg (0.14 mmol) of 4-decyloxybenzoic acid to give 44 mg (78 %) of **6(10)** as a white solid. The compound was further purified by recrystallization from isopropanol after passing through a 0.45 µm PTFE filter: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.87 (t, *J* = 7.0 Hz, 6H), 1.11-1.35 (m, 20H), 1.41-1.45 (m, 8H), 1.79-1.81 (m, 2H), 1.86-1.88 (m, 6H), 1.94 (s, 6H), 1.97 (s, 6H), 4.03 (t, *J* = 6.6 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H),

7.10 (s, 1H), 7.31 (s, 1H), 8.06 (d,  $J = 8.8$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  14.1, 14.1, 15.0, 15.1, 20.3, 20.4, 22.7, 23.3, 25.9, 28.5, 29.2, 29.3, 29.3, 29.5, 30.2, 30.4, 31.9, 32.8, 39.5, 41.2, 68.4, 114.5, 119.9, 123.5, 123.5, 129.6, 129.7, 132.7, 136.1, 136.1, 140.0, 140.0, 141.8, 141.9, 143.3, 163.6, 164.1, 175.5; MS (ESI)  $m/z$  806 ( $[\text{M} + \text{Na}]^+$ , 1), 803 (40), 577 (46), 413 (100), 365 (47); HRMS (ESI) calcd for  $\text{C}_{47}\text{H}_{62}\text{N}_2\text{O}_9\text{Na}$  821.4353, found 821.4361.

**(*R*)-4-((4-Dodecyloxybenzoyl)oxy)-2,2',6,6'-tetramethyl-3,3'-dinitro-4'-((4-pentylbicyclo[2.2.2]octan-1-yl)oxy)biphenyl (6(12))**

The procedure described for the synthesis of **4** was repeated with 32 mg (0.06 mmol) of **10** and 40 mg (0.13 mmol) of 4-dodecyloxybenzoic acid to give 38 mg (83%) of **6(12)** as a white solid. The compound was further purified by recrystallization from isopropanol after passing through a 0.45  $\mu\text{m}$  PTFE filter:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.87 (t,  $J = 7.1$  Hz, 6H), 1.11-1.35 (m, 24H), 1.41-1.45 (m, 8H), 1.79-1.81 (m, 2H), 1.86-1.88 (m, 6H), 1.94 (s, 6H), 1.97 (s, 6H), 4.03 (t,  $J = 6.7$  Hz, 2H), 6.96 (d,  $J = 8.8$  Hz, 2H), 7.10 (s, 1H), 7.31 (s, 1H), 8.06 (d,  $J = 8.8$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  14.1, 14.1, 15.0, 20.3, 20.3, 22.7, 23.3, 25.9, 28.5, 29.0, 29.3, 29.5, 29.6, 29.6, 31.2, 30.4, 31.9, 32.8, 39.5, 41.2, 68.4, 114.5, 119.9, 123.5, 123.5, 129.6, 129.7, 132.7, 136.1, 139.9, 140.0, 141.8, 141.9, 143.3, 143.4, 163.6, 164.1, 175.5; MS (ESI)  $m/z$  865 ( $[\text{M} + \text{K}]^+$ , 10), 381 (100), 313 (60); HRMS (ESI) calcd for  $\text{C}_{49}\text{H}_{66}\text{N}_2\text{O}_9\text{K}$  865.4405, found 865.4399.

**(*R*)-2,2',6,6'-Tetramethyl-3,3'-dinitro-4-((4-pentylbicyclo[2.2.2]octan-1-yl)oxy)-4'-((4-tetradecyloxybenzoyl)oxy)biphenyl (6(14))**

The procedure described for the synthesis of **4** was repeated with 23 mg (0.04 mmol) of **10** and 30 mg (0.09 mmol) of 4-tetradecyloxybenzoic acid to give 40 mg (88%) of **6(14)** as a white solid. The compound was further purified by recrystallization from isopropanol after passing through a 0.45  $\mu\text{m}$  PTFE filter:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.86-0.89 (m, 6H), 1.11-1.35 (m, 28H), 1.41-1.45 (m, 8H), 1.79-1.81 (m, 2H), 1.86-1.88 (m, 6H), 1.94 (s, 6H), 1.97 (s, 6H), 4.03 (t,  $J = 6.6$  Hz, 2H), 6.96 (d,  $J = 8.8$  Hz, 2H), 7.10 (s, 1H), 7.31 (s, 1H), 8.06 (d,  $J = 8.8$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  14.1, 14.1, 15.0, 15.1, 20.3, 20.4, 22.7, 23.3, 25.9, 28.5, 29.0, 29.3, 29.3, 29.5, 30.2, 30.2, 31.9, 32.7, 39.5, 41.2, 68.0, 114.5, 119.9, 123.5, 123.5, 129.6, 129.7, 132.7, 136.1, 136.1, 139.9, 140.0, 141.8, 141.9, 143.3, 163.6, 164.1, 175.5; MS (ESI)  $m/z$  893 ( $[\text{M} + \text{K}]^+$ , 100); HRMS (ESI) calcd for  $\text{C}_{51}\text{H}_{70}\text{N}_2\text{O}_9\text{K}$  893.4718, found 893.4729.

**(*R*)-4-Hydroxy-2,2',6,6'-tetramethyl-3,3'-dinitro-4'-((4-octyloxybenzoyl)oxy)biphenyl (11(8))**

Under an Ar atmosphere, solid DCC (325 mg, 1.58 mmol) was added to a solution of (*R*)-**8** (210 mg, 0.63 mmol), 4-octyloxybenzoic acid (156 mg, 0.62 mmol) and DMAP (145 mg, 1.19 mmol) in  $\text{CH}_2\text{Cl}_2$  (4 mL). After stirring overnight at room temperature, the mixture was filtered, diluted with EtOAc and washed twice with 20% aq HCl and water. The organic layer was dried ( $\text{MgSO}_4$ ) and concentrated to a pale yellow solid which was purified by flash chromatography on silica gel (7:3  $\text{CH}_2\text{Cl}_2$ /hexanes) to give 225 mg (64%) of **11(8)** as a yellow pasty solid:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  10.05 (s, 1H), 8.06 (d,  $J = 8.5$  Hz, 2H), 7.30 (s, 1H), 7.02 (s, 1H), 6.96 (d,  $J = 8.5$  Hz, 2H), 4.04 (t,  $J = 6.6$  Hz, 2H), 2.19 (s, 3H), 1.97 (s, 3H), 1.93 (s, 3H), 1.94 (s, 3H), 1.81 (quintet,  $J = 6.8$  Hz, 2H), 1.48 (quintet,  $J = 7.2$  Hz, 2H), 1.32 (br s, 10 H), 0.88 (t,  $J = 6.5$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  164.1, 163.6, 154.1, 145.3, 143.4, 141.8, 140.4, 136.8, 134.8, 134.0, 132.6, 131.5, 130.0, 123.4, 119.9, 118.7, 114.5, 68.4, 31.8, 29.3, 29.2, 29.0, 25.9, 22.6, 21.0, 20.4, 18.1, 15.1, 14.1; LRMS (EI)  $m/z$  587 ( $[\text{M} + \text{Na}]^+$ , 76), 365 (100), 332 (79), 186 (91); HRMS (EI) calcd for  $\text{C}_{31}\text{H}_{36}\text{N}_2\text{O}_8\text{Na}$  587.2369, found 587.2358.

**(*R*)-4-((4-Dodecyloxybenzoyl)oxy)-4'-hydroxy-2,2',6,6'-tetramethyl-3,3'-dinitrobiphenyl (11(12))**

The procedure described for the synthesis of **11(8)** was repeated with 400 mg (1.20 mmol) of (*R*)-**8** and 357 mg (1.16 mmol) of 4-dodecyloxybenzoic acid to give 394 mg (54%) of **11(12)** as a yellow pasty solid:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  9.3 (s, 1H), 8.07 (d,  $J$  = 8.8 Hz, 2H), 7.33 (s, 1H), 6.98 (s, 1H), 6.97 (d,  $J$  = 8.8 Hz, 2H), 4.05 (t,  $J$  = 6.4 Hz, 2H), 2.11 (s, 3H), 2.07 (s, 3H), 1.98 (s, 3H), 1.94 (s, 3H), 1.82 (quintet,  $J$  = 6.8 Hz, 2H), 1.44 (quintet,  $J$  = 7.2 Hz, 2H), 1.32 (br s, 18 H), 0.88 (t,  $J$  = 6.8 Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  164.3, 163.8, 149.1, 143.6, 143.4, 142.2, 140.5, 136.9, 136.7, 132.9, 131.8, 131.6, 130.2, 123.8, 120.3, 120.0, 114.8, 113.9, 68.6, 32.1, 29.9, 29.77, 29.74, 29.5, 29.2, 26.2, 22.9, 21.8, 20.7, 17.3, 15.4, 14.3; LRMS (EI)  $m/z$  620 ( $\text{M}^+$ ), 563 (20), 457 (**16**), 221 (100), 188 (**32**); HRMS (EI) calcd for  $\text{C}_{35}\text{H}_{44}\text{N}_2\text{O}_8$  620.3098, found 620.1949.

**(*R*)-2,2',6,6'-Tetramethyl-3,3'-dinitro-4-((4-octyloxybenzoyl)oxy)-4'-((4-octyloxybicyclo[2.2.2]octan-1-yl)oxy)biphenyl (7(8,8))**

Under an Ar atmosphere, solid DCC (208 mg, 1.0 mmol) was added to a solution of **11(8)** (225 mg, 0.4 mmol), **9(8)** (111 mg, 0.4 mmol) and DMAP (93 mg, 0.76 mmol) in  $\text{CH}_2\text{Cl}_2$  (3 mL). After stirring overnight at room temperature, the mixture was filtered, diluted with EtOAc and washed twice with 20% aq HCl and water. The organic layer was dried ( $\text{MgSO}_4$ ), concentrated and the residue purified by flash chromatography on silica gel (10:1 hexanes/EtOAc) to give 105 mg (30%) of **7(8,8)** as a white solid. The compound was further purified by recrystallization from acetonitrile after passing through a 0.45  $\mu\text{m}$  PTFE filter:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.08 (d,  $J$  = 8.8 Hz, 2H), 7.33 (s, 1H), 7.10 (s, 1H), 6.98 (d,  $J$  = 8.8 Hz, 2H), 4.05 (t,  $J$  = 6.8 Hz, 2H), 3.33 (t,  $J$  = 6.5 Hz, 2H), 2.08-2.04 (m, 6H), 1.99 (s, 6H), 1.96 (s, 3H), 1.95 (s, 3H), 1.82 (quintet,  $J$  = 8.4 Hz, 2H), 1.84-1.74 (m, 6H), 1.50 (quintet,  $J$  = 6.6 Hz, 4H), 1.27 (br s, 18 H), 0.89 (t,  $J$  = 7.0 Hz, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  175.0, 164.5, 163.9, 143.8, 143.7, 142.4, 142.0, 140.3, 140.2, 136.6, 136.3, 132.9, 130.3, 129.9, 123.8, 123.7, 120.3, 114.9, 73.1, 68.7, 61.7, 39.2, 32.1, 32.05, 30.9, 29.7, 29.5, 29.3, 26.5, 26.2, 22.9, 20.5, 15.3, 14.3; HRMS (ESI) calcd for  $\text{C}_{48}\text{H}_{64}\text{O}_{10}\text{N}_2\text{Na}$  851.4454, found 851.4453.

Anal. Calcd for  $\text{C}_{48}\text{H}_{64}\text{N}_2\text{O}_{10}$ : C, 69.54; H, 7.78; N, 3.38. Found: C, 69.53; H, 7.66; N, 3.43.

**(*R*)-4-((4-Dodecyloxybenzoyl)oxy)-4'-((4-dodecyloxybicyclo[2.2.2]octan-1-yl)oxy)-2,2',6,6'-tetramethyl-3,3'-dinitrobiphenyl (7(12,12))**

The procedure described for the synthesis of **7(8,8)** was repeated with 300 mg (0.46 mmol) of **11(12)** and 140 mg (0.42 mmol) of **9(12)** to give 140 mg (35%) of **7(12,12)** as a white solid. The compound was further purified by recrystallization from acetonitrile after passing through a 0.45  $\mu\text{m}$  PTFE filter:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.08 (d,  $J$  = 8.8 Hz, 2H), 7.33 (s, 1H), 7.10 (s, 1H), 6.98 (d,  $J$  = 8.8 Hz, 2H), 4.05 (t,  $J$  = 6.4 Hz, 2H), 3.33 (t,  $J$  = 6.8 Hz, 2H), 2.07-2.03 (m, 6H), 1.99 (s, 6H), 1.96 (s, 6H), 1.83 (quintet,  $J$  = 6.8 Hz, 2H), 1.84-1.74 (m, 6H), 1.51 (quintet,  $J$  = 6.6 Hz, 4H), 1.27 (br s, 34H), 0.87 (t,  $J$  = 8.9 Hz, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  175.0, 164.5, 163.9, 143.7, 143.6, 142.3, 142.0, 140.3, 140.2, 136.6, 136.3, 133.0, 130.1, 130.0, 123.9, 123.7, 120.2, 114.9, 73.1, 68.7, 61.7, 39.2, 32.2, 30.9, 29.9, 29.8, 29.78, 29.6, 29.5, 29.4, 29.3, 26.5, 26.2, 22.9, 20.6, 15.3, 14.3; HRMS (MALDI) calcd for  $\text{C}_{56}\text{H}_{80}\text{O}_{10}\text{N}_2$  941.5891, found 941.5938.

Anal. Calcd for  $\text{C}_{56}\text{H}_{80}\text{N}_2\text{O}_{10}$ : C, 71.46; H, 8.57; N, 2.98. Found: C, 71.02; H, 8.71; N, 2.97.

**(*R*)-4-((4-Dodecyloxybenzoyl)oxy)-4'-((4-butyloxybicyclo[2.2.2]octan-1-yl)oxy)-2,2',6,6'-tetramethyl-3,3'-dinitrobiphenyl (7(12,4))**

The procedure described for the synthesis of **7(8,8)** was repeated with 310 mg (0.5 mmol) of **11(12)** and 113 mg (0.5 mmol) of **9(4)** to give 150 mg (36%) of **7(12,4)** as a white solid. The compound was further purified by recrystallization from acetonitrile after passing through a 0.45  $\mu\text{m}$  PTFE filter:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 8.08 (d,  $J$  = 8.8 Hz, 2H), 7.33 (s, 1H), 7.10 (s, 1H), 6.98 (d,  $J$  = 8.8 Hz, 2H), 4.05 (t,  $J$  = 6.8 Hz, 2H), 3.35 (t,  $J$  = 6.8 Hz, 2H), 2.08-2.04 (m, 6H), 1.99 (6H), 1.96, 1.95 (s, 6H), 1.86 (q,  $J$  = 6.8 Hz, 2H),

1.83-1.77 (m, 6H), 1.54-1.50 (m, 4H), 1.42-1.36 (m, 4H), 1.28 (br s, 18H), 0.92 (t,  $J = 7.5$  Hz, 3H), 0.89 (t,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 164.4, 163.8, 143.6, 142.2, 141.9, 140.3, 140.2, 136.2, 132.9, 130.0, 123.8, 123.6, 120.1, 115.6, 114.8, 68.6, 61.3, 39.1, 32.8, 32.1, 29.9, 29.6, 29.4, 29.3, 29.26, 26.2, 22.9, 20.6, 19.6, 15.3, 14.3, 14.1; HRMS (MALDI) calcd for  $\text{C}_{48}\text{H}_{64}\text{N}_2\text{O}_{10}\text{Na}$  851.4459, found 851.4415. Anal. Calcd for  $\text{C}_{48}\text{H}_{64}\text{O}_{10}\text{N}_2$ : C, 69.54; H, 7.78; N, 3.38. Found: C, 69.34; H, 7.81; N, 3.49.

### Ferroelectric polarization measurements

The liquid crystal host **PhP** was obtained from commercial sources. Doped liquid crystal mixtures for ferroelectric measurements were loaded by capillary action into polyimide-coated ITO glass cells supplied by E.H.C. Co. ( $4\text{ }\mu\text{m}$  spacing,  $0.16\text{ cm}^2$  addressed area). Good alignment of the liquid crystal mixtures was achieved by slow cooling from isotropic to the  $\text{SmC}^*$  phase ( $0.5\text{--}2\text{ K/min}$ ). Spontaneous polarizations  $P_s$  were measured as a function of temperature by the triangular wave method ( $100\text{ Hz}$ ,  $6\text{ V}/\mu\text{m}$ ) using a LC Vision LCAS 1 liquid crystal analysis system.<sup>4</sup> Tilt angles  $\theta$  were measured by polarized microscopy as half the rotation between the two extinction positions corresponding to opposite polarization directions. 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.<sup>5</sup>

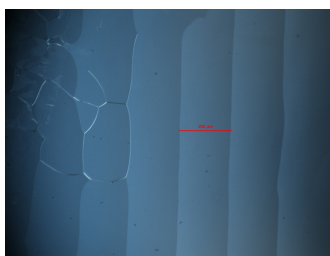
### $\text{N}^*$ pitch measurements

**a) Selective reflection.** Measurements of  $\text{N}^*$  pitch in the visible range of the spectrum were performed on cooling from the isotropic liquid phase by measuring the wavelength of selective reflection of thin films with planar alignment in commercial wedge cells (E.H.C.,  $\tan\theta = 0.0083$ ) mounted vertically in a Linkam LTS 350 hot stage using an Ocean Optics USB2000 Miniature Fiber Optic Spectrometer with Samples for helical pitch measurements were loaded by capillary action into wedge glass cells supplied by E.H.C. Co. ( $\tan\theta = 0.14$ ).

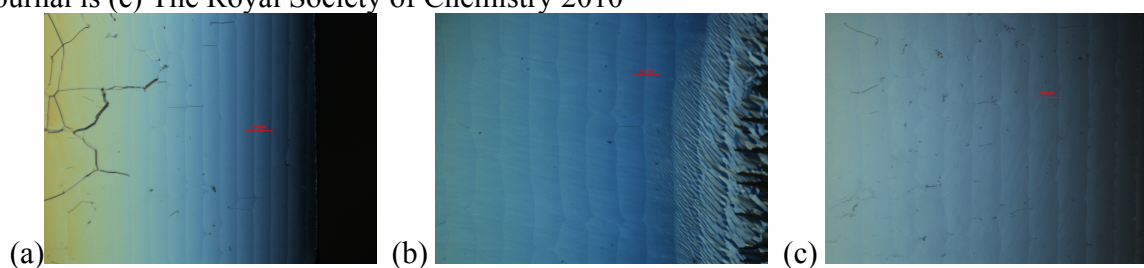
**b) Grandjean method.**<sup>6</sup> Measurements of  $\text{N}^*$  pitch greater than  $1\text{ }\mu\text{m}$  were performed by measuring the distance between Grandjean steps formed in a commercial wedge cell (E.H.C.,  $\tan\theta = 0.0083$ ) by slow cooling from isotropic to the  $\text{N}^*$  phase ( $0.5\text{--}2.0\text{ K/min}$ ).

### $\text{SmC}^*$ pitch measurements

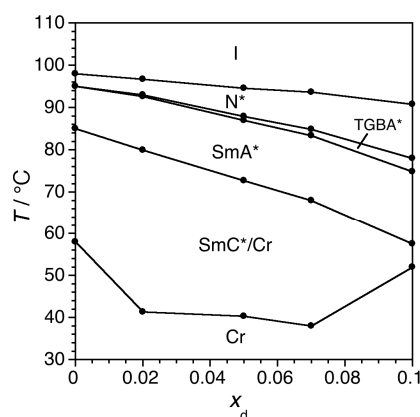
Measurements of  $\text{SmC}^*$  pitch were performed by polarized microscopy at  $T - T_C = -10\text{ K}$  by measuring the distance between dark fringes observed in focal conic domains formed by thick films ( $150\text{ }\mu\text{m}$ ) of the liquid crystal between parallel-rubbed glass slides and cover slips. The focal conic domains were obtained by slow cooling from the isotropic phase to the  $\text{SmC}^*$  phase.



**Fig. S1.** Grandjean steps formed by optically enriched **5(8)** (33% ee) in the  $\text{N}^*$  phase at  $T - T_{\text{NI}} = -10\text{ K}$  in a wedge cell with planar alignment ( $\tan\theta = 0.0083$ ) viewed by polarized optical microscopy ( $100\times$ ) on first cooling from the isotropic phase.



**Fig. S2.** Grandjean steps formed by 5 mol% mixtures of (a) **3(8)**, (b) **5(8)** and (c) **7(8,8)** in the N\* phase at  $T - T_{NI} = -5$  K in wedge cells with planar alignment ( $\tan\theta = 0.014$  for (a),  $\tan\theta = 0.083$  for (b) and (c)) viewed by polarized microscopy (100  $\times$ ).



**Fig. S3.** Partial phase diagrams for mixtures of **3(8)** in PhP. The notation SmC\*/Cr indicates that the dopant **3(8)** crystallizes out of the mixture upon standing in the SmC\* phase for several hours.

**Fitting functions for Fig. 4:** **6(14)**:  $y = 426.4 + 3.39x$ ; **6(12)**:  $y = 460.5 + 3.23x$ ; **6(10)**:  $y = 571.6 + 3.28x$ ; **6(8)**:  $y = 737.6 + 3.40x$ ; **7(8,8)**:  $y = 544.4 + 4.94x$ ; **7(12,12)**:  $y = 528.1 + 3.13x$ .

**Fitting function for Fig. 7:**  $y = 2.1 - 1226.5x$

## References

1. C. S. Hartley, R. Wang and R. P. Lemieux, *Chem. Mater.*, 2004, **16**, 5297.
2. D. Vizitiu, C. Lazar, B. J. Halden and R. P. Lemieux, *J. Am. Chem. Soc.*, 1999, **121**, 8229.
3. C. A. Grob and R. Rich, *Helv. Chim. Acta*, 1979, **62**, 2802.
4. K. Miyasato, S. Abe, H. Takezoe, A. Fukuda and E. Kuze, *Jpn. J. Appl. Phys.*, 1983, **22**, L661.
5. D. M. Walba, in *Advances in the Synthesis and Reactivity of Solids*, ed. T. E. Mallouck, JAI Press, Ltd., Greenwich, CT, 1991, p. 173.
6. M. F. Grandjean, *Acad. Sci.*, 1921, **172**, 71.