

**Remarkable smectic phase behaviour in odd-membered liquid crystal dimers: The CT6O.m series**

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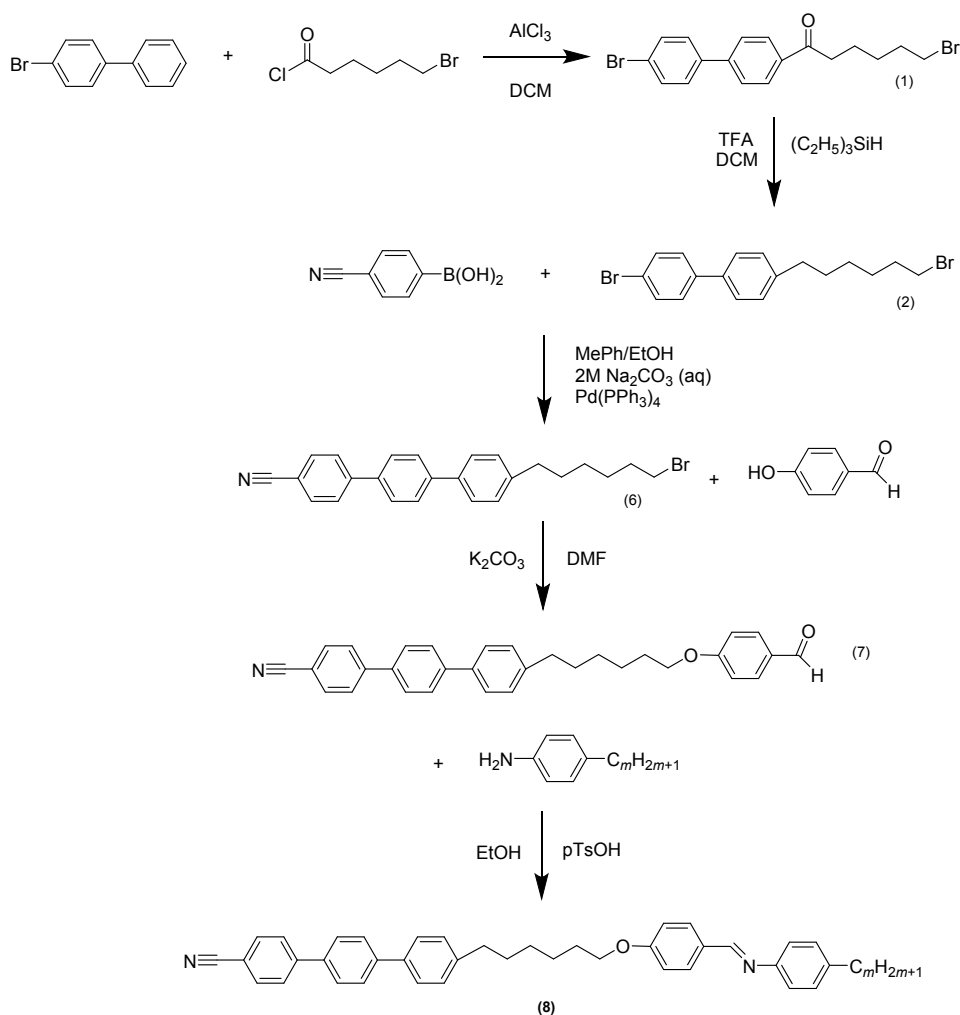
**Electronic Supplementary Information**

1. *Synthetic details and analytical data*
2. *Supporting figures*

1. Synthetic details and analytical data

All reagents and solvents were available commercially and purchased from Sigma Aldrich, Alfa Aesar or TCI Chemicals and used as received unless otherwise stated. Silica gel for column chromatography, grade 60 Å 40-63 micron, was purchased from Fluorochem. Reactions were monitored using Thin Layer Chromatography (TLC) and an appropriate solvent system. Silica gel coated aluminium plates were purchased from Merck KGaA. Spots were visualised using UV light (254 nm). The proposed structures of all the intermediates and final products were characterised using a combination of <sup>1</sup>H and <sup>13</sup>C NMR, and FT-IR spectroscopies. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on either a 400 MHz or 300 MHz Bruker Ultrashield NMR spectrometer. Infrared spectra were recorded on a Thermal Scientific Nicolet IR100 FT-IR spectrometer with an ATR diamond cell. The purities of the final products were verified using C, H, N microanalysis performed by the Centre for Chemical Instrumentation and Analytical Services in the Department of Chemistry at the University of Sheffield.

The synthesis of the CT6O.m series followed the route outlined in *Scheme 1*. The route to (2) is identical to that reported earlier for the synthesis of CB6O.m, thus procedures and analytical data for intermediates (1) and (2) are also reported elsewhere.<sup>[1]</sup>



**Scheme 1.** Synthetic route to the CT60.*m* series.

### 1-Bromo-6-(4'-cyanoterphenyl-4-yl)hexane (3)

4-(6-Bromohexyl)-4'-bromo-1,1'-biphenyl (13.5 g, 0.03 mol), 4-cyanophenylboronic acid (5.00 g, 0.03 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.25 g, 0.22 mmol) were added into a mixture of toluene (40 mL), ethanol (20 mL), and sodium bicarbonate (20 mL) and heated at reflux for 24 hours. The reaction mixture was poured into dichloromethane (100 mL) and distilled water (200 mL). The layers were separated and the aqueous layer washed with dichloromethane (2 x 100 mL). The organic fractions were combined and dried over anhydrous  $\text{MgSO}_4$  before removal of the solvent *in vacuo*. The crude was purified using silica gel chromatography using dichloromethane as the eluent to obtain the title compound as a yellow powder. Yield: 7.36 g, 53%.

M.P. = 118 °C.  $T_{\text{NI}}$  = 217 °C. IR  $\bar{\nu}$   $\text{cm}^{-1}$ : 2930, 2854, 2220 (C≡N stretch), 1601 (para di-substituted benzene), 1488, 1003, 808, 635, 553, 512.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 7.76 (s, 4H, Ar), 7.73 (d, J = 8.7 Hz, 2H, Ar), 7.68 (d, J = 8.7 Hz, 2H, Ar), 7.59 (d, J = 8.2 Hz, 2H, Ar), 7.30 (d, J = 8.4 Hz, 2H, Ar), 3.44 (t, J = 6.8 Hz, 2H,  $\text{ArCH}_2(\text{CH}_2)_4\text{CH}_2\text{Br}$ ), 2.70 (t, 2H,  $\text{ArCH}_2(\text{CH}_2)_4\text{CH}_2\text{Br}$ ), 1.89 (m, 2H,  $\text{Ar}(\text{CH}_2)_4\text{CH}_2\text{CH}_2\text{Br}$ ), 1.71 (p, J = 7.5 Hz, 2H,  $\text{ArCH}_2\text{CH}_2(\text{CH}_2)_4\text{Br}$ ), 1.48 (m, 4H,  $\text{ArCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 145.22, 142.33, 141.48, 137.66, 137.60, 132.67, 129.00, 127.63, 127.55, 126.97, 119.02, 110.83, 35.47, 34.02, 32.73, 31.25, 28.43, 28.04.

#### **4-[[6-(4-Cyanoterphenyl-4'-yl)hexyl]oxy}benzaldehyde (4)**

1-Bromo-6-(4'-cyanoterphenyl-4-yl)hexane (2.61 g, 6.23 mmol), 4-hydroxybenzaldehyde (0.79 g, 6.50 mmol), sodium iodide (0.09 g, 0.63 mmol), and potassium carbonate (1.95 g, 0.014 mol) were combined in dimethylformamide (20 mL) and stirred at reflux for approximately 24 hours. The reaction mixture was added to distilled water (200 mL), the resulting precipitate collected and recrystallised from EtOH to give the title compound as a white solid. Yield: 1.352 g, 47%.

M.P. 110 °C.  $T_{NI}$  = 201 °C. IR  $\bar{\nu}$  cm<sup>-1</sup>: 2933, 2856, 2228 (C≡N stretch), 1684 (C=O aldehyde), 1602 (para di-substituted benzene), 1510, 1488, 1260, 1159, 1002, 811, 511. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ ppm: 9.90 (s, 1H, ArCOH), 7.85 (d, J = 8.4 Hz, 2H, Ar-H), 7.77 (s, 4H, Ar-H), 7.73 (d, J = 8.3 Hz, 2H, Ar-H), 7.69 (d, J = 8.2 Hz, 2H, Ar-H), 7.58 (d, J = 7.8 Hz, 2H, Ar-H), 7.31 (d, J = 8.1 Hz, 2H, Ar-7H), 7.01 (d, J = 8.4 Hz, 2H, Ar-H), 4.07 (t, J = 6.5 Hz, 2H, ArCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>O), 2.72 (t, J = 7.7 Hz, 2H, ArCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>O), 1.86 (p, J = 6.8 Hz, 2H, Ar(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>O), 1.74 (p, J = 7.8 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>O), 1.50 (m, 4H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ ppm: 190.81, 164.22, 145.21, 142.36, 141.46, 137.70, 137.61, 132.66, 132.01, 129.81, 129.00, 127.61, 127.59, 127.55, 126.96, 118.99, 114.76, 110.88, 68.31, 35.50, 31.31, 28.99, 28.93, 25.87. Elemental Analysis: Calculated for C<sub>32</sub>H<sub>29</sub>NO<sub>2</sub>: C 83.63 %, H 6.36 %, N 3.05 %, Found: C 83.55 %, H 6.45 %, N 2.92 %.

#### **4'-(6-(4-((4-Alkylphenyl)imino)methyl)phenoxy)hexyl)[1,1'-terphenyl]-4-carbonitrile (5)**

4-[[6-(4-Cyanoterphenyl-4'-yl)hexyl]oxy}benzaldehyde (1 eq.), the desired alkyaniline (1 eq.) and a crystal of *p*-toluenesulfonic acid were combined in EtOH (30 mL) and heated at 90 °C for 3 h. The resulting white precipitate was collected by hot vacuum filtration and did not require further purification. Yields of 46-74 % were obtained.

**CT60.1:** IR  $\bar{\nu}$  cm<sup>-1</sup>: 2916, 2853, 2228 (C≡N stretch), 1604 (para di-substituted benzene), 1571, 1510, 1489, 1249, 1161, 1003, 807. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ ppm: 8.41 (s, 1H, CH=N), 7.85 (d, J = 8.4 Hz, 2H, Ar), 7.75 (s, 4H, Ar), 7.72 (d, J = 8.3 Hz, 2H, Ar), 7.68 (d, J = 8.3 Hz, 2H, Ar), 7.58 (d, J = 7.8 Hz, 2H, Ar), 7.31 (d, J = 8.1 Hz, 2H, Ar), 7.21 (d, J = 8.0 Hz, 2H, Ar), 7.14 (d, J = 8.0 Hz, 2H, Ar), 6.98 (d, J = 8.4 Hz, 2H, Ar), 4.05 (t, J = 6.5 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAr), 2.72 (t, J = 7.7 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAr), 2.39 (s, 3H, ArCH<sub>3</sub>), 1.86 (p, J = 6.8 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAr), 1.74 (p, J = 7.6 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAr), 1.56 (d, J = 7.8 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAr), 1.49 (q, J = 7.6 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAr). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ ppm: 161.70, 158.99, 149.80, 145.22, 142.41, 141.49, 137.65, 137.57, 135.34, 132.65, 130.39, 129.74, 129.24, 129.03, 127.62, 127.58, 127.54, 126.95, 120.79, 119.00, 114.67, 110.85, 68.04, 35.47, 31.29, 29.08, 28.89, 25.87, 21.01. Elemental Analysis: Calculated for C<sub>39</sub>H<sub>36</sub>N<sub>2</sub>O: C 85.37 %, H 6.61 %, N 5.11 %, Found: C 84.90 %, H 6.57 %, N 4.97 %.

**CT60.2:** IR  $\bar{\nu}$  cm<sup>-1</sup>: 2934, 2857, 2223 (C≡N stretch), 1604 (para di-substituted benzene), 1568, 1510, 1489, 1244, 1164, 1003, 811. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ ppm: 8.41 (s, 1H, CH=N), 7.85 (d, J = 8.4 Hz, 2H, Ar), 7.75 (s, 4H, Ar), 7.72 (d, J = 8.3 Hz, 2H, Ar), 7.68 (d, J = 8.2 Hz, 2H, Ar), 7.58 (d, J = 7.8 Hz, 2H, Ar), 7.31 (d, J = 8.0 Hz, 2H, Ar), 7.23 (d, J = 8.0 Hz, 2H, Ar), 7.16 (d, J = 8.0 Hz, 2H, Ar), 6.98 (d, J = 8.4 Hz, 2H, Ar), 4.05 (t, J = 6.5 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAr), 2.70 (m, 4H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAr, ArCH<sub>2</sub>CH<sub>3</sub>), 1.86 (p, J = 6.8 Hz, 2H), 1.74 (p, J = 7.6 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAr), 1.53 (m, 4H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAr), 1.28 (t, J = 7.6 Hz, 3H, ArCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ ppm: 161.70, 159.02, 150.00, 145.22, 142.41, 141.78, 141.50, 137.65, 137.58, 132.65, 130.40, 129.26, 129.03, 128.54, 127.63, 127.58, 127.55, 126.95, 120.85, 119.00, 114.67, 110.85, 68.04, 35.48, 31.30, 29.09, 28.90, 28.43, 25.87, 15.69. Elemental Analysis: Calculated for C<sub>40</sub>H<sub>38</sub>N<sub>2</sub>O: C 85.37 %, H 6.81 %, N 4.98 %, Found: C 85.43 %, H 6.80 %, N 4.80 %.

**CT60.3:** IR  $\bar{\nu}$  cm<sup>-1</sup>: 2930, 2856, 2224 (C≡N stretch), 1603 (para di-substituted benzene), 1570, 1510, 1488, 1248, 1161, 1003, 810. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ ppm: 8.41 (s, 1H, CH=N), 7.84 (d, J = 8.7 Hz, 2H, Ar), 7.75 (m, 4H, Ar), 7.68 (d, J = 8.7 Hz, 2H, Ar), 7.57 (d, J = 8.1 Hz, 2H, Ar), 7.31 (d, J = 8.3 Hz, 2H, Ar), 7.21 (d, J = 8.3 Hz, 2H, Ar), 7.15 (d, J = 8.4 Hz, 2H, Ar), 6.98 (d, J = 8.7 Hz, 2H, Ar), 4.04 (t, J = 6.4 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAr), 2.71 (t, J = 7.6 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAr), 2.66 – 2.58 (m, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.91 – 1.43 (m, 10H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAr, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.98 (t, J = 7.3 Hz, 3H, Ar(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ ppm: 161.70, 158.98, 149.98, 145.22, 142.41, 141.50, 140.23, 137.65, 137.58, 132.65, 132.01, 130.40, 129.15, 129.03, 127.62, 127.58, 127.55, 126.95, 120.76, 119.00, 114.76, 114.67, 110.85, 68.04, 37.60, 35.48, 31.30, 29.09, 28.90, 25.87, 24.65, 13.85. Elemental Analysis: Calculated for C<sub>39</sub>H<sub>36</sub>N<sub>2</sub>O: C 85.38 %, H 6.99 %, N 4.86 %, Found: C 85.46 %, H 6.91 %, N 4.68 %.

**CT60.4:** IR  $\bar{\nu}$  cm<sup>-1</sup>: 2925, 2855, 2222 (C≡N stretch), 1603 (para di-substituted benzene), 1569, 1510, 1488, 1245, 1165, 1003, 812. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ ppm: 8.42 (s, 1H, CH=N), 7.85 (d, J = 8.4 Hz, 2H, Ar), 7.76 (s, 4H, Ar), 7.72 (d, J = 8.3 Hz, 2H, Ar), 7.68 (d, J = 8.2 Hz, 2H, Ar), 7.58 (d, J = 7.8 Hz, 2H, Ar), 7.31 (d, J = 8.0 Hz, 2H, Ar), 7.21 (d, J = 8.1 Hz, 2H, Ar), 7.15 (d, J = 8.0 Hz, 2H, Ar), 6.98 (d, J = 8.5 Hz, 2H, Ar), 4.05 (t, J = 6.4 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAr), 2.72 (t, J = 7.7 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAr), 2.65 (t, J = 7.7 Hz, 2H, ArCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 1.86 (p, J = 6.9 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAr), 1.74 – 1.34 (m, 10H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAr, ArCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 0.96 (t, J = 7.3 Hz, 3H, Ar(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ ppm: 161.70, 158.97, 149.94, 145.22, 142.42, 141.50, 140.46, 137.65, 137.58, 132.66, 130.40, 129.09, 129.04, 127.63, 127.59, 127.55, 126.96, 120.78, 114.68, 110.86, 68.05, 35.48, 35.20, 33.75, 31.31, 29.09, 28.91, 25.88, 22.39, 14.00. Elemental Analysis: Calculated for C<sub>42</sub>H<sub>42</sub>N<sub>2</sub>O: C 85.38 %, H 7.17 %, N 4.74 %, Found: C 85.06 %, H 7.15 %, N 4.62 %.

**CT60.5:** IR  $\bar{\nu}$  cm<sup>-1</sup>: 2928, 2855, 2224 (C≡N stretch), 1605 (para di-substituted benzene), 1570, 1511, 1489, 1245, 1160, 1004, 814. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ ppm: 8.42 (s, 1H, CH=N), 7.85 (d, J = 8.4 Hz, 2H, Ar), 7.76 (s, 4H, Ar), 7.72 (d, J = 8.3 Hz, 2H, Ar), 7.68 (d, J = 8.1 Hz, 2H, Ar), 7.58 (d, J = 7.8 Hz, 2H, Ar), 7.31 (d, J = 8.2 Hz, 2H, Ar), 7.21 (d, J = 8.1 Hz, 2H, Ar), 7.15 (d, J = 8.3 Hz, 2H, Ar), 6.98 (d, J = 8.5 Hz, 2H, Ar), 4.05 (t, J = 6.5 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAr), 2.72 (t, J = 7.7 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAr), 2.64 (t, J = 7.8 Hz, 2H, ArCH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 1.86 (t, J = 7.3 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAr), 1.61 (m, 8H, ArCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAr), 1.42 – 1.30 (m, 4H, ArCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 0.95 – 0.89 (m, 3H, Ar(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ ppm: 161.69, 158.96, 149.93, 145.22, 142.41, 141.50, 140.50, 137.65, 137.58, 132.65, 132.01, 130.39, 129.27, 129.15, 129.08, 129.03, 127.62, 127.58, 127.55, 126.95, 120.78, 119.00, 115.21, 114.76, 114.67, 110.85, 68.04, 35.48, 35.06, 31.53, 31.30, 31.27, 29.09, 28.99, 28.90, 25.87, 22.58, 14.07. Elemental Analysis: Calculated for C<sub>43</sub>H<sub>44</sub>N<sub>2</sub>O: C 85.39 %, H 7.33 %, N 4.63 %, Found: C 85.46 %, H 7.21 %, N 4.50 %.

**CT60.6:** IR  $\bar{\nu}$  cm<sup>-1</sup>: 2926, 2854, 2223 (C≡N stretch), 1604 (para di-substituted benzene), 1569, 1510, 1489, 1245, 1162, 1003, 811. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ ppm: 8.42 (s, 1H, CH=N), 7.85 (d, J = 8.4 Hz, 2H, Ar), 7.76 (s, 4H, Ar), 7.72 (d, J = 8.3 Hz, 2H, Ar), 7.68 (d, J = 8.2 Hz, 2H, Ar), 7.58 (d, J = 7.8 Hz, 2H, Ar), 7.31 (d, J = 8.2 Hz, 2H, Ar), 7.21 (d, J = 8.1 Hz, 2H, Ar), 7.15 (d, J = 8.0 Hz, 2H, Ar), 6.98 (d, J = 8.4 Hz, 2H, Ar), 4.05 (t, J = 6.5 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 2.72 (t, J = 7.7 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 2.64 (t, J = 7.8 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.86 (p, J = 6.7 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 1.74 – 1.49 (m, 8H, ArCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAr), 1.34 (m, 6H, ArCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 0.95 – 0.88 (m, 3H, Ar(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ ppm: 161.69, 158.96, 149.94, 145.22, 142.41, 141.50, 140.50, 137.65, 137.58, 132.65, 130.39, 129.28, 129.08, 129.03, 127.62, 127.58, 127.55, 126.95, 120.78, 119.00, 114.67, 110.85, 68.04, 35.52, 35.48, 31.76,

31.56, 31.30, 29.09, 29.00, 28.91, 25.87, 22.64, 14.13. Elemental Analysis: Calculated for C<sub>44</sub>H<sub>46</sub>N<sub>2</sub>O: C 85.40 %, H 7.49 %, N 4.53 %, Found: C 85.55 %, H 7.45 %, N 4.35 %.

**CT60.7:** IR  $\bar{\nu}$  cm<sup>-1</sup>: 2925, 2854, 2224 (C≡N stretch), 1604 (para di-substituted benzene), 1590, 1510, 1488, 1248, 1160, 1003, 809. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm: 8.42 (s, 1H, CH=N), 7.85 (d, J = 8.3 Hz, 2H, Ar), 7.76 (s, 4H, Ar), 7.73 (d, J = 8.2 Hz, 2H, Ar), 7.68 (d, J = 8.1 Hz, 2H, Ar), 7.58 (d, J = 7.7 Hz, 2H, Ar), 7.31 (d, J = 8.1 Hz, 2H, Ar), 7.21 (d, J = 7.9 Hz, 2H, Ar), 7.15 (d, J = 8.0 Hz, 2H, Ar), 6.98 (d, J = 8.4 Hz, 2H, Ar), 4.05 (t, J = 6.5 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 2.72 (t, J = 7.7 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 2.64 (t, J = 7.8 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.86 (p, J = 6.9 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 1.74 - 1.48 (m, 8H, ArCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAr), 1.33 (d, J = 19.1 Hz, 8H, ArCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 0.91 (t, J = 6.4 Hz, 3H, Ar(CH<sub>2</sub>)<sub>6</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  ppm: 161.68, 158.94, 149.93, 145.20, 142.40, 141.48, 140.49, 137.63, 137.56, 132.64, 130.39, 129.28, 129.07, 129.02, 127.61, 127.57, 127.53, 126.94, 120.78, 118.99, 114.67, 110.84, 68.04, 35.52, 35.48, 31.86, 31.61, 31.31, 29.31, 29.22, 29.10, 28.92, 25.88, 22.70, 14.15. Elemental Analysis: Calculated for C<sub>45</sub>H<sub>48</sub>N<sub>2</sub>O: C 85.40 %, H 7.64 %, N 4.43 %, Found: C 85.57 %, H 7.52 %, N 4.27 %.

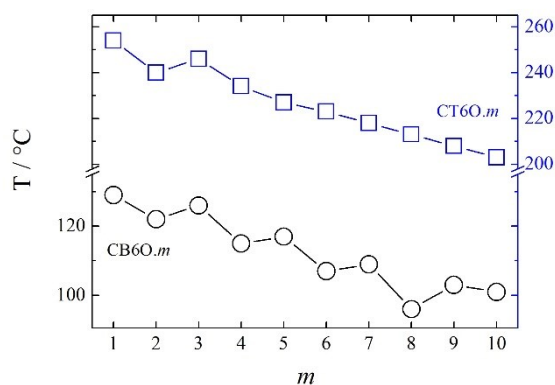
**CT60.8:** IR  $\bar{\nu}$  cm<sup>-1</sup>: 2922, 2851, 2222 (C≡N stretch), 1723, 1605 (para di-substituted benzene), 1510, 1248, 808, 541. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm: 8.42 (s, 1H, CH=N), 7.85 (d, J = 8.4 Hz, 2H, Ar), 7.76 (s, 4H, Ar), 7.70 (q, J = 8.2 Hz, 4H, Ar), 7.58 (d, J = 7.8 Hz, 2H, Ar), 7.31 (d, J = 8.8 Hz, 2H, Ar), 7.23 - 7.12 (m, 4H, Ar), 6.98 (d, J = 8.4 Hz, 2H, Ar), 4.05 (t, J = 6.5 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 2.72 (t, J = 7.7 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 2.64 (t, J = 7.8 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.85 (p, J = 7.0 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 1.74 - 1.43 (m, 8H, ArCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAr), 1.32 (m, 10H, ArCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>), 0.91 (t, J = 6.6 Hz, 3H, ArCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  ppm: 161.67, 158.94, 149.92, 145.21, 142.40, 141.48, 140.49, 137.63, 137.56, 132.64, 130.38, 129.27, 129.07, 129.02, 127.61, 127.57, 127.53, 126.94, 120.76, 118.99, 114.66, 110.84, 68.04, 35.52, 35.48, 31.91, 31.60, 31.30, 29.51, 29.35, 29.30, 29.09, 28.91, 25.87, 22.70, 14.14. Elemental Analysis: Calculated for C<sub>46</sub>H<sub>50</sub>N<sub>2</sub>O: C 85.41 %, H 7.79 %, N 4.33 %, Found: C 85.62 %, H 7.91 %, N 4.20%.

**CT60.9:** IR  $\bar{\nu}$  cm<sup>-1</sup>: 2922, 2851, 2222 (C≡N stretch), 1723, 1605 (para di-substituted benzene), 1510, 1247, 807, 542. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm: 8.42 (s, 1H, CH=N), 7.85 (d, J = 8.4 Hz, 2H, Ar), 7.80 - 7.64 (m, 8H, Ar), 7.58 (d, J = 7.9 Hz, 2H, Ar), 7.31 (d, J = 8.0 Hz, 2H, Ar), 7.24 - 7.10 (m, 4H, Ar), 6.98 (d, J = 8.4 Hz, 2H, Ar), 4.05 (t, J = 6.5 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 2.72 (t, J = 7.7 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 2.64 (t, J = 7.8 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.86 (p, J = 6.9 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 1.74 (p, J = 7.6 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 1.69 - 1.43 (m, 6H, ArCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>CH<sub>3</sub>, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAr), 1.32 (m, 12H, ArCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>CH<sub>3</sub>), 0.91 (t, J = 6.6 Hz, 3H, ArCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  ppm: 161.67, 158.93, 149.93, 145.20, 142.40, 141.48, 140.49, 137.63, 137.56, 132.64, 130.38, 129.27, 129.07, 129.02, 127.61, 127.57, 127.53, 126.94, 120.77, 118.99, 114.66, 110.84, 68.04, 35.52, 35.48, 31.93, 31.60, 31.31, 29.60, 29.56, 29.35, 29.09, 28.91, 25.88, 22.71, 14.15. Elemental Analysis: Calculated for C<sub>47</sub>H<sub>52</sub>N<sub>2</sub>O: C 85.41 %, H 7.93 %, N 4.24 %, Found: C 85.55 %, H 8.07 %, N 4.11 %.

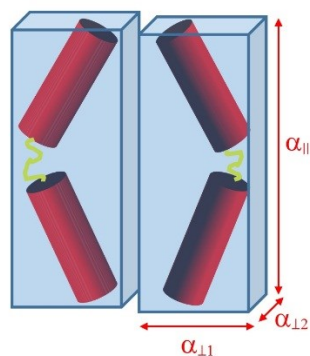
**CT60.10:** IR  $\bar{\nu}$  cm<sup>-1</sup>: 2914, 2848, 2225 (C≡N stretch), 1606 (para di-substituted benzene), 1575, 1514, 1489, 1253, 1170, 1005, 819. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm: 8.42 (s, 1H, CH=N), 7.85 (d, J = 8.4 Hz, 2H, Ar), 7.76 (s, 4H, Ar), 7.73 (d, J = 8.3 Hz, 2H, Ar), 7.68 (d, J = 8.2 Hz, 2H, Ar), 7.58 (d, J = 7.8 Hz, 2H, Ar), 7.31 (d, J = 8.1 Hz, 2H, Ar), 7.21 (d, J = 8.1 Hz, 2H, Ar), 7.15 (d, J = 8.0 Hz, 2H, Ar), 6.98 (d, J = 8.4 Hz, 2H, Ar), 4.05 (t, J = 6.5 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAr), 2.72 (t, J = 7.7 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAr), 2.64 (t, J = 7.7 Hz, 2H, ArCH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub>), 1.86 (p, J = 6.7 Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAr), 1.74 (m, 8H, ArCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>7</sub>CH<sub>3</sub>, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAr), 1.32 (m,

14H, ArCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>7</sub>CH<sub>3</sub>, 0.91 (t, J = 6.6 Hz, 3H, Ar(CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>). Elemental Analysis: Calculated for C<sub>48</sub>H<sub>54</sub>N<sub>2</sub>O: C 85.41 %, H 8.06 %, N 4.15 %, Found: C 85.22 %, H 7.79 %, N 4.00 %.

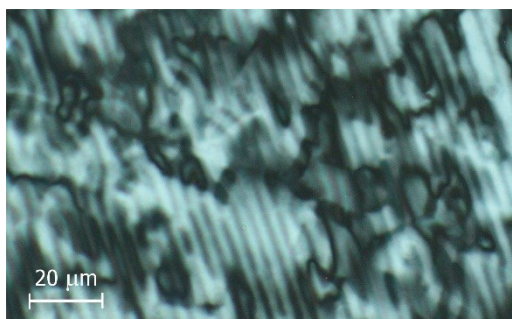
## 2. Supporting figures



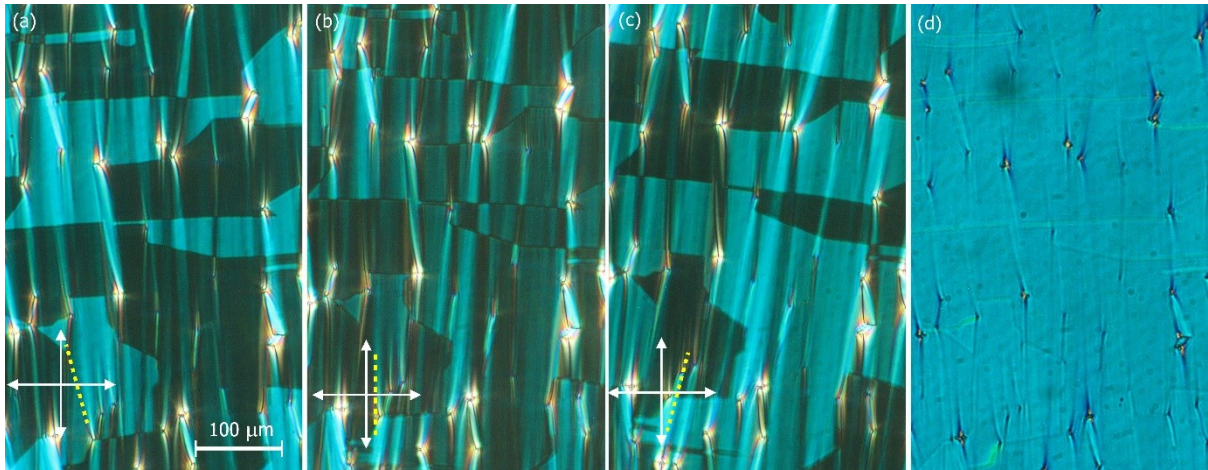
**Figure S1.** The dependence of clearing temperature,  $T_{NI}$ , on terminal chain length  $m$  for the CB6O. $m$  series (black circles) and CT6O. $m$  series (blue squares).



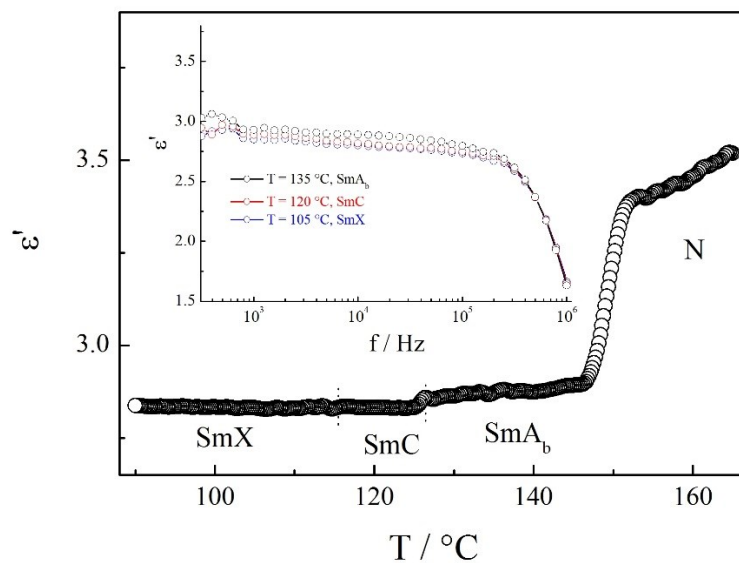
**Figure S2.** Schematic drawing showing that restricted rotation of bent dimeric molecules in SmA<sub>b</sub> phase results in the optical biaxiality of the phase, as three distinct molecular polarizabilities ( $\alpha_{\perp 1}$ ,  $\alpha_{\perp 2}$ ,  $\alpha_{\parallel}$ ) translate into three distinct refractive indices.



**Figure S3.** Stripe texture of SmA<sub>b</sub> phase formed by CB6O.10 compound in wedge cell with homeotropic anchoring. The stripes are due to periodic changes of optical retardation magnitude.



**Figure S4.** Texture of SmC phase formed by CB6O.9 compound in cell with planar anchoring; tilted domains visible in (a)-(c) can be brought into extinction by rotation of the cell with respect to crossed linear polarizers (arrows) by  $\pm 5$  deg. Dashed lines indicate rubbing direction. In (d) the same area observed between crossed circular polarizers showing no difference in birefringence between domains.



**Figure S5.** Real part of dielectric permittivity,  $\epsilon'$ , of CB6O.9 compound vs. temperature. In the inset dispersion of dielectric permittivity measured in SmAb, SmC and SmX phases. No dielectrically active collective modes are visible in any phase. Cut-off above 300 kHz is due to limited conductivity of ITO electrodes.

## References

- [1] R. Walker, D. Pocięcha, G. J. Strachan, J. M. D. Storey, E. Gorecka, C. T. Imrie, *Soft Matter* **2019**, *15*, 3188–3197.