Supplementary Information

Molecular curvature, specific intermolecular interactions and the twist bend nematic phase: the synthesis and characterisation of the 1-(4-cyanobiphenyl-4'-yl)-6-(4-alkylanilinebenzylidene-4'-oxy)hexanes (CB6O.*m*)

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Section 1: Materials/ General methods/ Instrumentation

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 ^{1}H and ^{13}C NMR, and FT-IR spectroscopies. ^{1}H and ^{13}C NMR spectra were recorded on either a 400 MHz Varian Unity INOVA, or a 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.

Section 2: Synthetic procedures

Synthesis of the CB6O.m series

The synthesis of the 1-(4-cyanobiphenyl-4'-yl)-6-(4-alkylanilinebenzylidene-4'- oxy)hexanes (CB6O.*m*) involved the condensation of 4-{4-[6-(4-formylphenoxy)hexyl]phenyl}benzonitrile [1] with the appropriate 4-alkylaniline. Thus, 4'-[6-(4-formylphenoxy)hexyl][1,1'-biphenyl]-4-carbonitrile (1 equiv), the appropriate 4-alkylaniline (1 equiv) and a crystal of *p*-toluenesulfonic acid were combined in EtOH (10 mL) and heated at reflux for 2-3 h. The mixture was cooled to room temperature and the resulting precipitate collected by vacuum filtration. The crude product was recrystallised twice from ethanol to give the title compound as an off-white solid.

CB6O.1: IR $\bar{\nu}$ cm^{-1}: 2928, 2855, 2225 (C≡N stretch), 1622 (C=N), 1605, 1509, 1247, 1167, 532, 543. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.41 (s, 1H, CH=N), 7.85 (d, J = 8.4 Hz, 2H, Ar), 7.71 (q, J = 8.2 Hz, 4H, Ar), 7.53 (d, J = 7.9 Hz, 2H, Ar), 7.32 (d, J = 8.0 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, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 2.71 (t, J = 7.7 Hz, 2H, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 2.39 (s, 3H, $ArCH_3$), 1.85 (p, J = 6.7 Hz, 2H, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 1.73 (p, J = 7.6 Hz, 2H, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 1.57 (m, 2H, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 1.48 (p, J = 7.7 Hz, 2H, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 161.67, 158.92, 149.76, 145.56, 143.49, 136.53, 135.34, 132.56, 130.38, 129.73,

129.25, 129.20, 127.47, 127.11, 120.78, 119.03, 114.66, 110.57, 68.03, 35.49, 31.24, 29.09, 28.93, 25.87, 21.00. Elemental Analysis: Calculated for $C_{33}H_{32}N_2O$: C 83.68 %, H 6.82 %, N 5.71 %, Found: C 83.86 %, H 6.82 %, N 5.93 %.

CB6O.2: IR $\bar{\nu}$ cm^{-1}: 2928, 2857, 2224 (C≡N stretch), 1621 (C=N), 1605 (para di-substituted benzene), 1509, 1247, 1166, 832, 542. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.42 (s, 1H, CH=N), 7.85 (d, *J* = 8.4 Hz, 2H, Ar), 7.71 (q, *J* = 8.2 Hz, 4H, Ar), 7.53 (d, *J* = 7.9 Hz, 2H, Ar), 7.32 (d, *J* = 7.9 Hz, 2H, Ar), 7.24 (d, *J* = 8.1 Hz, 2H, Ar), 7.17 (d, *J* = 8.1 Hz, 2H, Ar), 6.98 (d, *J* = 8.4 Hz, 2H, Ar), 4.05 (t, *J* = 6.5 Hz, 2H, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 2.70 (m, 4H, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$, Ar-$CH_2CH_3$), 1.85 (p, *J* = 6.8 Hz, 2H, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 1.73 (p, *J* = 7.6 Hz, 2H, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 1.52 (m, 4H, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 1.28 (t, *J* = 7.6 Hz, 3H, $ArCH_2CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 161.65, 158.94, 149.96, 145.56, 143.49, 136.55, 132.56, 130.37, 129.82, 129.27, 129.18, 128.51, 127.47, 127.10, 120.82, 119.01, 115.26, 114.65, 110.58, 68.02, 35.49, 31.22, 29.08, 28.92, 27.97, 25.86, 15.66. Elemental Analysis: Calculated for $C_{34}H_{34}N_2O$: C 83.91 %, H 7.04 %, N 5.76 %, Found: C 83.75 %, H 7.03 %, N 5.64 %.

CB6O.3: IR $\bar{\nu}$ cm^{-1}: 2930, 1856, 2225 (C≡N stretch), 1623 (C=N), 1605 (para di-substituted benzene), 1509, 1245, 1167, 832, 540. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.43 (s, 1H, CH=N), 7.86 (d, *J* = 8.3 Hz, 2H, Ar), 7.71 (q, *J* = 8.2 Hz, 4H, Ar), 7.54 (d, *J* = 7.7 Hz, 2H, Ar), 7.33 (d, *J* = 7.8 Hz, 2H, Ar), 7.23 (d, *J* = 8.0 Hz, 2H, Ar), 7.17 (d, *J* = 8.0 Hz, 2H, Ar), 6.99 (d, *J* = 8.3 Hz, 2H, Ar), 4.05 (t, *J* = 6.4 Hz, 2H, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 2.72 (t, *J* = 7.7 Hz, 2H, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 2.64 (t, *J* = 7.6 Hz, 2H, $ArCH_2CH_2CH_3$), 1.86 (p, *J* = 6.8 Hz, 2H, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 1.71 (m, 4H, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$, $ArCH_2CH_2CH_3$), 1.63 – 1.43 (m, 4H, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 1.00 (t, *J* = 7.3 Hz, 3H, $Ar(CH_2)_2CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 161.67, 158.92, 149.97, 145.56, 144.11, 143.51, 140.23, 136.53, 132.58, 130.40, 129.30, 129.22, 129.16, 127.49, 127.13, 120.78, 119.06, 115.19, 114.67, 110.57, 68.04, 37.61, 35.52, 31.27, 29.11, 28.96, 25.90, 24.66, 13.87. Elemental Analysis: Calculated for $C_{35}H_{36}N_2O$: C 83.96 %, H 7.25 %, N 5.60 %, Found: C 84.05 %, H 7.31 %, N 5.47 %.

CB6O.4: IR $\bar{\nu}$ cm^{-1}: 2933, 2853, 2223 (C≡N stretch), 1623 (C=N), 1605 (para di-substituted benzene), 1510, 1245, 1162, 836, 545. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.42 (s, 1H, CH=N), 7.85 (d, *J* = 8.4 Hz, 2H, Ar), 7.71 (q, *J* = 8.2 Hz, 4H, Ar), 7.53 (d, *J* = 7.8 Hz, 2H, Ar), 7.32 (d, *J* = 7.9 Hz, 2H, Ar), 7.22 (d, *J* = 8.1 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, Ar-$CH_2CH_2CH_2CH_2CH_2CH_2O$-Ar), 2.72 (t, *J* = 7.7 Hz, 2H, Ar-$CH_2CH_2CH_2CH_2CH_2CH_2O$-Ar),), 2.65 (t, *J* = 7.8 Hz, 2H, Ar-$CH_2(CH_2)_2CH_3$), 1.85 (p, *J* = 6.8 Hz, 2H, Ar-$CH_2CH_2CH_2CH_2CH_2CH_2O$-Ar), 1.79 – 1.34 (m, 10H, Ar-$CH_2CH_2CH_2CH_2CH_2CH_2O$-Ar, Ar-$CH_2(CH_2)_2CH_3$), 0.97 (t, *J* = 7.4 Hz, 3H, Ar-$(CH_2)_3CH_3$). ^{13}C NMR (101

MHz, $CDCl_3$) δ ppm: 161.64, 158.92, 149.92, 145.57, 143.50, 140.45, 136.54, 132.57, 130.37, 129.28, 129.20, 129.08, 127.49, 127.12, 120.76, 119.04, 114.65, 110.57, 68.02, 35.50, 35.19, 33.74, 31.25, 30.95, 29.09, 28.94, 25.88, 22.37, 13.99. Elemental Analysis: Calculated for $C_{36}H_{38}N_2O$: C 84.01 %, H 7.44 %, N 5.44 %, Found: C 83.83 %, H 7.49 %, N 5.28 %.

CB6O.5: IR $\bar{\nu}$ cm^{-1}: 2924, 2854, 2223 (C≡N stretch), 1623 (C=N), 1605 (para di-substituted benzene), 1510, 1246, 1167, 814, 538. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.42 (s, 1H, CH=N), 7.85 (d, *J* = 8.4 Hz, 2H, Ar), 7.71 (q, *J* = 8.2 Hz, 4H, Ar), 7.53 (d, *J* = 7.9 Hz, 2H, Ar), 7.32 (d, *J* = 7.8 Hz, 2H, Ar), 7.25 – 7.12 (m, 4H, Ar), 6.98 (d, *J* = 8.4 Hz, 2H, Ar), 4.05 (t, *J* = 6.5 Hz, 2H, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 2.71 (t, *J* = 7.7 Hz, 2H, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 2.64 (t, *J* = 7.8 Hz, 2H, $ArCH_2(CH_2)_3CH_3$), 1.85 (p, *J* = 6.9 Hz, 2H, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 1.61 (m, 8H, $ArCH_2CH_2(CH_2)_2CH_3$, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 1.42 – 1.30 (m, 4H, $ArCH_2CH_2(CH_2)_2CH_3$), 0.98 – 0.88 (m, 3H, $Ar(CH_2)_4CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 161.67, 158.91, 149.92, 145.56, 143.51, 140.50, 136.53, 132.58, 130.40, 129.30, 129.22, 129.10, 127.49, 127.13, 120.80, 119.06, 114.67, 110.57, 68.04, 35.52, 35.50, 31.55, 31.29, 31.27, 29.12, 28.96, 25.90, 22.60, 14.11. Elemental Analysis: Calculated for $C_{37}H_{40}N_2O$: C 84.05 %, H 7.63 %, N 5.30 %, Found: C 84.03 %, H 7.76 %, N 5.17 %.

CB6O.6: IR $\bar{\nu}$ cm^{-1}: 2925, 2854, 2222 (C≡N stretch), 1627 (C=N), 1593 (para di-substituted benzene), 1511, 1253, 1160, 815, 562. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.42 (s, 1H, CH=N), 7.85 (d, *J* = 8.4 Hz, 2H, Ar), 7.71 (q, *J* = 8.2 Hz, 4H, Ar), 7.53 (d, *J* = 7.9 Hz, 2H, Ar), 7.32 (d, *J* = 7.9 Hz, 2H, Ar), 7.21 (d, *J* = 8.1 Hz, 2H, Ar), 7.15 (d, *J* = 8.1 Hz, 2H, Ar), 6.98 (d, *J* = 8.4 Hz, 2H, Ar), 4.05 (t, *J* = 6.5 Hz, 2H, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 2.71 (t, *J* = 7.7 Hz, 2H, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 2.64 (t, *J* = 7.8 Hz, 2H, $ArCH_2(CH_2)_4CH_3$), 1.85 (p, *J* = 6.9 Hz, 2H, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 1.61 (m, 8H, $ArCH_2CH_2(CH_2)_3CH_3$, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 1.34 (m, 6H, $ArCH_2CH_2(CH_2)_3CH_3$), 0.98 – 0.86 (m, 3H, $Ar(CH_2)_5CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 161.66, 158.91, 149.92, 145.57, 143.51, 140.51, 136.54, 132.58, 130.39, 129.30, 129.21, 129.09, 127.49, 127.13, 120.78, 119.05, 114.66, 110.57, 68.04, 35.53, 35.51, 31.78, 31.56, 31.27, 29.11, 29.02, 28.95, 25.90, 22.66, 14.15. Elemental Analysis: Calculated for $C_{38}H_{42}N_2O$: C 84.09 %, H 7.80 %, N 5.16 %, Found: C 84.12 %, H 7.86 %, N 5.02 %.

CB6O.7: IR $\bar{\nu}$ cm^{-1}: 2924, 2852, 2223 (C≡N stretch), 1627 (C=N), 1594 (para di-substituted benzene), 1495, 1253, 1159, 814, 561. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.42 (s, 1H, CH=N), 7.84 (d, *J* = 8.5 Hz, 2H, Ar), 7.71 (q, *J* = 8.2 Hz, 4H, Ar), 7.53 (d, *J* = 8.0 Hz, 2H, Ar), 7.32 (d, *J* = 8.0 Hz, 2H, Ar), 7.21 (d, *J* = 8.1 Hz, 2H, Ar), 7.15 (d, *J* = 8.1 Hz, 2H, Ar), 6.98 (d, *J* = 8.5 Hz, 2H, Ar), 4.05 (t, *J* = 6.5 Hz, 2H, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 2.71 (t, *J* = 7.7 Hz, 2H, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 2.64 (t, *J* = 7.8 Hz, 2H, $ArCH_2(CH_2)_5CH_3$), 1.85 (p, *J* = 6.8 Hz, 2H, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 1.79 – 1.42 (m, 8H, $ArCH_2CH_2(CH_2)_4CH_3$, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 1.32 (m, 8H, $ArCH_2CH_2(CH_2)_4CH_3$), 0.91 (t, *J* = 6.5

Hz, 3H, $Ar(CH_2)_6CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 161.65, 158.92, 149.90, 145.57, 143.50, 140.51, 136.54, 132.58, 130.38, 129.20, 129.08, 127.49, 127.12, 120.77, 119.05, 114.66, 110.57, 68.03, 35.51, 31.86, 31.60, 31.26, 29.30, 29.22, 29.10, 28.94, 25.89, 22.70, 14.14. Elemental Analysis: Calculated for $C_{39}H_{44}N_2O$: C 84.13 %, H 7.97 %, N 5.03 %, Found: C 84.24 %, H 7.92 %, N 5.00 %.

CB6O.8: IR $\bar{\nu}$ cm^{-1}: 2921, 2850, 2224 (C≡N stretch), 1626 (C=N), 1595 (para di-substituted benzene), 1514, 1257, 1167, 814, 538. ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 8.42 (s, 1H, CH=N), 7.85 (d, *J* = 8.3 Hz, 2H, Ar), 7.71 (q, *J* = 8.2 Hz, 4H, Ar), 7.53 (d, *J* = 7.9 Hz, 2H, Ar), 7.32 (d, *J* = 7.9 Hz, 2H, Ar), 7.24 – 7.12 (m, 4H, Ar), 6.98 (d, *J* = 8.5 Hz, 2H, Ar), 4.05 (t, *J* = 6.5 Hz, 2H, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 2.72 (t, *J* = 7.7 Hz, 2H, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 2.64 (t, *J* = 7.8 Hz, 2H, $ArCH_2(CH_2)_6CH_3$), 1.84 (p, *J* = 6.7 Hz, 2H, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 1.61 (m, 8H, $ArCH_2CH_2(CH_2)_5CH_3$, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 1.42 – 1.22 (m, 10H, $ArCH_2CH_2(CH_2)_5CH_3$), 0.91 (t, *J* = 6.6 Hz, 3H, $Ar(CH_2)_7CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.64, 158.88, 149.90, 145.58, 143.49, 140.49, 132.56, 131.97, 130.36, 129.29, 129.18, 129.11, 129.06, 127.47, 127.10, 120.74, 119.01, 114.74, 114.65, 110.60, 68.02, 35.50, 35.09, 31.89, 31.57, 31.23, 29.49, 29.28, 29.08, 28.98, 28.92, 25.86, 22.68, 14.11. Elemental Analysis: Calculated for $C_{40}H_{46}N_2O$: C 84.17 %, H 8.12 %, N 4.91 %, Found: C 84.01 %, H 8.06 %, N 4.84 %.

CB6O.9: IR $\bar{\nu}$ cm^{-1}: 2921, 2850, 2224 (C≡N stretch), 1626 (C=N), 1595 (para di-substituted benzene), 1514, 1256, 1167, 814, 538. ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 8.42 (s, 1H, CH=N), 7.85 (d, *J* = 8.4 Hz, 2H, Ar), 7.71 (q, *J* = 8.2 Hz, 4H, Ar), 7.53 (d, *J* = 7.9 Hz, 2H, Ar), 7.32 (d, *J* = 7.9 Hz, 2H, Ar), 7.21 (d, *J* = 8.1 Hz, 2H, Ar), 7.15 (d, *J* = 8.1 Hz, 2H, Ar), 6.98 (d, *J* = 8.5 Hz, 2H, Ar), 4.05 (t, *J* = 6.5 Hz, 2H, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 2.72 (t, *J* = 7.7 Hz, 2H, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 2.64 (t, *J* = 7.8 Hz, 2H, $ArCH_2(CH_2)_7CH_3$), 1.85 (p, *J* = 6.8 Hz, 2H, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 1.61 (m, 8H, $ArCH_2CH_2(CH_2)_6CH_3$, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 1.32 (m, 12H, $ArCH_2CH_2(CH_2)_6CH_3$), 0.91 (t, *J* = 6.6 Hz, 3H, $Ar(CH_2)_8CH_3$)). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 161.64, 158.90, 149.85, 145.54, 143.46, 140.50, 136.54, 132.56, 130.36, 129.28, 129.18, 129.06, 127.47, 127.10, 120.74, 114.73, 114.64, 110.58, 68.02, 35.49, 31.90, 31.57, 31.24, 29.57, 29.53 29.33, 29.08, 28.92, 25.87, 22.68, 14.12. Elemental Analysis: Calculated for $C_{42}H_{48}N_2O$: C 84.20 %, H 8.27 %, N 4.79 %, Found: C 84.17 %, H 8.27 %, N 4.62 %.

CB6O.10: IR $\bar{\nu}$ cm^{-1}: 2923, 2851, 2225 (C≡N stretch), 1623 (C=N), 1606 (para di-substituted benzene), 1511, 1245, 1167, 815, 535. ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 8.41 (s, 1H, CH=N), 7.85 (d, *J* = 8.4 Hz, 2H, Ar), 7.71 (q, *J* = 8.2 Hz, 4H, Ar), 7.53 (d, *J* = 7.9 Hz, 2H, Ar), 7.31 (d, *J* = 7.9 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), 4.04 (t, *J* = 6.5 Hz, 2H, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 2.71 (t, *J* = 7.7 Hz, 2H, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 2.64 (t, *J* = 7.8 Hz, 2H $ArCH_2(CH_2)_8CH_3$), 1.85 (p, *J* = 6.9 Hz, 2H, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 1.62 (m, 8H,

$ArCH_2CH_2(CH_2)_7CH_3$, $ArCH_2CH_2CH_2CH_2CH_2CH_2OAr$), 1.40 – 1.21 (m, 14H, $ArCH_2CH_2(CH_2)_7CH_3$), 0.90 (t, *J* = 6.7 Hz, 3H, $Ar(CH_2)_9CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 161.68, 158.91, 149.86, 145.57, 143.51, 140.53, 136.54, 132.58, 130.41, 129.27, 129.21, 129.09, 127.49, 127.12, 120.78, 119.05, 114.67, 110.57, 68.04, 35.53, 31.95, 31.60, 31.27, 29.67, 29.65, 29.57, 29.38, 29.36, 29.11, 28.96, 25.90, 22.73, 14.17. Elemental Analysis: Calculated for $C_{42}H_{50}N_2O$: C 84.23 %, H 8.42 %, N 4.68 %, Found: C 84.11 %, H 8.58 %, N 4.54 %.

Synthesis of CBO5O.4[2]

4-{4-[(5-Bromopentyl)oxy]phenyl}benzonitrile

4-Cyano-4'-hydroxybiphenyl (8.119 g, 0.041 mol), 1,5-dibromopentane (55.8 mL, 0.41 mol) and anhydrous potassium carbonate (42.5 g, 0.31 mol) were added to acetone (250 mL), and the reaction mixture was refluxed for 24 h. The mixture was filtered and the inorganic residual precipitate was washed with copious amounts of acetone. The solvent was removed *in vacuo* and the resulting liquid was poured into ice-cold petroleum ether (350 mL). After several hours, the resulting precipitate was collected and washed with petroleum ether. The crude product was recrystallised twice with EtOH to give the title compound as a white solid. Yield: 9.321 g, 65.9 %.

M.P. = 82 °C. T_{NI} = 64 °C. IR $\bar{\nu}$ cm^{-1}: 2945, 2869, 2223 (C≡N stretch), 1603 (para di-substituted benzene), 1494, 1245, 1178, 1038, 828, 809, 531. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 7.76 – 7.62 (m, 4H, Ar), 7.60 – 7.51 (m, 2H, Ar), 7.06 – 6.96 (m, 2H, Ar), 4.05 (t, *J* = 6.3 Hz, 2H, $ArOCH_2CH_2CH_2CH_2CH_2Br$), 3.48 (t, *J* = 6.7 Hz, 2H, $ArOCH_2CH_2CH_2CH_2CH_2Br$), 2.04 – 1.93 (m, 2H, $ArOCH_2CH_2CH_2CH_2CH_2Br$), 1.93 – 1.81 (m, 2H, $ArOCH_2CH_2CH_2CH_2CH_2Br$), 1.76 – 1.62 (m, 2H, $ArOCH_2CH_2CH_2CH_2CH_2Br$). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 159.68, 145.22, 132.56, 131.43, 128.35, 127.09, 119.10, 115.07, 110.09, 67.90, 33.57, 32.46, 28.40, 24.83.

4-4-{[5-(4-Formylphenoxy)pentyl]oxy}phenyl)benzonitrile

A stirred mixture of 4-{4-[*5*-bromopentyl)oxy]phenyl}benzonitrile (4.091 g, 0.012 mol), 4-hydroxybenzaldehyde (1.465 g, 0.012 mol) and potassium carbonate (5.065 g, 0.036 mol) in N,N-dimethylformamide (25 mL) was heated under reflux for 20 h. The reaction mixture was allowed to cool to room temperature before addition to water (600 mL) and the resulting precipitate was

collected by vacuum filtration. The crude product was recrystallised from ethanol to give the title compound as a white solid. Yield: 3.310 g, 71.6 %.

CBO5OAH: M.P. = 101 °C. T_{NI} = 73 °C. IR $\bar{\nu}$ cm^{-1}: 2950, 2869, 2219 (C≡N stretch), 1688 (C=O aldehyde), 1595 (para di-substituted benzene), 1468, 1245, 1111, 823, 533. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 9.90 (s, 1H, ArC=OH), 7.91 – 7.80 (m, 2H, Ar), 7.76 – 7.61 (m, 4H, Ar), 7.61 – 7.50 (m, 2H, Ar), 7.07 – 6.97 (m, 4H, Ar), 4.09 (m, 4H, $OCH_2CH_2CH_2CH_2CH_2O$), 1.94 (m, 4H, $OCH_2CH_2CH_2CH_2CH_2O$), 1.81 – 1.64 (m, 2H, $OCH_2CH_2CH_2CH_2CH_2O$). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 190.92, 164.10, 159.61, 145.20, 132.61, 132.06, 131.41, 129.79, 128.38, 127.10, 119.18, 115.02, 114.72, 110.04, 68.13, 67.80, 28.96, 28.84, 22.74.

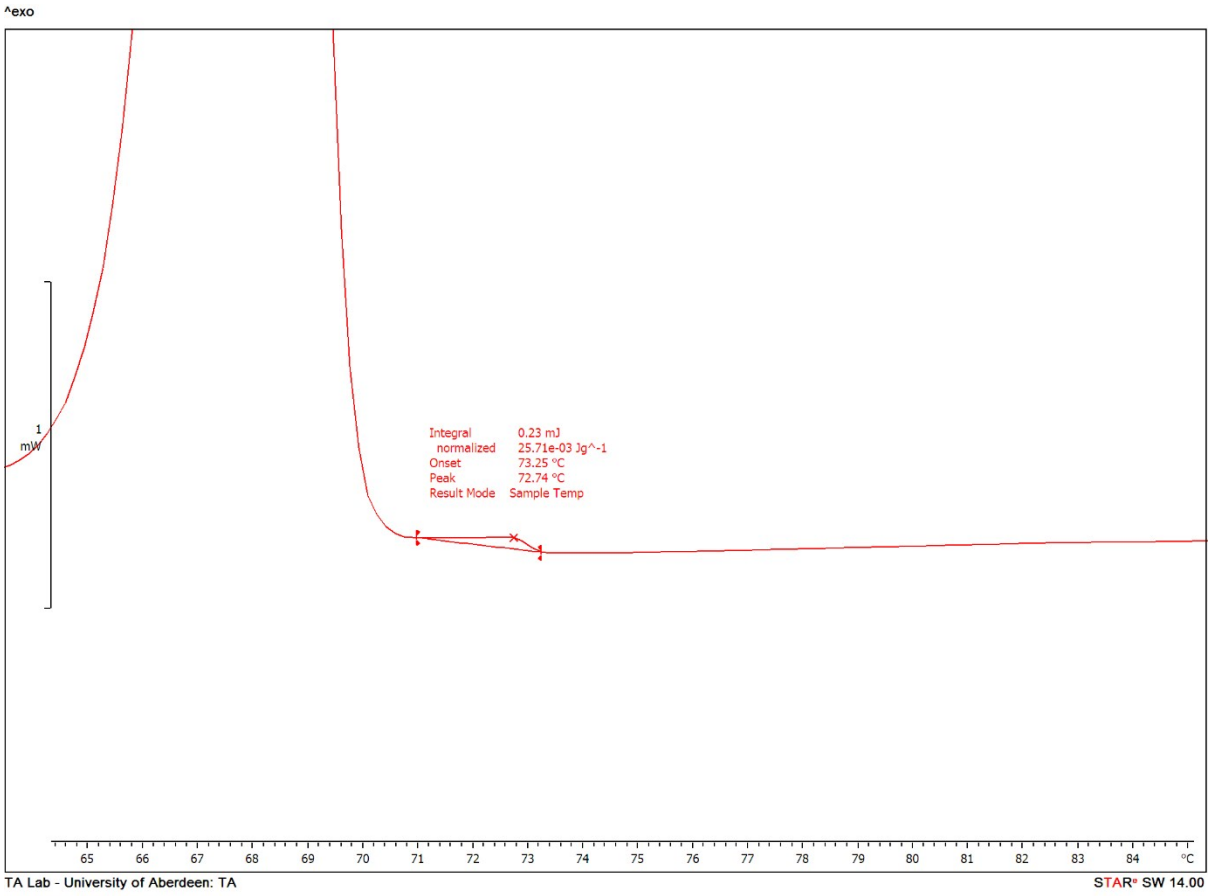
4-{4-[(5-{4-[(E)-N-(4-Butylphenyl)carboximidoyl]phenoxy}alkyl)oxy]phenyl}benzonitrile

4-4-{[5-(4-Formylphenoxy)pentyl]oxy}phenyl)benzonitrile (0.515 g, 0.0013 mol), *n*-butylaniline (0.4 mL, 0.0017 mol) and a few crystals of *p*-toluenesulfonic acid were combined in EtOH (20 mL) and heated at 80 °C for 3 h. The mixture was cooled to room temperature and the resulting precipitate collected by vacuum filtration. The crude product was recrystallised three times from ethanol to give the title compound as a white solid. Yield: 0.451 g, 67.2 %.

IR $\bar{\nu}$ cm^{-1}: 2942, 2867, 2232 (C≡N stretch), 1605 (para di-substituted benzene), 1511, 1495, 1251, 1171, 1016, 822, 530. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 8.42 (s, 1H, ArCHNAr), 7.92 – 7.78 (m, 2H, Ar), 7.78 – 7.61 (m, 4H, Ar), 7.61 – 7.48 (m, 2H, Ar), 7.28 – 7.10 (m, 4H, Ar), 7.10 – 6.90 (m, 4H, Ar), 4.09 (m, 4H, $OCH_2CH_2CH_2CH_2CH_2O$), 2.74 – 2.55 (t, J = 8.0 Hz, 2H, $ArCH_2CH_2CH_2CH_3$), 2.06 – 1.85 (m, 4H, $OCH_2CH_2CH_2CH_2CH_2O$), 1.83 – 1.54 (m, 4H, $OCH_2CH_2CH_2CH_2CH_2O$, $ArCH_2CH_2CH_2CH_3$), 1.40 (h, *J* = 9 Hz, 2H, $ArCH_2CH_2CH_2CH_3$), 0.96 (t, *J* = 7.3 Hz, 3H, $ArCH_2CH_2CH_2CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 161.56, 159.66, 158.95, 149.88, 145.23, 140.48, 132.59, 131.38, 130.39, 129.32, 129.09, 128.37, 127.09, 120.77, 119.15, 115.07, 114.63, 110.05, 67.87, 35.20, 33.75, 28.96, 22.75, 22.39, 14.02. Elemental Analysis: Calculated for $C_{35}H_{36}N_2O_2$: C 81.36 %, H 7.02 %, N 5.42 %, Found: C 81.39 %, H 7.23 %, N 5.22 %.

Section 3: DSC data

Figure SI. DSC trace obtained on cooling for CBO5O.4 showing the N_{TB}-N transition prior to crystallisation.



Section 4: References

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