

Twist-Bend Nematogenic Supramolecular Dimers and Trimers Formed by Hydrogen Bonding.

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Electronic Supplementary Information

Materials

Reagents The reagents and solvents available commercially were purchased from Sigma Aldrich, Alfa Aesar, ACROS Organics or TCI Chemicals and used as received unless otherwise stated.

TLC and Column Chromatography Reactions were monitored using thin-layer chromatography (TLC) carried out on aluminium-backed plates with a coating of Merck Kieselgel 60 F254 silica, using an appropriate solvent system. Silica gel coated aluminium plates were purchased from Merck KGaA. Spots were visualised using UV light (254 nm) or by oxidation using potassium permanganate stain. Separation via column chromatography was carried out using silica gel grade 60 Å 40–63 µm particle size, purchased from Fluorochem.

Purity Analysis The proposed structures of all final products and their intermediates were characterised using a combination of ¹H and ¹³C NMR, and FT-IR spectroscopies. ¹H and ¹³C NMR spectra were recorded on either a 400 MHz 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 Micro Analytical Laboratory in the School of Chemistry at the University of Manchester or Sheffield Analytical and Scientific Services Elemental Microanalysis Service at the University of Sheffield.

Synthetic Procedures and Analytical Data

6-Bromo-1-(4'-bromo[1,1'-biphenyl]-4-yl)hexan-1-one (1)

With all items of glassware wrapped in tin foil to exclude light, a mixture of 4-bromobiphenyl (24.821 g, 0.106 mol) and 6-bromohexanoyl chloride (25 g, 0.117 mol) dissolved in dichloromethane (50 mL) was added dropwise to a stirred suspension of aluminium (III) chloride (15.766 g, 0.117 mol) in dichloromethane (150 mL), cooled to 0 °C in an ice bath. The resulting mixture was stirred at 0 °C for 1 h, then warmed to room temperature and stirring continued for 7 h. The mixture was then added to crushed ice (400 g) and extracted using dichloromethane (2 × 100 mL). The organic fractions were combined, dried over anhydrous MgSO₄ and the solvent removed in vacuo. The crude product was recrystallised from ethanol to give the title compound as off-white crystals. Yield: 33.185 g, 76.3 %.

M.P. = 87 °C. IR $\bar{\nu}$ cm⁻¹: 2952, 2866, 1680 (C = O ketone), 1604 (para di-substituted benzene), 1467, 1357, 1258, 1185, 1076, 971, 807, 665. ¹H NMR (300 MHz, CDCl₃) δ ppm: 1.50 - 1.66 (m, 2H. ArCOCH₂CH₂CH₂CH₂CH₂Br), 1.75 - 1.88 (m, 2H. -ArCOCH₂CH₂CH₂CH₂CH₂Br), 1.90 - 2.02 (m, 2H. ArCOCH₂CH₂CH₂CH₂CH₂Br), 3.05 (t, J = 7.25 Hz, 2H. -ArCOCH₂CH₂CH₂CH₂CH₂Br), 3.47 (t, J = 6.69

Hz, 2H. ArCOCH₂CH₂CH₂CH₂CH₂Br), 7.48–7.55 (m, 2H. Ar), 7.59–7.70 (m, 4 H. Ar), 8.02–8.08 (m, 2H. Ar). ¹³C NMR (75 MHz, CDCl₃) δ ppm: 23.38, 27.89, 32.63, 33.56, 38.35, 122.65, 127.05, 128.72, 128.80, 132.11, 135.99, 138.80, 144.39, 199.40.

4-(6-Bromohexyl)-4'-bromo-1,1'-biphenyl (2)

With all items of glassware wrapped in tin foil to exclude light, triethylsilane (57.5 mL, 0.36 mol) was added dropwise to a mixture of 6-bromo-1-(4'-bromo[1,1'-biphenyl]-4-yl)hexan-1-one (37.082 g, 0.09 mol) and trifluoroacetic acid (55.5 mL, 0.72 mol) in dichloromethane (20 mL), cooled to 0 °C in an ice bath. The resulting mixture was stirred for 16 h at room temperature before addition to water (300 mL) and dichloromethane (100 mL). The layers were separated, and the aqueous layer washed with dichloromethane (2 × 100 mL). The organic fractions were combined and dried over anhydrous MgSO₄ before removal of the solvent in vacuo. The crude product was recrystallised from ethanol to give the title compound as a white solid. Yield: 31.839 g, 89.4 %.

M.P. = 76 °C. IR $\bar{\nu}$ cm⁻¹: 2932, 2856, 1607 (para di-substituted benzene), 1480, 1390, 1235, 1077, 1000, 804, 647. ¹H NMR (300 MHz, CDCl₃) δ ppm: 1.33–1.55 (m, 4 H. –ArCH₂CH₂CH₂CH₂CH₂CH₂Br), 1.61–1.75 (m, 2H. –ArCH₂CH₂CH₂CH₂CH₂CH₂Br), 1.89 (p, *J* = 7.06 Hz, 2H. –ArCH₂CH₂CH₂CH₂CH₂CH₂Br), 2.62–2.77 (m, 2H. –ArCH₂CH₂CH₂CH₂CH₂CH₂Br), 3.43 (t, *J* = 6.78 Hz, 2 H. –ArCH₂CH₂CH₂CH₂CH₂CH₂Br), 7.21–7.30 (m, 2H. Ar), 7.41–7.53 (m, 4H. Ar), 7.53–7.61 (m, 2H. Ar). ¹³C NMR (75 MHz, CDCl₃) δ ppm: 28.02, 28.39, 31.18, 32.73, 33.90, 35.43, 121.21, 126.83, 128.56, 128.95, 131.81, 137.42, 140.04, 142.18.

Methyl 4-[[6-(4'-bromo[1,1'-biphenyl]-4-yl)hexyl]oxy]benzoate (3)

A stirred mixture of 4-(6-bromohexyl)-4'-bromo-1,1'-biphenyl (1 eq), methyl 4-hydroxybenzoate (1.1 eq) and potassium carbonate (2 eq) in N,N-dimethylformamide (60 mL) was heated at reflux for 20 h. The reaction mixture was cooled to room temperature before addition to water (300 mL). NaCl (s) was added to the resulting suspension to encourage a precipitate which was collected by vacuum filtration. The crude product was recrystallised from ethyl acetate to give the title compound as an off-white solid. Yields in the range 46–62 % were obtained.

M.P. = 104 °C. IR $\bar{\nu}$ cm⁻¹: 2931, 2866, 1709 (C=O ester), 1609 (para di-substituted benzene), 1436, 1281, 1167, 1105, 1001, 810, 771. ¹H NMR (300 MHz, CDCl₃) δ ppm: 1.40–1.62 (m, 4H. ArCH₂CH₂CH₂CH₂CH₂CH₂OAr), 1.65–1.77 (m, 2H. ArCH₂CH₂CH₂CH₂CH₂CH₂OAr), 1.77–1.90 (m, 2H. ArCH₂CH₂CH₂CH₂CH₂CH₂OAr), 2.68 (t, *J* = 7.63 Hz, 2H. ArCH₂CH₂CH₂CH₂CH₂CH₂OAr), 3.90 (s, 3H. ArCOOCH₃), 4.02 (t, *J* = 6.40 Hz, 2H. ArCH₂CH₂CH₂CH₂CH₂CH₂OAr), 6.91 (d, *J* = 9.04 Hz, 2 H), 7.22–7.31 (m, 2H. Ar), 7.41–7.52 (m, 4H. Ar), 7.53–7.59 (m, 2H. Ar), 8.00 (d, *J* = 8.85 Hz, 2H. Ar). ¹³C NMR (75 MHz, CDCl₃) δ ppm: 25.86, 28.93, 29.03, 31.31, 35.46, 51.86, 68.07, 114.06, 121.21, 122.35, 126.81, 128.56, 128.97, 131.58, 131.81, 137.39, 140.01, 142.26, 162.91, 166.93.

Methyl 4-[[ω-(4'-cyano[1,1'-biphenyl]-4-yl)alkyl]oxy]benzoate (4)

Methyl 4-[[6-(4'-bromo[1,1'-biphenyl]-4-yl)hexyl]oxy]benzoate (1 eq.) was added to a stirred mixture of copper (I) cyanide (2.6 eq.) and N-methyl-2-pyrrolidone (70 mL) and heated at 200 °C for 4 h. The mixture was cooled to 80 °C and combined with a 60 °C solution of iron (III) chloride (13 eq. (5 eq. wrt moles of CN), concentrated HCl (32%, 16 mL) and water (30 mL). This was allowed to cool and stirred at room temperature for 1 h before addition to dichloromethane (300 mL) and water (300 mL). The layers were separated, and the aqueous layer washed with dichloromethane (3 × 100 mL). The organic fractions were combined, washed with water (3 × 100 mL) and dried over anhydrous MgSO₄ before removing the solvent in vacuo to yield a liquid. This was added to water and the resulting precipitate collected by vacuum filtration. The crude product was purified by silica gel chromatography using dichloromethane as eluent, followed by recrystallisation from ethanol to give the title compound as a white solid. Yields in the range 54%–62% were obtained.

M.P. = 86 °C. $\bar{\nu}$ cm⁻¹: 2948, 2928, 2858, 2223 (C≡N stretch), 1707 (C=O ester), 1604 (para di-substituted benzene), 1513, 1496, 1432, 1252, 1167, 1107, 999, 818, 771, 649, 522. ¹H NMR (300 MHz,

CDCl₃) δ ppm 1.35–1.62 (m, 4H. ArCH₂CH₂CH₂CH₂CH₂CH₂OAr), 1.63–1.78 (m, 2H. ArCH₂CH₂CH₂CH₂CH₂CH₂OAr), 1.78–1.91 (m, 2H. ArCH₂CH₂CH₂CH₂CH₂CH₂OAr), 2.61–2.79 (m, 2H. ArCH₂CH₂CH₂CH₂CH₂CH₂OAr), 3.90 (s, 3H. ArCOOCH₃), 4.02 (t, $J = 6.40$ Hz, 2H. ArCH₂CH₂CH₂CH₂CH₂CH₂OAr), 6.91 (d, $J = 9.04$ Hz, 2 H. Ar), 7.29–7.34 (m, 2 H. Ar), 7.53 (d, $J = 8.29$ Hz, 2H. Ar), 7.63–7.80 (m, 4 H. Ar), 8.00 (d, $J = 9.04$ Hz, 2H. Ar). ¹³C NMR (75 MHz, CDCl₃) δ ppm: 25.86, 28.91, 29.02, 31.26, 35.49, 51.89, 68.03, 110.55, 114.04, 119.07, 122.36, 127.12, 127.49, 129.20, 131.58, 132.59, 136.55, 143.48, 145.56, 162.88, 166.91.

6-(4'-Cyanobiphenyl-4-yl)hexyloxybenzoic acid, CB6OBA (5)

NaOH (40 eq.) was dissolved in H₂O (100 mL) and tetrahydrofuran (100 mL). Methyl 4-[[6-(4'-cyano[1,1'-biphenyl]-4-yl)hexyl]oxy]benzoate (1 eq.) was added and the resulting mixture heated at 55 °C with constant stirring for 144 h. The tetrahydrofuran was removed in vacuo, the pH of the water was lowered to pH 1 by addition of concentrated hydrochloric acid (32%) and the resulting white precipitate was collected by vacuum filtration. The crude product was added to dichloromethane (250 mL) and heated at reflux for 12 h. Any remaining solid was removed by vacuum filtration and the filtrate evaporated to yield the title compound, and subsequent recrystallisation from EtOAc gave the pure material as a white solid. Yields in the range 54%–72% were obtained.

IR $\bar{\nu}$ cm⁻¹: 3000–2250 (broad, OH), 2932, 2853, 2228 (C≡N stretch), 1679 (C=O carboxylic acid), 1606 (para di-substituted benzene), 1430, 1295, 1255, 1168, 982, 845, 813, 769, 646, 545. ¹H NMR (300 MHz, CDCl₃) δ ppm: 1.40–1.62 (m, 4H. ArCH₂CH₂CH₂CH₂CH₂CH₂OAr), 1.72 (p, $J = 7.58$ Hz, 4H. ArCH₂CH₂CH₂CH₂CH₂CH₂OAr), 1.79–1.92 (m, 2H. ArCH₂CH₂CH₂CH₂CH₂CH₂OAr), 2.71 (t, $J = 7.63$ Hz, 2 H. ArCH₂CH₂CH₂CH₂CH₂CH₂OAr), 4.05 (t, $J = 6.40$ Hz, 2H. ArCH₂CH₂CH₂CH₂CH₂CH₂OAr), 6.90–7.00 (m, 2H. Ar), 7.31 (d, $J = 8.29$ Hz, 2H. Ar), 7.53 (d, $J = 8.29$ Hz, 2H. Ar), 7.65–7.77 (m, 4H. Ar), 8.02–8.10 (m, 2H. Ar). ¹³C NMR (75 MHz, CDCl₃) δ ppm: 25.84, 28.90, 28.98, 31.24, 35.49, 68.13, 110.56, 114.19, 119.06, 121.40, 127.12, 127.48, 129.20, 132.35, 132.59, 136.55, 143.47, 145.56, 163.61, 171.65.

4-[(E)-2-(Pyridin-4-yl)ethenyl]phenol, HOS (6)

A stirred mixture of 4-methylpyridine (10 ml, 0.103 mol) and 4-hydroxybenzaldehyde (15.270 g, 0.125 mol) in acetic anhydride (21.5 ml, 0.226 mol) was heated under reflux for 23 hr. After cooling to room temperature, the mixture was poured into ice water (600 ml) and stirred for 1 h. The resulting precipitate was collected using vacuum filtration and refluxed in alcoholic potassium hydroxide (0.75 N) for 2 h. Acetic acid (20 ml) was added to precipitate the crude product, which was recrystallised from ethanol to give the title compound as a dark yellow solid. Yield: 6.852 g, 33.7 %.

M.P. = 282 °C. IR $\bar{\nu}$ cm⁻¹: 3250–2000 (broad, OH), 1636 (C=C), 1581, 1512, 1250, 1192, 973, 829, 547. ¹H NMR (300 MHz, DMSO-*d*₆) δ ppm: 6.80 (d, $J = 8.67$ Hz, 2H), 7.01 (d, $J = 16.58$ Hz, 1H. ArCH=CHAr), 7.39–7.53 (m, 5H. ArCH=CHAr, Ar), 8.46–8.54 (m, 2H. Ar, adj. to N), 9.77 (s, 1H. OHAr). ¹³C NMR (75 MHz, CDCl₃) δ ppm: 115.64, 120.45, 122.43, 127.17, 128.63, 133.02, 144.76, 149.86, 158.18.

4-[(E)-2-(4-Alkoxyphenyl)ethenyl]pyridines, *n*OS (7)

A stirred mixture of 4-hydroxystilbazole (1 eq.), *n*-bromoalkane (1 eq.) and potassium carbonate (3 eq.) in acetone was heated under reflux for 96 h. After cooling to room temperature, undissolved inorganic solid was removed by vacuum filtration and the filtrate removed in vacuo to yield a dark red solid. The crude product was purified by first passing through silica, washing through with copious amounts of ethyl acetate and subsequent recrystallisation: *n* = 1–5, CN and (S)-(2-Me)₄ from a mixture of ethyl acetate and hexane, *n* = 6–9 from ethyl acetate and *n* = 10 from toluene. Yields in the range of 30%–56% were obtained.

1OS: M.P. = 132 °C. IR $\bar{\nu}$ cm⁻¹: 3024, 1586, 1508, 1256, 1175, 1023, 970, 833, 546. ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.57 (d, $J = 4.9$ Hz, 2H, Ar adj. to N), 7.57–7.45 (m, 2H, Ar), 7.37–7.23 (m, 3H, Ar, ArCH=CHAr), 7.05–6.82 (m, 3H, Ar, ArCH=CHAr), 3.86 (d, $J = 1.6$ Hz, 3H, OCH₃). ¹³C NMR (101 MHz,

CDCl₃) δ 160.17, 150.06, 145.03, 132.75, 128.90, 128.40, 123.72, 120.66, 114.30, 55.36. Elemental Analysis: Calculated for C₁₄H₁₃NO₂: C 79.59%, H 6.20%, N 6.63%, Found: C 79.19%, H 6.27%, N 6.26%.

2OS: M.P. = 151 °C. IR $\bar{\nu}$ cm⁻¹: 2983, 1603, 1590, 1510, 1255, 1176, 973, 825, 551. ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.56 (d, *J* = 5.1 Hz, 2H, Ar adj. to N), 7.48 (d, *J* = 8.2 Hz, 2H, Ar), 7.44–7.18 (m, 3H, Ar, ArCHCHAr), 7.03–6.78 (m, 3H, Ar, ArCHCHAr), 4.08 (q, *J* = 7.0 Hz, 2H, OCH₂CH₃), 1.45 (t, *J* = 7.0 Hz, 3H, OCH₂CH₃). ¹³C NMR (101 MHz, CDCl₃) δ 159.57, 150.11, 145.00, 132.76, 128.74, 128.39, 123.60, 120.62, 114.80, 63.56, 14.81. Elemental Analysis: Calculated for C₁₅H₁₅NO: C 79.97%, H 6.71%, N 6.22%, Found: C 79.78%, H 6.86%, N 6.04%.

3OS: M.P. = 112 °C. IR $\bar{\nu}$ cm⁻¹: 2962, 2881, 1606, 1588, 1509, 1258, 1174, 1014, 970, 835, 545. ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.55 (d, *J* = 5.0 Hz, 2H, Ar adj. to N), 7.46 (d, *J* = 8.2 Hz, 2H, Ar), 7.37–7.17 (m, 3H, Ar, ArCHCHAr), 6.96–6.76 (m, 3H, Ar, ArCHCHAr), 3.94 (t, *J* = 6.6 Hz, 2H, OCH₂CH₂CH₃), 1.83 (h, *J* = 7.0 Hz, 2H, OCH₂CH₂CH₃), 1.06 (t, *J* = 7.4 Hz, 3H, OCH₂CH₂CH₃). ¹³C NMR (101 MHz, CDCl₃) δ 159.77, 150.10, 144.99, 132.76, 128.67, 128.38, 123.52, 120.61, 114.82, 69.58, 22.57, 10.53. Elemental Analysis: Calculated for C₁₆H₁₇NO: C 80.30%, H 7.16%, N 5.85%, Found: C 80.41%, H 7.33%, N 5.72%.

4OS: M.P. = 95 °C. IR $\bar{\nu}$ cm⁻¹: 2939, 2876, 1604, 1589, 1257, 1176, 970, 836, 544. ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.55 (d, *J* = 5.1 Hz, 2H, Ar adj. to N), 7.46 (d, *J* = 8.2 Hz, 2H, Ar), 7.35–7.17 (m, 3H, Ar, ArCHCHAr), 6.96–6.79 (m, 3H, Ar, ArCHCHAr), 3.98 (t, *J* = 6.5 Hz, 2H, OCH₂CH₂CH₂CH₃), 1.79 (p, *J* = 6.8 Hz, 2H, OCH₂CH₂CH₂CH₃), 1.51 (h, *J* = 7.5 Hz, 2H, OCH₂CH₂CH₂CH₃), 1.00 (t, *J* = 7.3 Hz, 3H, OCH₂CH₂CH₂CH₃). ¹³C NMR (101 MHz, CDCl₃) δ 159.79, 150.10, 144.98, 132.76, 128.65, 128.38, 123.52, 120.61, 114.81, 67.78, 31.28, 19.25, 13.88. Elemental Analysis: Calculated for C₁₇H₁₉NO: C 80.60%, H 7.56%, N 5.53%, Found: C 80.76%, H 7.76%, N 5.38%.

5OS: M.P. = 88 °C. IR $\bar{\nu}$ cm⁻¹: 2966, 2877, 1588, 1251, 1020, 971, 831, 545. ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.57 (d, *J* = 4.8 Hz, 2H, Ar adj. to N), 7.54–7.44 (m, 2H, Ar), 7.37–7.23 (m, 3H, Ar, ArCHCHAr), 6.99–6.82 (m, 3H, Ar, ArCHCHAr), 4.00 (t, *J* = 6.6 Hz, 2H, OCH₂CH₂(CH₂)₂CH₃), 1.82 (p, *J* = 6.7 Hz, 2H, OCH₂CH₂(CH₂)₂CH₃), 1.45 (m, 4H, OCH₂CH₂(CH₂)₂CH₃), 0.96 (t, *J* = 6.9 Hz, 3H, OCH₂CH₂(CH₂)₂CH₃). ¹³C NMR (101 MHz, CDCl₃) δ 159.78, 150.11, 145.01, 132.78, 128.68, 128.37, 123.56, 120.61, 114.82, 77.38, 77.06, 76.75, 68.12, 28.94, 28.20, 22.48, 14.04. Elemental Analysis: Calculated for C₁₈H₂₁NO: C 80.86%, H 7.92%, N 5.24%, Found: C 80.90%, H 8.11%, N 5.04%.

6OS: M.P. = 88 °C. IR $\bar{\nu}$ cm⁻¹: 2938, 2857, 1605, 1589, 1509, 1282, 1176, 1025, 969, 834, 543. ¹H NMR (300 MHz, CDCl₃) δ ppm: 8.62–8.47 (m, 2H, Ar adj. to N), 7.56–7.44 (m, 2H, Ar), 7.42–7.19 (m, 3H, Ar, ArCHCHAr), 7.03–6.78 (m, 3H, Ar, ArCHCHAr), 4.00 (t, *J* = 6.6 Hz, 2H, OCH₂CH₂(CH₂)₃CH₃), 1.91–1.71 (m, 2H, OCH₂CH₂(CH₂)₃CH₃), 1.62–1.29 (m, 6H, OCH₂CH₂(CH₂)₃CH₃), 1.00–0.86 (m, 3H, OCH₂CH₂(CH₂)₃CH₃). ¹³C NMR (101 MHz, CDCl₃) δ ppm: 159.80, 150.09, 145.02, 132.79, 128.67, 128.37, 123.54, 120.61, 114.83, 68.13, 31.59, 29.21, 25.72, 22.61, 14.05. Elemental Analysis: Calculated for C₁₉H₂₃NO: C 81.10%, H 8.24%, N 4.98%, Found: C 81.27%, H 8.42%, N 4.80%.

7OS: M.P. = 89 °C. IR $\bar{\nu}$ cm⁻¹: 2937, 2853, 1604, 1588, 1511, 1255, 1175, 970, 834, 544. ¹H NMR (300 MHz, CDCl₃) δ ppm: 8.62–8.50 (m, 2H, Ar adj. to N), 7.57–7.40 (m, 2H, Ar), 7.38–7.32 (m, 2H, Ar), 7.26 (d, *J* = 10.9 Hz, 1H, ArCHCHAr), 6.98–6.81 (m, 3H, Ar, ArCHCHAr), 4.00 (t, *J* = 6.6 Hz, 2H, OCH₂CH₂(CH₂)₄CH₃), 1.90–1.62 (m, 2H, OCH₂CH₂(CH₂)₄CH₃), 1.62–1.19 (m, 8H, OCH₂CH₂(CH₂)₄CH₃), 1.07–0.76 (m, 3H, OCH₂CH₂(CH₂)₄CH₃). ¹³C NMR (75 MHz, CDCl₃) δ 159.75, 150.13, 144.99, 132.76, 128.62, 128.38, 123.52, 120.62, 114.79, 68.11, 31.81, 29.24, 29.10, 26.02, 22.66, 14.16. Elemental Analysis: Calculated for C₂₀H₂₅NO: C 81.31%, H 8.53%, N 4.74%, Found: C 81.41%, H 8.74%, N 4.57%.

8OS: M.P. = 89 °C. IR $\bar{\nu}$ cm⁻¹: 2920, 2854, 1606, 1588, 1511, 1282, 1175, 969, 834, 544. ¹H NMR (300 MHz, CDCl₃) δ ppm: 8.62–8.46 (m, 2H, Ar adj. to N), 7.55–7.42 (m, 2H, Ar), 7.38–7.33 (m, 2H, Ar), 7.27 (m, 1H, ArCHCHAr), 6.98–6.82 (m, 3H, Ar, ArCHCHAr), 4.00 (t, *J* = 6.6 Hz, 2H, OCH₂CH₂(CH₂)₅CH₃), 1.81 (m, 2H, OCH₂CH₂(CH₂)₅CH₃), 1.57–1.21 (m, 10H, OCH₂CH₂(CH₂)₅CH₃), 0.98–0.83 (m, 3H, OCH₂CH₂(CH₂)₅CH₃). ¹³C NMR (101 MHz, CDCl₃) δ 159.79, 150.12, 145.02, 132.79, 128.67, 128.37, 123.56, 120.61, 114.83, 68.14, 31.83, 29.37, 29.25, 26.05, 22.68, 14.12. Elemental Analysis: Calculated for C₂₁H₂₇NO: C 81.51%, H 8.79%, N 4.53%, Found: C 81.30%, H 8.96%, N 4.39%.

9OS: M.P. = 89 °C. IR $\bar{\nu}$ cm⁻¹: 2937, 2850, 1606, 1589, 1510, 1254, 969, 835, 544. ¹H NMR (300 MHz, CDCl₃) δ ppm: 8.74 (d, J = 6.7 Hz, 2H, Ar adj. to N), 7.93–7.82 (m, 2H, Ar), 7.73–7.54 (m, 3H, Ar, ArCHCHAr), 7.10–6.89 (m, 3H, Ar, ArCHCHAr), 4.02 (t, J = 6.5 Hz, 2H, OCH₂CH₂(CH₂)₆CH₃), 1.91–1.74 (m, 2H, OCH₂CH₂(CH₂)₆CH₃), 1.68–1.18 (m, 13H, OCH₂CH₂(CH₂)₆CH₃), 0.99–0.84 (m, 3H, OCH₂CH₂(CH₂)₆CH₃). ¹³C NMR (75 MHz, CDCl₃) δ ppm: 161.66, 154.66, 141.39, 141.10, 130.01, 126.96, 122.52, 119.98, 115.20, 68.33, 31.87, 29.52, 29.37, 29.25, 29.13, 25.99, 22.67, 14.12. Elemental Analysis: Calculated for C₂₂H₂₉NO: C 81.49%, H 9.04%, N 4.33%, Found: C 81.27%, H 8.70%, N 4.23%.

10OS: M.P. = 87 °C. IR $\bar{\nu}$ cm⁻¹: 2918, 2851, 1606, 1589, 1511, 1256, 1019, 834, 544. ¹H NMR (300 MHz, CDCl₃) δ ppm: 8.57 (d, J = 5.3 Hz, 2H, Ar adj. to N), 7.52–7.45 (m, 2H, Ar), 7.40–7.33 (m, 2H, Ar), 7.27 (d, J = 7.8 Hz, 1H, ArCHCHAr), 6.97–6.83 (m, 3H, Ar, ArCHCHAr), 4.00 (t, J = 6.6 Hz, 2H, OCH₂CH₂(CH₂)₇CH₃), 1.81 (p, J = 6.7 Hz, 2H, OCH₂CH₂(CH₂)₇CH₃), 1.56–1.18 (m, 14H, OCH₂CH₂(CH₂)₇CH₃), 0.94–0.84 (m, 3H, OCH₂CH₂(CH₂)₇CH₃). ¹³C NMR (101 MHz, CDCl₃) δ ppm: 159.87, 149.73, 145.43, 133.14, 128.59, 128.44, 123.39, 120.69, 114.85, 77.38, 77.06, 76.75, 68.15, 31.92, 29.59, 29.58, 29.41, 29.34, 29.24, 26.05, 22.70, 14.14. Elemental Analysis: Calculated for C₂₃H₃₁NO: C 81.95%, H 9.26%, N 4.15%, Found: C 81.85%, H 9.43%, N 4.16%.

Table 1. Transition temperatures and associated entropy changes for CB6OBA.

n	T _{Cr} /°C	T _{N_{TB}N} /°C	T _{Nl} /°C	$\Delta S_{Cr/R}$	$\Delta S_{N_{TB}N/R}$	$\Delta S_{Nl/R}$
6	162	159	197	7.08	0.17	0.89

Procedure for Resonant Soft X-Ray Diffraction (RSoXS)

Experiments were performed on the soft x-ray scattering beam line (11.0.1.2) at Advanced Light Source, Lawrence Berkeley National Laboratory. The X-ray beam was tuned to the carbon absorption K-edge, ~283 eV. Samples with thickness ~1 μ m were placed between two 100-nm-thick Si₃N₄ slides. The scattering intensity was recorded using the Princeton PI-MTE CCD detector, cooled to -45°C, having a pixel size of 27 μ m, with an adjustable distance from the sample. The adjustable position of the detector allowed to cover a broad range of q vectors, corresponding to periodicities from approximately 5–300 nm.