Sulfur-linked cyanoterphenyl-based liquid crystal dimers and the twist-bend nematic phase

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Experimental Procedures

Synthesis

Reagents

All reagents and solvents that were available commercially were purchased from Sigma Aldrich, Fisher Scientific or Fluorochem and were used without further purification unless otherwise stated.

Thin Layer Chromatography

Reactions were monitored using thin layer chromatography, and the appropriate solvent system, using aluminium-backed plates with a coating of Merck Kieselgel 60 F254 silica which were purchased from Merck KGaA. The spots on the plate were visualised by UV light (254 nm) or by oxidation using either a potassium permanganate stain or iodine dip.

Column Chromatography

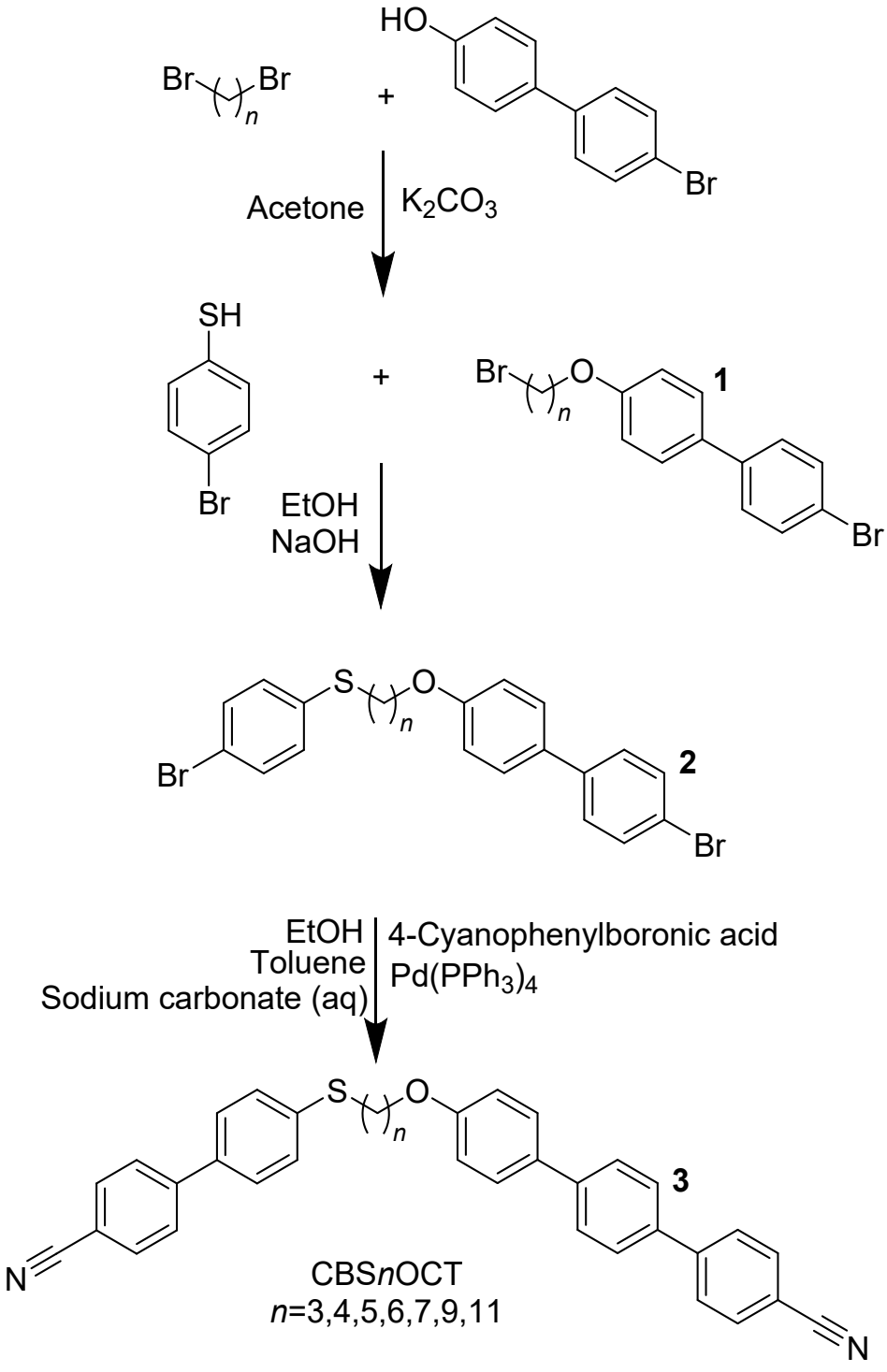
For normal phase column chromatography, the separations were carried out using silica gel grade 60 Å, 40-63 μm particle size, purchased from Fluorochem and using an appropriate solvent system.

Structure Characterisation

All final products and intermediates that were synthesised were characterised using ^{1}H NMR, ^{13}C NMR and infrared spectroscopies. The NMR spectra were recorded on a 400 MHz Bruker Avance III HD NMR spectrometer. The infrared spectra were recorded on a Perkin Elmer Spectrum Two FTIR spectrometer with an ATR diamond cell.

Purity Analysis

In order to determine the purity of the final products, high-resolution mass spectrometry was carried out using a Waters XEVO G2 QTof mass spectrometer by Dr. Morag Douglas at the University of Aberdeen.



Scheme 1. Synthesis of the CBS*n*OCT series.

The synthesis of the CBS*n*OCT series follows the steps outlined in **Scheme 1**. The CBS*n*OCT series (**3**) was synthesised using a Williamson ether reaction[12] followed by a modified Williamson ether reaction[10] and subsequently by a Suzuki-Miyaura cross-coupling reaction[2] to form the desired product.

1 4-Bromo-4'-[(ω-bromoalkyl)oxy]-1,1'-biphenyls

To a pre-dried flask, flushed with argon and fitted with a condenser, 4'-bromo-(1,1'-biphenyl)-4-ol (1 eq) and potassium carbonate (2 eq) were added. Acetone (50 mL) was added along with the appropriate 1,ω-dibromoalkane (6 eq) and stirred. The reaction mixture was refluxed overnight, and the extent of the reaction monitored by TLC using dichloromethane as the solvent system (RF values quoted in the product data). The quantities of the reagents used in each reaction are listed in **Table S1**. The reaction mixture was cooled to room temperature, filtered and the residue washed with acetone (100 mL). The filtrate was concentrated under vacuum to give a yellow solution which was added to 40:60 petroleum ether (100 mL). The resulting white precipitate was collected and recrystallised from hot ethanol (200 mL).

Table S1. Quantities of reagents used in the syntheses of 4-bromo-4'-[(ω-bromoalkyl)oxy]-1,1'-biphenyls (**1**).

n	1,ω-Dibromoalkane	4-Bromo-(1,1-biphenyl)-4-ol	Potassium carbonate
3	4.9 mL, 9.73 g, 4.82×10^{-2} mol	2.00 g, 8.03×10^{-3} mol	2.20 g, 1.61×10^{-2} mol
4	5.8 mL, 10.4 g, 4.82×10^{-2} mol	2.00 g, 8.03×10^{-3} mol	2.20 g, 1.61×10^{-2} mol
5	6.6 mL, 11.1 g, 4.82×10^{-2} mol	2.00 g, 8.03×10^{-3} mol	2.20 g, 1.61×10^{-2} mol
6	7.4 mL, 11.8 g, 4.82×10^{-2} mol	2.00 g, 8.03×10^{-3} mol	2.20 g, 1.61×10^{-2} mol
7	6.0 mL, 9.0 g, 3.49×10^{-2} mol	1.45 g, 5.82×10^{-3} mol	1.61 g, 1.16×10^{-2} mol
9	5.3 mL, 7.5 g, 2.62×10^{-2} mol	1.09 g, 4.37×10^{-3} mol	1.21 g, 8.74×10^{-3} mol
11	5.6 mL, 7.5 g, 2.39×10^{-2} mol	0.99 g, 3.98×10^{-3} mol	1.10 g, 7.96×10^{-3} mol

1.1 4-Bromo-4'-[(3-bromopropyl)oxy]-1,1'-biphenyl

Yield: 2.06 g, 69.3 %. RF: 0.74. MP: 117 °C

ν_{max}/cm^{-1}: 1604, 1516, 1479, 1389, 1281, 1240, 1196, 1176, 1059, 1028, 998, 919, 844, 811, 723, 616, 550, 511

δ_H/ppm (400 MHz, $CDCl_3$): 7.53 (2 H, d, J 8.2 Hz, Ar-H), 7.49 (2 H, d, J 8.4 Hz, Ar-H), 7.41 (2 H, d, J 8.2 Hz, Ar-H), 6.98 (2 H, d, J 8.4 Hz, Ar-H), 4.15 (2 H, t, J 5.8 Hz, O-$\underline{CH_2}$-CH_2-), 3.63 (2 H, t, J 6.3 Hz, Br-$\underline{CH_2}$-CH_2-), 2.35 (2 H, tt, J 5.8 Hz, 6.3 Hz, O-CH_2-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 158.52, 139.68, 132.77, 131.81, 128.31, 128.03, 120.85, 115.15, 114.93, 65.41, 32.35, 29.98

2.2 4-Bromo-4'-[(4-bromobutyl)oxy]-1,1'-biphenyl

Yield: 1.71 g, 55.4 %. RF: 0.75. MP: 118 °C

v_{max}/cm^{-1}: 2948, 2870, 1604, 1514, 1480, 1392, 1279, 1242, 1172, 1045, 1029, 1008, 998, 843, 815, 735, 653, 617, 546, 518, 492, 440

δ_H/ppm (400 MHz, $CDCl_3$): 7.53 (2 H, d, J 8.3 Hz, Ar-H), 7.47 (2 H, d, J 8.5 Hz, Ar-H), 7.40 (2 H, d, J 8.3 Hz, Ar-H), 6.95 (2 H, d, J 8.5 Hz, Ar-H), 4.04 (2 H, t, J 5.9 Hz, O-$\underline{CH_2}$-CH_2-), 3.50 (2 H, t, J 6.7 Hz, Br-$\underline{CH_2}$-CH_2-), 2.08 (2 H, tt, J 6.7 Hz, 5.9 Hz, O-CH_2-$\underline{CH_2}$-CH_2-) 1.97 (2 H, quin, J 6.7 Hz, Br-CH_2-$\underline{CH_2}$-CH_2-),

δ_C/ppm (100 MHz, $CDCl_3$): 158.69, 139.71, 132.56, 131.79, 128.29, 128.00, 120.81, 114.86, 66.96, 33.43, 29.47, 27.91

1.3 4-Bromo-4'-[(5-bromopentyl)oxy]-1,1'-biphenyl

Yield: 2.06 g, 69.3 %. RF: 0.80. MP: 114 °C

v_{max}/cm^{-1}: 2938, 2867, 1604, 1580, 1519, 1480, 1392, 1288, 1245, 1202, 1198, 1094, 1070, 1040, 997, 820, 804, 731, 649, 617, 501, 479

δ_H/ppm (400 MHz, $CDCl_3$): 7.53 (2 H, d, J 8.2 Hz, Ar-H), 7.47 (2 H, d, J 8.5 Hz, Ar-H), 7.41 (2 H, d, J 8.2 Hz, Ar-H), 6.96 (2 H, d, J 8.5 Hz, Ar-H), 4.01 (2 H, t, J 6.2 Hz, O-$\underline{CH_2}$-CH_2-), 3.45 (2 H, t, J 6.8 Hz, Br-$\underline{CH_2}$-CH_2-),1.96 (2 H, tt, J 6.2 Hz, 6.8 Hz, O-CH_2-$\underline{CH_2}$-CH_2-), 1.84 (2 H, quin, J 6.8 Hz, Br-CH_2-$\underline{CH_2}$-CH_2-), 1.65 (2 H, quin, J 6.8 Hz, O-CH_2-CH_2-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 158.81, 139.75, 132.44, 131.78, 128.28, 127.98, 120.77, 114.88, 67.69, 33.60, 32.49, 28.45, 24.86

1.4 4-Bromo-4'-[(6-bromohexyl)oxy]-1,1'-biphenyl

Yield: 2.10 g, 63.4 %. RF: 0.81. MP: 110 °C

v_{max}/cm^{-1}: 2937, 2862, 1604, 1580, 1521, 1472, 1392, 1285, 1247, 1198, 1177, 1081. 1031, 995, 809, 734, 647, 496

δ_H/ppm (400 MHz, $CDCl_3$): 7.52 (2 H, d, J 8.3 Hz, Ar-H), 7.47 (2 H, d, J 8.5 Hz, Ar-H), 7.41 (2 H, d, J 8.3 Hz, Ar-H), 6.95 (2 H, d, J 8.5 Hz, Ar-H), 4.00 (2 H, t, J 6.4 Hz, O-$\underline{CH_2}$-CH_2-), 3.41 (2 H, t, J 6.8, Br-$\underline{CH_2}$-CH_2-), 1.91 (2 H, tt, J 7.2 Hz, 6.4 Hz, O-CH_2-$\underline{CH_2}$-CH_2-),1.81 (2 H, quin, J 6.8 Hz, Br-CH_2-$\underline{CH_2}$-CH_2-), 1.43 (4 H, m, O-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 158.89, 139.77, 132.37, 131.78, 128.28, 127.96, 120.75, 114.88, 67.84, 33.80, 32.69, 29.10, 27.94, 25.32

1.5 4-Bromo-4'-[(7-bromoheptyl)oxy]-1,1'-biphenyl

Yield: 1.29 g, 52.0 %. RF: 0.83. MP: 84 °C

ν_{max}/cm^{-1}: 2935, 2854, 1604, 1518, 1482, 1391, 1287, 1243, 1190. 1172, 1073, 1031, 998, 819, 806, 730, 639, 548, 498

δ_H/ppm (400 MHz, $CDCl_3$): 7.52 (2 H, d, J 8.1 Hz, Ar-H), 7.47 (2 H, d, J 8.3 Hz, Ar-H), 7.41 (2 H, d, J 8.1 Hz, Ar-H), 6.96 (2 H, d, J 8.3 Hz, Ar-H), 3.99 (2 H, t, J 6.5 Hz, O-$\underline{CH_2}$-CH_2-), 3.42 (2 H, t, J 6.9 Hz, Br-$\underline{CH_2}$-CH_2-), 1.89 (2 H, tt, J 7.0 Hz, 6.5 Hz, O-CH_2-$\underline{CH_2}$-CH_2-), 1.81 (2 H, quin, J 6.9 Hz, Br-CH_2-$\underline{CH_2}$-CH_2-), 1.47 (6 H, m, O-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 158.93, 139.78, 132.31, 131.77, 128.27, 127.95, 120.73, 114.88, 67.96, 33.93, 32.72, 29.16, 28.53, 28.09, 25.91

1.6 4-Bromo-4'-[(9-bromononyl)oxy]-1,1'-biphenyl

Yield: 1.32 g, 66.5 %. RF: 0.78. MP: 98 °C

ν_{max}/cm^{-1}: 2929, 2856, 1604, 1515, 1472, 1391, 1285, 1242, 1197, 1174, 1078, 1011, 999, 810, 734, 641, 550, 495

δ_H/ppm (400 MHz, $CDCl_3$): 7.53 (2 H, d, J 8.4 Hz, Ar-H), 7.47 (2 H, d, J 8.3 Hz, Ar-H), 7.41 (2 H, d, J 8.4 Hz, Ar-H), 6.96 (2 H, d, J 8.3 Hz, Ar-H), 3.99 (2 H, t, J 6.5 Hz, O-$\underline{CH_2}$-CH_2-), 3.41 (2 H, t, J 6.9 Hz, Br-$\underline{CH_2}$-CH_2-), 1.83 (4 H, m, O-CH_2-$\underline{CH_2}$-CH_2-CH_2-CH_2-CH_2-CH_2-$\underline{CH_2}$-CH_2-), 1.43 (10 H, m, O-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 158.97, 139.80, 132.27, 131.77, 128.27, 127.94, 120.72, 114.89, 68.07, 34.03, 32.81, 29.36, 29.27, 29.25, 28.70, 28.15, 26.02

1.7 4-Bromo-4'-[(11-bromoundecyl)oxy]-1,1'-biphenyl

Yield: 1.15 g, 60.0 %. RF: 0.85. MP: 70 °C

ν_{max}/cm^{-1}: 2918, 2849, 1607, 1518, 1466, 1391, 1286, 1249, 1188, 1174, 1074, 1033, 997, 808, 722, 636, 547, 504, 472

δ_H/ppm (400 MHz, $CDCl_3$): 7.52 (2 H, d, J 8.1 Hz, Ar-H), 7.47 (2 H, d, J 8.3, Ar-H), 7.41 (2 H, d, J 8.1 Hz, Ar-H), 6.96 (2 H, d, J 8.3 Hz, Ar-H), 3.99 (2 H, t, J 6.5, O-$\underline{CH_2}$-CH_2-), 3.41 (2 H, t, J 6.9, Br-$\underline{CH_2}$-CH_2-), 1.83 (4 H, m, O-CH_2-$\underline{CH_2}$-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$\underline{CH_2}$-CH_2-), 1.39 (14 H, m, O-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 158.99, 139.80, 132.25, 131.77, 128.27, 127.93, 120.71, 114.90, 68.11, 34.07, 32.84, 29.52, 29.47, 29.42, 29.37, 29.27, 28.77, 28.18, 26.05

2 4-Bromo-4'-({ω-[(4-bromophenyl)thio]alkyl}oxy)-1,1'-biphenyls

To a pre-dried flask flushed with argon, 4-bromothiophenol (1.1 eq) was added. Sodium hydroxide (1.32 eq) dissolved in ethanol (20 mL), sonicated to ensure all the solid was in solution, was added and the mixture was stirred for 2 h at room temperature. Compound **1** (1 eq) in tetrahydrofuran (5 mL) was added and the reaction mixture was stirred at room temperature for 24 h. The quantities of the reagents used in each reaction are listed in **Table S2**. The extent of the reaction was monitored by TLC using dichloromethane as the solvent system (RF values quoted in the product data). The resulting white precipitate was collected and recrystallised from hot ethanol (100 mL).

Table S2. Quantities of reagents used in the syntheses of 4-Bromo-4'-({ω-[(4-bromophenyl)thio]alkyl}oxy)-1,1'-biphenyls (**2**).

n	(**1**)	4-Bromothiophenol	Sodium hydroxide
3	1.00 g, 2.70×10^{-3} mol	0.562 g, 2.97×10^{-3} mol	0.142 g, 3.56×10^{-3} mol
4	2.50 g, 6.52×10^{-3} mol	1.36 g, 7.17×10^{-3} mol	0.344 g, 8.61×10^{-3} mol
5	1.50 g, 3.77×10^{-3} mol	0.783 g, 4.14×10^{-3} mol	0.199 g, 4.97×10^{-3} mol
6	1.50 g, 3.64×10^{-3} mol	0.756 g, 4.00×10^{-3} mol	0.192 g, 4.80×10^{-3} mol
7	1.00 g, 2.35×10^{-3} mol	0.488 g, 2.58×10^{-3} mol	0.124 g, 3.10×10^{-3} mol
9	1.00 g, 2.20×10^{-3} mol	0.458 g, 2.42×10^{-3} mol	0.116 g, 2.91×10^{-3} mol
11	2.00 g, 4.15×10^{-3} mol	0.862 g, 4.56×10^{-3} mol	0.219 g, 5.48×10^{-3} mol

2.1 4-Bromo-4'-({3-[(4-bromophenyl)thio]propyl}oxy)-1,1'-biphenyl

Yield: 0.815 g, 63.1 %. RF: 0.75. MP: 112 °C

ν_{max}/cm^{-1}: 2964, 1603, 1580, 1521, 1481, 1472, 1391, 1286, 1249, 1201, 1177, 1091, 1035, 997, 816, 806, 729, 478

δ_H/ppm (400 MHz, $CDCl_3$): 7.53 (2 H, d, J 8.3 Hz, Ar-H), 7.47 (2 H, d, J 8.5 Hz, Ar-H), 7.40 (4 H, m, Ar-H), 7.22 (2 H, d, J 8.5 Hz, Ar-H), 6.94 (2 H, d, J 8.5 Hz, Ar-H), 4.10 (2 H, t, J 5.9 Hz, O-$\underline{CH_2}$-CH_2-), 3.12 (2 H, t, J 7.0 Hz, S-$\underline{CH_2}$-CH_2-), 2.12 (2 H, tt, J 7.0 Hz, 5.9 Hz, S-CH_2-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 158.54, 139.69, 135.43, 132.68, 131.98, 131.80, 130.72, 128.31, 128.00, 120.83, 119.84, 114.88, 65.93, 30.29, 28.83

2.2 4-Bromo-4'-({4-[(4-bromophenyl)thio]butyl}oxy)-1,1'-biphenyl

Yield: 1.90 g, 59.2 %. RF: 0.80. MP: 142 °C

ν_{max}/cm^{-1}: 2948, 1606, 1517, 1480, 1470, 1397, 1284, 1243, 1198, 1089, 1041, 1006, 805, 724, 501, 479

δ_H/ppm (400 MHz, $CDCl_3$): 7.55 (2 H, d, J 8.5 Hz, Ar-H), 7.50 (2 H, d, J 8.8 Hz, Ar-H), 7.42 (4 H, m, Ar-H), 7.22 (2 H, d, J 8.7 Hz, Ar-H), 6.96 (2 H, d, J 8.8 Hz, Ar-H), 4.12 (2 H, t, J 6.0 Hz, O-$\underline{CH_2}$-CH_2-), 3.01 (2 H, t, J 7.1 Hz, S-$\underline{CH_2}$-CH_2-), 1.97 (2 H, quin, J 6.0 Hz, O-CH_2-$\underline{CH_2}$-CH_2-), 1.87 (2 H, tt, J 7.1 Hz, 6.0 Hz, S-CH_2-$\underline{CH_2}$-CH_2-),

δ_C/ppm (100 MHz, $CDCl_3$): 158.70, 139.71, 135.73, 132.52, 131.92, 131.79, 130.71, 128.28, 127.98, 120.79, 119.71, 114.86, 67.29, 33.48, 28.23, 25.68

2.3 4-Bromo-4'-({5-[(4-bromophenyl)thio]pentyl}oxy)-1,1'-biphenyl

Yield: 0.985 g, 51.6 %. RF: 0.75. MP: 99 °C

ν_{max}/cm^{-1}: 2942, 2859, 1603, 1579, 1521, 1470, 1391, 1286, 1248, 1198, 1178, 1094, 1071, 1005, 997, 808, 732, 498, 477

δ_H/ppm (400 MHz, $CDCl_3$): 7.52 (2 H, d, J 8.3 Hz, Ar-H), 7.47 (2 H, d, J 8.6 Hz, Ar-H), 7.39 (4 H, m, Ar-H), 7.18 (2 H, d, J 8.6 Hz, Ar-H), 6.94 (2 H, d, J 8.6 Hz, Ar-H), 3.99 (2 H, t, J 6.3 Hz, O-$\underline{CH_2}$-CH_2-), 2.93 (2 H, t, J 7.3, S-$\underline{CH_2}$-CH_2-), 1.82 (2 H, tt, J 6.9 Hz, 6.3 Hz, O-CH_2-$\underline{CH_2}$-CH_2-), 1.73 (2 H, quin, J 7.3 Hz, S-CH_2-$\underline{CH_2}$-CH_2-), 1.63 (2 H, m, S-CH_2-CH_2-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 158.83, 139.75, 135.96, 132.42, 131.89, 131.78, 130.59, 128.28, 127.97, 120.77, 119.59, 114.88, 67.71, 33.64, 28.79, 28.73, 25.30

2.4 4-Bromo-4'-({6-[(4-bromophenyl)thio]hexyl}oxy)-1,1'-biphenyl

Yield: 0.350 g, 18.5 %. RF: 0.80. MP: 120 °C

ν_{max}/cm^{-1}: 2937, 2859, 1606, 1581, 1523, 1482, 1391, 1286, 1252, 1198, 1178, 1090, 1031, 997, 809, 733, 484

δ_H/ppm (400 MHz, $CDCl_3$):): 7.52 (2 H, d, J 8.1 Hz, Ar-H), 7.47 (2 H, d, J 8.3 Hz, Ar-H), 7.40 (4 H, m, Ar-H), 7.18 (2 H, d, J 8.4 Hz, Ar-H), 6.94 (2 H, d, J 8.3 Hz, Ar-H), 3.98 (2 H, t, J 6.5 Hz, O-$\underline{CH_2}$-CH_2-), 2.91 (2 H, t, J 7.2 Hz, S-$\underline{CH_2}$-CH_2-), 1.80 (2 H, tt, J 7.1 Hz, 6.5 Hz, O-CH_2-$\underline{CH_2}$-CH_2-), 1.68 (2 H, quin, J 7.2 Hz, S-CH_2-$\underline{CH_2}$-CH_2-), 1.63 (4 H, m, S-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 158.89, 139.76, 136.11, 132.35, 131.87, 131.77, 130.44, 128.27, 127.95, 120.74, 119.48, 114.87, 67.86, 33.61, 29.12, 28.92, 28.49, 25.66

2.5 4-Bromo-4'-({7-[(4-bromophenyl)thio]heptyl}oxy)-1,1'-biphenyl

Yield: 0.887 g, 70.6 %. RF: 0.78. MP: 94 °C

ν_{max}/cm^{-1}: 2829, 2852, 1603, 1579, 1521, 1482, 1470, 1389, 1288, 1250, 1199, 1178, 1094, 1069, 996, 808, 733, 479

δ_H/ppm (400 MHz, $CDCl_3$): 7.53 (2 H, d, J 8.1 Hz, Ar-H), 7.47 (2 H, d, J 8.5 Hz, Ar-H), 7.40 (4 H, m, Ar-H), 7.18 (2 H, d, J 8.4 Hz, Ar-H), 6.96 (2 H, d, J 8.5 Hz, Ar-H), 4.00 (2 H, t, J 6.4, O-$\underline{CH_2}$-CH_2-), 2.90 (2 H, t, J 7.3 Hz, S-$\underline{CH_2}$-CH_2-), 1.81 (2 H, tt, J 7.0 Hz, 6.4 Hz, O-CH_2-$\underline{CH_2}$-CH_2-), 1.66 (2 H, quin, J 7.3 Hz, S-CH_2-$\underline{CH_2}$-CH_2-), 1.46 (6 H, m, S-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 158.93, 139.78, 136.20, 132.31, 131.85, 131.78, 130.39, 128.27, 127.95, 120.74, 119.42, 114.88, 67.97, 33.65, 29.17, 28.91, 28.88, 28.67, 25.93

2.6 4-Bromo-4'-({9-[(4-bromophenyl)thio]nonyl}oxy)-1,1'-biphenyl

Yield: 0.941 g, 76.1 %. RF: 0.78. MP: 90 °C

ν_{max}/cm^{-1}: 2922, 2850, 1605, 1580, 1483, 1469, 1389, 1288, 1252, 1200, 1178, 1094, 1070, 1005, 997, 808, 727, 497, 479

δ_H/ppm (400 MHz, $CDCl_3$): 7.52 (2 H, d, J 8.1 Hz, Ar-H), 7.47 (2 H, d, J 7.9 Hz, Ar-H), 7.40 (4 H, m, Ar-H), 7.22 (2 H, d, J 8.4 Hz, Ar-H), 6.94 (2 H, d, J 7.9 Hz, Ar-H), 3.99 (2 H, t, J 6.4 Hz, O-$\underline{CH_2}$-CH_2-), 2.89 (2 H, t, J 7.2 Hz, S-$\underline{CH_2}$-CH_2-), 1.79 (2 H, tt, J 6.9 Hz, 6.4 Hz, O-CH_2-$\underline{CH_2}$-CH_2-), 1.62 (2 H, quin, J 7.2 Hz, S-CH_2-$\underline{CH_2}$-CH_2-), 1.37 (10 H, m, S-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 158.97, 139.79, 136.28, 132.27, 131.83, 131.77, 130.35, 128.27, 127.94, 120.72, 119.37, 114.89, 68.07, 33.66, 29.39, 29.28, 29.25, 29.06, 28.97, 28.75, 26.02

2.7 4-Bromo-4'-({11-[(4-bromophenyl)thio]undecyl}oxy)-1,1'-biphenyl

Yield: 0.808 g, 33.0 %. RF: 0.78. MP: 82 °C

ν_{max}/cm^{-1}: 2937, 2917, 2847, 1606, 1483, 1471, 1392, 1287, 1253, 1199, 1178, 1093, 1083, 1031, 998, 811, 798, 734, 719, 480

δ_H/ppm (400 MHz, $CDCl_3$): 7.53 (2 H, d, J 8.1 Hz, Ar-H), 7.47 (2 H, d, J 8.2 Hz, Ar-H), 7.40 (4 H, m, Ar-H), 7.17 (2 H, d, J 8.0 Hz, Ar-H), 6.96 (2 H, d, J 8.2 Hz, Ar-H), 3.99 (2 H, t, J 6.5 Hz, O-$\underline{CH_2}$-CH_2), 2.89 (2 H, t, J 7.4 Hz, S-$\underline{CH_2}$-CH_2), 1.80 (2 H, tt, J 6.9 Hz, 6.5 Hz, O-CH_2-$\underline{CH_2}$-CH_2-), 1.63 (2 H, quin, J 7.4, S-CH_2-$\underline{CH_2}$-CH_2-), 1.30 (14 H, m, S-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 158.99, 139.80, 136.31, 132.25, 131.83, 131.77, 130.33, 128.27, 127.93, 120.72, 119.35, 114.89, 68.11, 33.66, 29.53, 29.48, 29.45, 29.37, 29.27, 29.13, 28.99, 28.78, 26.05

3 3^4-({ω-[(4'-Cyano-[1,1'-biphenyl]-4-yl)thio]alkyl}oxy)-[1^1,2^1:2^4,3^1-terphenyl]-1^4-carbonitriles (CBS*n*OCT)

To a pre-dried flask flushed with argon and fitted with a condenser, compound **2** (1 eq), 4-cyanophenylboronic acid (2.5 eq) and tetrakis(triphenylphosphine)palladium(0) (0.05 eq) were added. A mixture of an aqueous solution of sodium carbonate (2 M, 5 mL), ethanol (2.5 mL) and toluene (20 mL) were added, and the reaction mixture was heated to 85 °C for 24 h with stirring. The quantities of the reagents used in each reaction are listed in **Table S3**. The reaction mixture was cooled to room temperature, before 32 % hydrochloric acid (5 mL) was added dropwise until effervescence was no longer observed. The resulting mixture was filtered to remove the palladium catalyst, and the solvents were removed under vacuum. Water (100 mL) and dichloromethane (100 mL) were added to the solid obtained. The organic layer was washed with water (2 × 50 mL), dried over anhydrous magnesium sulfate and the solvent removed under vacuum to give a brown solid. The product was purified using a silica gel column with the eluent being 20 % 40:60 petroleum ether and 80 % dichloromethane (RF values quoted in product data). The eluent fractions of interest were evaporated under vacuum to leave a white solid which was recrystallised from hot toluene (50 mL).

Table S3. Quantities of reagents used in the syntheses of 3^4-({ω-[(4'-cyano-[1,1'-biphenyl]-4-yl)thio]alkyl}oxy)-[1^1,2^1:2^4,3^1-terphenyl]-1^4-carbonitriles (**3**).

n	(**2**)	4-Cyanophenylboronic acid	Tetrakis(triphenylphosphine) palladium(0)
3	0.750 g, 1.57×10^{-3} mol	0.576 g, 3.92×10^{-3} mol	0.091 g, 7.85×10^{-5} mol
4	1.75 g, 3.55×10^{-3} mol	1.30 g, 8.88×10^{-3} mol	0.205 g, 1.78×10^{-4} mol
5	0.900 g, 1.78×10^{-3} mol	0.654 g, 4.45×10^{-3} mol	0.103 g, 8.90×10^{-5} mol
6	0.300 g, 5.77×10^{-4} mol	0.212 g, 1.44×10^{-3} mol	0.033 g, 2.89×10^{-5} mol
7	0.600 g, 1.12×10^{-3} mol	0.412 g, 2.81×10^{-3} mol	0.065 g, 5.60×10^{-5} mol
9	0.850 g, 1.51×10^{-3} mol	0.555 g, 3.78×10^{-3} mol	0.087 g, 7.55×10^{-5} mol
11	0.400 g, 6.77×10^{-4} mol	0.249 g, 1.69×10^{-3} mol	0.039 g, 3.39×10^{-5} mol

3.1 3^4-({3-[(4'-Cyano-[1,1'-biphenyl]-4-yl)thio]propyl}oxy)-[1^1,2^1:2^4,3^1-terphenyl]-1^4-carbonitrile (CBS3OCT)

Yield: 0.270 g, 32.9 %. RF: 0.27

T_{CrN} 166 °C $T_{N_{TB}N}$ (100 °C) T_{NI} 277 °C

ν_{max}/cm^{-1}: 2941, 2227, 1608, 1486, 1466, 1394, 1285, 1250, 1180, 1096, 1030, 1001, 808, 558, 518

δ_H/ppm (400 MHz, $CDCl_3$): 7.67 (12 H, m, Ar-H), 7.56 (2 H, d, J 8.3 Hz, Ar-H), 7.49 (2 H, d, J 8.2 Hz, Ar-H), 7.44 (2 H, d, J 8.2 Hz, Ar-H), 6.98 (2 H, d, J 8.3 Hz, Ar-H), 4.15 (2 H, t, J 5.9 Hz, O-$\underline{CH_2}$-CH_2-), 3.21 (2 H, t, J 6.9 Hz, S-$\underline{CH_2}$-CH_2-), 2.20 (2 H, tt, J 6.9 Hz, 5.9 Hz, S-CH_2-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 158.67, 145.15, 144.81, 141.03, 137.67, 137.37, 136.46, 132.76, 132.66, 132.64, 129.02, 128.10, 127.60, 127.59, 127.50, 127.35, 127.27, 119.00, 118.92, 114.93, 110.83, 110.82, 65.91, 29.69, 29.01

EA: Calculated for $C_{35}H_{26}N_2OS$: C = 80.43 %, H = 5.01 %, N = 5.36 %, S = 6.13 %; Found: C = 80.22 %, H = 5.13 %, N = 5.21 %, S = 5.99 %

3.2 3^4-({4-[(4'-Cyano-[1,1'-biphenyl]-4-yl)thio]butyl}oxy)-[1^1,2^1:2^4,3^1-terphenyl]-1^4-carbonitrile (CBS4OCT)

Yield: 0.075 g, 3.9 %. RF: 0.24

T_{CrN} 210 °C T_{NI} 316 °C

ν_{max}/cm^{-1}: 2956, 2233, 1599, 1485, 1394, 1285, 1255, 1179, 1101, 1040, 993, 810, 557, 518

δ_H/ppm (400 MHz, $CDCl_3$): 7.69 (12 H, m, Ar-H), 7.56 (2 H, d, J 8.4 Hz, Ar-H), 7.51 (2 H, d, J 8.3 Hz, Ar-H), 7.42 (2 H, d, J 8.3 Hz, Ar-H), 6.98 (2 H, d, J 8.4 Hz, Ar-H), 4.06 (2 H, t, J 5.9 Hz, O-$\underline{CH_2}$-CH_2-), 3.08 (2 H, t, J 7.0 Hz, S-$\underline{CH_2}$-CH_2-), 1.96 (4 H, quin, m , S-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 158.84, 145.25, 144.81, 141.26, 137.45, 137.22, 136.42, 132.76, 132.65, 132.64, 129.11, 128.11, 127.58, 127.57, 127.49, 127.35, 127.28, 119.01, 118.92, 114.90, 110.81, 110.80, 67.32, 32.89, 28.33, 25.75

EA: Calculated for $C_{36}H_{28}N_2OS$: C = 80.57 %, H = 5.26 %, N = 5.22 %, S = 5.97 %; Found: C = 80.25 %, H = 5.24 %, N = 5.09 %, S = 5.57 %

3.3 3^4-({5-[(4'-Cyano-[1,1'-biphenyl]-4-yl)thio]pentyl}oxy)-[1^1,2^1:2^4,3^1-terphenyl]-1^4-carbonitrile (CBS5OCT)

Yield: 0.265 g, 27.0 %. RF: 0.19

T_{CN-} 185 °C $T_{N_{TB}N}$ (129 °C) T_{NI} 271 °C

ν_{max}/cm^{-1}: 2935, 2228, 1601, 1510, 1487, 1392, 1287, 1256, 1183, 1096, 1045, 1001, 961, 811, 722, 563, 520

δ_H/ppm (400 MHz, $CDCl_3$): 7.69 (12 H, m, Ar-H), 7.56 (2 H, d, J 8.2 Hz, Ar-H), 7.50 (2 H, d, J 8.3 Hz, Ar-H), 7.41 (2 H, d, J 8.3 Hz, Ar-H), 6.97 (2 H, d, J 8.2 Hz, Ar-H), 4.02 (2 H, t, J 6.3 Hz, O-$\underline{CH_2}$-CH_2), 3.03 (2 H, t, J 7.2 Hz, S-$\underline{CH_2}$-CH_2), 1.82 (4 H, m, O-CH_2-$\underline{CH_2}$-CH_2-$\underline{CH_2}$-CH_2-), 1.69 (2 H, m, S-CH_2-CH_2-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 158.95, 145.19, 144.88, 141.13, 138.22, 137.32, 136.26, 132.66, 132.65, 132.55, 128.87, 128.08, 127.58, 127.54, 127.50, 127.33, 127.27, 118.99, 118.92, 114.91, 110.82, 110.81, 67.71, 33.05, 28.80, 28.73, 25.37.

EA: Calculated for $C_{37}H_{30}N_2OS$: C = 80.70 %, H = 5.49 %, N = 5.09 %, S = 5.82 %; Found: C = 80.21 %, H = 5.38 %, N = 5.14 %, S = 6.06 %

3.4 3^4-({6-[(4'-Cyano-[1,1'-biphenyl]-4-yl)thio]hexyl}oxy)-[1^1,2^1:2^4,3^1-terphenyl]-1^4-carbonitrile (CBS6OCT)

Yield: 0.048 g, 14.7 %. RF: 0.35

T_{CrN} 203 °C T_{NI} 296 °C

ν_{max}/cm^{-1}: 2917, 2851, 2231, 1601, 1487, 1393, 1290, 1254, 1181, 1097, 1001, 812, 723, 562, 520

δ_H/ppm (400 MHz, $CDCl_3$): 7.68 (12 H, m, Ar-H), 7.56 (2 H, d, J 8.4 Hz, Ar-H), 7.51 (2 H, d, J 8.3 Hz, Ar-H), 7.40 (2 H, d, J 8.3 Hz, Ar-H), 6.99 (2 H, d, J 8.4 Hz, Ar-H), 4.01 (2 H, t, J 6.5 Hz, O-$\underline{CH_2}$-CH_2-), 3.00 (2 H, t, J 7.3 Hz, S-$\underline{CH_2}$-CH_2-), 1.79 (4 H, m, O-CH_2-$\underline{CH_2}$-CH_2-CH_2-$\underline{CH_2}$-CH_2-), 1.55 (4 H, m, S-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 159.01, 145.20, 144.91, 141.17, 138.42, 137.28, 136.17, 132.65, 132.64, 132.51, 128.69, 128.09, 127.57, 127.53, 127.49, 127.33, 127.27, 118.99, 118.93, 114.90, 110.80, 110.79, 67.88, 33.01, 29.15, 28.96, 28.57, 25.70

EA: Calculated for $C_{38}H_{32}N_2OS$: C = 80.82 %, H = 5.71 %, N = 4.96 %, S = 5.68 %; Found: C = 80.32 %, H = 5.39 %, N = 4.96 %, S = 5.83 %

3.5 3^4-({7-[(4'-Cyano-[1,1'-biphenyl]-4-yl)thio]heptyl}oxy)-[1^1,2^1:2^4,3^1-terphenyl]-1^4-carbonitrile (CBS7OCT)

Yield: 0.317 g, 48.9 %. RF: 0.29

T_{CrN} 151 °C $T_{N_{TB}N}$ (130 °C) T_{NI} 265 °C

ν_{max}/cm^{-1}: 2922, 2851, 2228, 1603, 1487, 1392, 1290, 1245, 11178, 1096, 1001, 856, 807, 723, 563, 519

δ_H/ppm (400 MHz, $CDCl_3$): 7.69 (12 H, m, Ar-H), 7.56 (2 H, d, J 8.3 Hz, Ar-H), 7.51 (2 H, d, J 8.1 Hz, Ar-H), 7.40 (2 H, d, J 8.1 Hz, Ar-H), 6.98 (2 H, d, J 8.3 Hz, Ar-H), 4.02 (2 H, t, J 6.5 Hz, O-$\underline{CH_2}$-CH_2-), 2.99 (2 H, t, J 7.3 Hz, S-$\underline{CH_2}$-CH_2-), 1.76 (4 H, m, O-CH_2-$\underline{CH_2}$-CH_2-CH_2-CH_2-$\underline{CH_2}$-CH_2-), 1.47 (6 H, m, S-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 159.05, 145.21, 144.92, 141.18, 138.50, 137.27, 136.12, 132.65, 132.58, 132.47, 128.65, 128.08, 127.57, 127.52, 127.49, 127.32, 127.27, 119.00, 118.93, 114.91, 110.80, 110.78, 67.99, 33.04, 29.19, 28.92, 28.89, 28.73, 25.95

EA: Calculated for $C_{39}H_{34}N_2OS$: C = 80.93 %, H = 5.92 %, N = 4.84 %, S = 5.54 %; Found: C = 80.72 %, H = 5.93 %, N = 4.88 %, S = 5.75 %

3.6 3^4-({9-[(4'-Cyano-[1,1'-biphenyl]-4-yl)thio]nonyl}oxy)-[1^1,2^1:2^4,3^1-terphenyl]-1^4-carbonitrile (CBS9OCT)

Yield: 0.487 g, 53.1 %. RF: 0.42

T_{CrN} 120 °C $T_{N_{TB}N}$ (119 °C) T_{NI} 245 °C

ν_{max}/cm^{-1}: 2940, 2853, 2228, 1604, 1486, 1475, 1391, 1290, 1242, 1176, 1095, 1023, 1000, 856, 807, 726, 563, 518

δ_H/ppm (400 MHz, $CDCl_3$): 7.68 (12 H, m, Ar-H), 7.56 (2 H, d, J 8.3 Hz, Ar-H), 7.51 (2 H, d, J 8.1 Hz, Ar-H), 7.39 (2 H, d, J 8.1 Hz, Ar-H), 6.99 (2 H, d, J 8.3 Hz, Ar-H), 4.00 (2 H, t, J 6.5 Hz, O-$\underline{CH_2}$-CH_2-), 2.98 (2 H, t, J 7.4 Hz, S-$\underline{CH_2}$-CH_2-), 1.80 (2 H, tt, J 7.0 Hz, 6.5 Hz, O-CH_2-$\underline{CH_2}$-CH_2-), 1.69 (2 H, quin, J 7.4 Hz, S-CH_2-$\underline{CH_2}$-CH_2-), 1.67 (10 H, m, S-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 159.09, 145.22, 144.94, 141.21, 138.60, 137.25, 136.07, 132.64, 132.60, 132.43, 128.59, 128.07, 127.56, 127.50, 127.48, 127.32, 127.28, 119.00, 118.94, 114.92, 110.79, 110.77, 68.09, 33.05, 29.40, 29.30, 29.27, 29.08, 28.99, 28.82, 26.04

EA: Calculated for $C_{41}H_{38}N_2OS$: C = 81.15 %, H = 6.31 %, N = 4.62 %, S = 5.28 %; Found: C = 81.10 %, H = 6.21 %, N = 4.98 %, S = 5.02 %

3.7 3^4-({11-[(4'-Cyano-[1,1'-biphenyl]-4-yl)thio]undecyl}oxy)-[1^1,2^1:2^4,3^1-terphenyl]-1^4-carbonitrile (CBS11OCT)

Yield: 0.255 g, 59.3 %. RF: 0.35

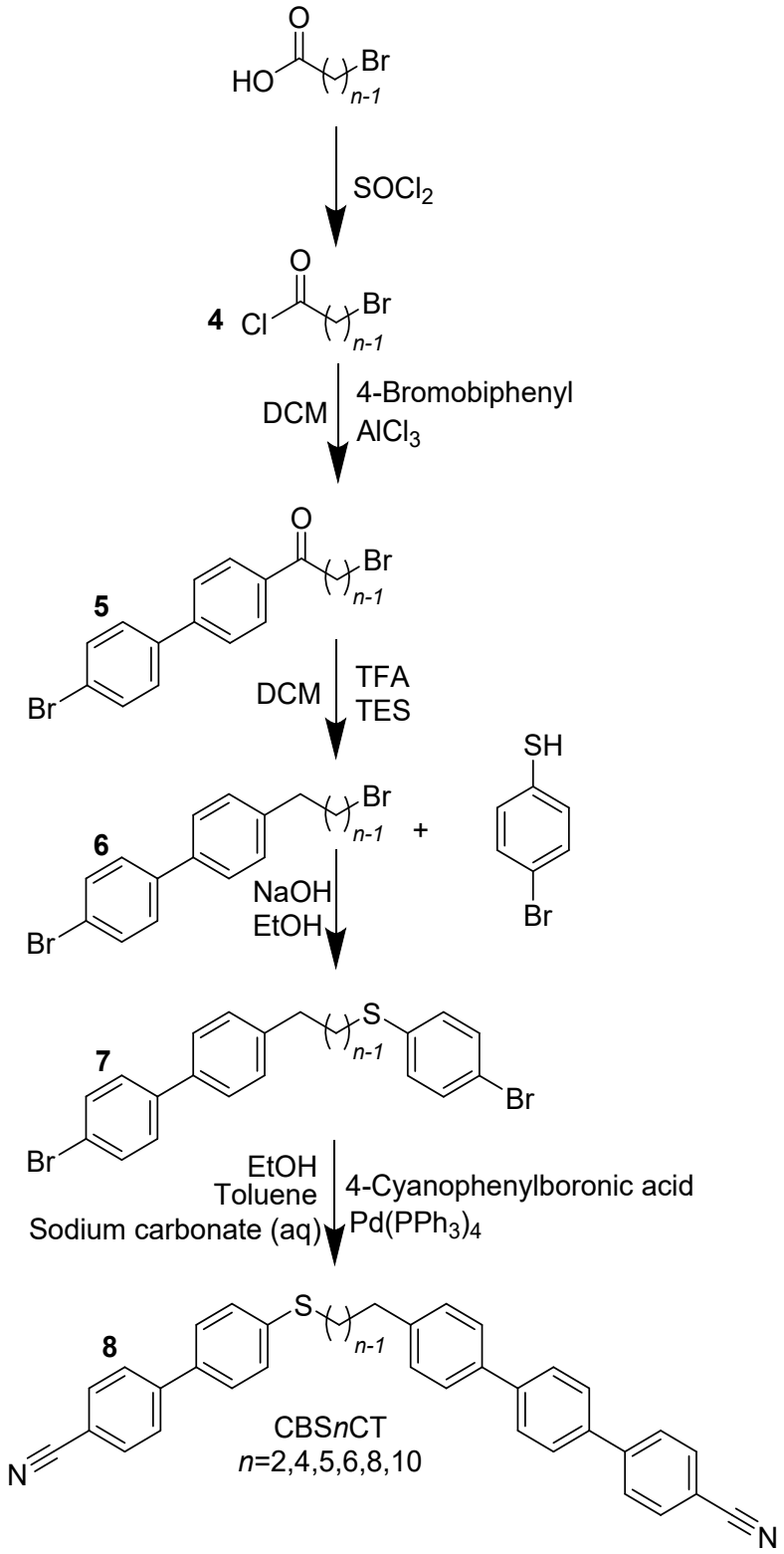
T_{CrN} 128 °C $T_{N_{TB}N}$ (115 °C) T_{NI} 236 °C

ν_{max}/cm^{-1}: 2917, 2850, 2229, 1604, 1487, 1473, 1391, 1290, 1240, 1178, 1096, 1001, 856, 809, 723, 563, 519

δ_H/ppm (400 MHz, $CDCl_3$): 7.69 (12 H, m, Ar-H), 7.57 (2 H, d, J 8.3 Hz, Ar-H), 7.50 (2 H, d, J 8.1 Hz, Ar-H), 7.39 (2 H, d, J 8.1 Hz, Ar-H), 6.99 (2 H, d, J 8.3 Hz, Ar-H), 4.01 (2 H, t, J 6.5 Hz, O-$\underline{CH_2}$-CH_2-), 2.98 (2 H, t, J 7.3 Hz, S-$\underline{CH_2}$-CH_2-), 1.81 (2 H, tt, J 7.0 Hz, 6.5 Hz, O-CH_2-$\underline{CH_2}$-CH_2-), 1.70 (2 H, quin, J 7.3, S-CH_2-$\underline{CH_2}$-CH_2-), 1.67 (14 H, m, S-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 159.10, 145.22, 144.94, 141.22, 138.64, 137.24, 136.05, 132.64, 132.62, 132.41, 128.56, 128.07, 127.56, 127.50, 127.48, 127.32, 127.28, 119.00, 118.94, 114.92, 110.78, 110.76, 68.13, 33.05, 29.54, 29.50, 29.48, 29.40, 29.30, 29.16, 29.02, 28.87, 26.07

EA: Calculated for $C_{43}H_{42}N_2OS$: C = 81.35 %, H = 6.67 %, N = 4.41 %, S = 5.05 %; Found: C = 81.36 %, H = 6.75 %, N = 4.37 %, S = 4.93 %



Scheme 2. Synthesis of the CBS*n*CT series.

The synthesis of the CBS*n*CT series follows the steps outlined in **Scheme 2**. In the synthesis of the CBS*n*CT series (**8**), the bromoalkanoic acid was converted to an acid chloride before it underwent a Friedel-Crafts acylation and a subsequent hydrosilane reduction in a method described by Abberley *et*

al.[14] This was followed by a modified Williamson ether reaction[10] and a subsequent Suzuki-Miyaura cross-coupling reaction[2] to form the desired product.

4 ω-Bromoalkanoyl chlorides

To a pre-dried flask flushed with argon, the starting ω-bromoalkanoic acid (1 eq) was added. The acid was azeotroped with dry toluene (2 × 15 mL) and once all the toluene had been removed, thionyl chloride (5.0 eq) was syringed in with stirring. The quantities of the reagents used in each reaction are listed in **Table S4**. The mixture was heated to 70 °C for 2 h which generated a yellow/brown liquid. The excess of thionyl chloride remaining in the flask was removed using high vacuum. To ensure all the thionyl chloride had been removed dry toluene (1 × 10 mL) was added to the flask before also being removed under high vacuum. The yellow/brown liquid remaining was used without any further purification.

Table S4. Quantities of reagents used in the preparation of ω-bromoalkanoyl chlorides (**4**).

n	ω-Bromoalkanoic acid	Thionyl chloride
8	11.0 g, 0.0493 mol	18.0 mL, 29.4 g, 0.247 mol
10	6.50 g, 0.0259 mol	9.41 mL, 15.3 g, 0.129 mol

***2-Bromoethanoyl chloride* -** Was purchased commercially from Sigma Aldrich and used without further purification.

***4-Bromobutanoyl chloride* -** Was purchased commercially from Sigma Aldrich and used without further purification.

***5-Bromopentanoyl chloride* -** Was purchased commercially from Sigma Aldrich and used without further purification.

***6-Bromohexanoyl chloride* -** Was purchased commercially from Fisher Scientific and used without further purification.

4.1 8-Bromooctanoyl chloride

Yield: 11.8 g, 99.0 %

4.2 10-Bromodecanoyl chloride

Yield: 6.94 g, 99.4 %

5 ω-Bromo-1-(4'-bromo-[1,1'-biphenyl]-4-yl)alkan-1-ones

To a pre-dried flask flushed with argon, aluminium chloride (1.2 eq) was added along with dry dichloromethane (60 mL) while being stirred. The outside of the flask was wrapped in aluminium foil to prevent light from interfering with the reaction and placed into an ice bath in order to keep the reaction mixture at 0 °C. 4-Bromobiphenyl (1.1 eq) and compound **4** (1 eq) were mixed along with dry dichloromethane (60 mL) and added dropwise into the flask. The quantities of the reagents used in each reaction are listed in **Table S5**. The ice bath was removed, and the reaction proceeded at room temperature overnight. The extent of the reaction was monitored by TLC using dichloromethane as the solvent system (RF values quoted in the product data). The mixture was added to a slurry of ice (50 g) with 6 M hydrochloric acid (12 mL) and extracted with dichloromethane (200 mL). The extracted organic layer was washed with water (3 × 50 mL) and dried over anhydrous magnesium sulfate. The magnesium sulfate was removed using vacuum filtration and the solvent evaporated under vacuum to leave an off-white solid which was recrystallised using hot ethanol (250 mL).

Table S5. Quantities of reagents used in the preparation of ω-bromo-1-(4'-bromo-[1,1'-biphenyl]-4-yl)alkan-1-ones (**5**).

n	(**4**)	4-Bromobiphenyl	Aluminium chloride
2	2.30 mL, 4.34 g, 0.0276 mol	4.06 g, 0.0304 mol	2.55 g, 0.0331 mol
4	3.06 mL, 4.90 g, 0.0264 mol	6.76 g, 0.0290 mol	4.23 g, 0.0317 mol
5	2.41 mL, 3.59 g, 0.0180 mol	4.62 g, 0.0198 mol	2.88 g, 0.0216 mol
6	7.19 mL, 10.0 g, 0.0470 mol	12.1 g, 0.0517 mol	7.25 g, 0.0564 mol
8	11.8 mL, 11.8 g, 0.0488 mol	12.5 g, 0.0537 mol	7.80 g, 0.0586 mol
10	5.55 mL, 5.55 g, 0.0146 mol	6.80 g, 0.0292 mol	4.28 g, 0.0321 mol

5.1 2-Bromo-1-(4'-bromo-[1,1'-biphenyl]-4-yl)ethan-1-one

Yield: 6.48 g, 66.3 %. RF: 0.57. MP: 145 °C

ν_{max}/cm^{-1}: 1685, 1602, 1474, 1416, 1387, 1280, 1191, 1074, 993, 808, 698, 634, 565, 528, 481

δ_H/ppm (400 MHz, $CDCl_3$): 8.06 (2 H, d, J 7.9 Hz, Ar-H), 7.68 (2 H, d, J 7.9 Hz, Ar-H), 7.61 (2 H, d, J 8.1 Hz, Ar-H), 7.50 (2 H, d, J 8.1 Hz, Ar-H), 4.47 (2 H, s, Br-$\underline{CH_2}$-C(=O)-)

δ_C/ppm (100 MHz, $CDCl_3$): 190.82, 145.37, 138.47, 132.93, 132.20, 129.69, 128.84, 127.29, 122.98, 30.71

Data consistent with reported values.[15]

5.2 4-Bromo-1-(4'-bromo-[1,1'-biphenyl]-4-yl)butan-1-one

Yield: 7.21 g, 71.5 %. RF: 0.62. MP: 116 °C

ν_{max}/cm^{-1}: 1675, 1603, 1404, 1387, 1281, 1225, 1187, 1070, 1001, 851, 847, 810, 666, 568, 529, 453

δ_H/ppm (400 MHz, $CDCl_3$): 8.02 (2 H, d, J 8.0 Hz, Ar-H), 7.64 (2 H, d, J 8.0 Hz, Ar-H), 7.59 (2 H, d, J 8.2 Hz, Ar-H), 7.49 (2 H, d, J 8.2 Hz, Ar-H), 3.47 (2 H, t, J 6.4 Hz, Br-$\underline{CH_2}$-CH_2-), 3.04 (2 H, t, J 6.9 Hz, C(=O)-$\underline{CH_2}$-CH_2-), 1.95 (4 H, m, Br-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 198.28, 144.62, 138.72, 135.73, 132.13, 128.82, 128.74, 127.11, 122.72, 36.64, 33.65, 26.89

Data consistent with reported values.[16]

5.3 5-Bromo-1-(4'-bromo-[1,1'-biphenyl]-4-yl)pentan-1-one

Yield: 5.64 g, 79.1 %. RF: 0.56. MP: 118 °C

ν_{max}/cm^{-1}: 2957, 1676, 1604, 1474, 1456, 1388, 1372, 1275, 1185, 1076, 1001, 978, 812, 722, 640, 574, 531, 515, 457

δ_H/ppm (400 MHz, $CDCl_3$): 8.02 (2 H, d, J 8.3 Hz, Ar-H), 7.65 (2 H, d, J 8.3 Hz, Ar-H), 7.59 (2 H, d, J 8.4 Hz, Ar-H), 7.49 (2 H, d, J 8.4 Hz, Ar-H), 3.44 (2 H, t, J 7.1 Hz, Br-$\underline{CH_2}$-CH_2-), 3.03 (2 H, t, J 7.1 Hz, C(=O)-$\underline{CH_2}$-CH_2-), 1.93 (2 H, quin, J 7.1 Hz, Br-CH_2-$\underline{CH_2}$-CH_2-), 1.79 (2 H, quin, J 7.1 Hz, C(=O)-CH_2-$\underline{CH_2}$-CH_2-), 1.56 (2 H, quin, J 7.1 Hz, Br-CH_2-CH_2-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 199.03, 144.48, 138.75, 135.82, 132.12, 128.82, 128.74, 127.09, 122.69, 37.52, 33.34, 32.22, 22.82

Data consistent with reported values.[1]

5.4 6-Bromo-1-(4'-bromo-[1,1'-biphenyl]-4-yl)hexan-1-one

Yield: 10.15 g, 53.2 %. RF: 0.53. MP: 81 °C

ν_{max}/cm^{-1}: 2938, 1678, 1604, 1477, 1389, 1365, 1262, 1208, 1189, 1070, 1000, 969, 822, 794, 723, 664, 574

δ_H/ppm (400 MHz, $CDCl_3$): 8.02 (2 H, d, J 8.3 Hz, Ar-H), 7.65 (2 H, d, J 8.3 Hz, Ar-H), 7.59 (2 H, d, J 8.4 Hz, Ar-H), 7.49 (2 H, d, J 8.4 Hz, Ar-H), 3.44 (2 H, t, J 7.1 Hz, Br-$\underline{CH_2}$-CH_2-), 3.03 (2 H, t, J 7.1 Hz, C(=O)-$\underline{CH_2}$-CH_2-), 1.93 (2 H, quin, J 7.1 Hz, Br-CH_2-$\underline{CH_2}$-CH_2-), 1.79 (2 H, quin, J 7.1 Hz, C(=O)-CH_2-$\underline{CH_2}$-CH_2-), 1.56 (2 H, quin, J 7.1 Hz, Br-CH_2-CH_2-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 199.45, 144.40, 138.78, 135.94, 132.11, 128.82, 128.73, 127.07, 122.66, 38.37, 33.65, 32.64, 27.90, 23.37

Data consistent with reported values.[14]

5.5 8-Bromo-1-(4'-bromo-[1,1'-biphenyl]-4-yl)octan-1-one

Yield: 3.18 g, 14.9 %. RF: 0.49. MP: 64 °C

ν_{max}/cm^{-1}: 2928, 2851, 1675, 1602, 1480, 1465, 1408, 1389, 1270, 1197, 1077, 1001, 974, 809, 764, 724, 563, 522

δ_H/ppm (400 MHz, $CDCl_3$): 8.03 (2 H, d, J 8.4 Hz, Ar-H), 7.64 (2 H, d, J 8.4 Hz, Ar-H), 7.59 (2 H, d, J 8.5 Hz, Ar-H), 7.49 (2 H, d, J 8.5 Hz, Ar-H), 3.40 (2 H, t, J 6.9 Hz, Br-$\underline{CH_2}$-CH_2-), 2.97 (2 H, t, J 7.1 Hz, C(=O)-$\underline{CH_2}$-CH_2-), 1.86 (2 H, quin, J 6.9 Hz, Br-CH_2-$\underline{CH_2}$-CH_2-), 1.76 (2 H, quin, J 7.1 Hz, C(=O)-CH_2-$\underline{CH_2}$-CH_2-), 1.43 (6 H, m, Br-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 199.87, 144.31, 138.82, 136.04, 132.10, 128.81, 128.76, 127.04, 122.62, 38.58, 33.95, 32.75, 29.16, 28.64, 28.02, 24.25

Data consistent with reported values.[16]

5.6 10-Bromo-1-(4'-bromo-[1,1'-biphenyl]-4-yl)decan-1-one

Yield: 3.02 g, 44.4 %. RF: 0.43. MP: 95 °C

ν_{max}/cm^{-1}: 2929, 2847, 1675, 1602, 1587, 1474, 1390, 1252, 1226, 1195, 1078, 1000, 974, 282, 810, 754, 690, 562, 468

δ_H/ppm (400 MHz, $CDCl_3$): 8.03 (2 H, d, J 7.9 Hz, Ar-H), 7.64 (2 H, d, J 7.9 Hz, Ar-H), 7.57 (2 H, d, J 8.1 Hz, Ar-H), 7.49 (2 H, d, J 8.1 Hz, Ar-H), 3.40 (2 H, t, J 6.6 Hz, Br-$\underline{CH_2}$-CH_2-), 2.95 (2 H, t, J 7.3 Hz, C(=O)-$\underline{CH_2}$-CH_2-), 1.85 (2 H, tt, J 7.1 Hz, 6.6 Hz, Br-CH_2-$\underline{CH_2}$-CH_2-), 1.75 (2 H, quin, J 7.3 Hz, C(=O)-CH_2-$\underline{CH_2}$-CH_2-), 1.37 (10 H, m, Br-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 200.02, 144.27, 138.84, 136.07, 132.10, 128.81, 128.77, 127.03, 122.61, 38.68, 34.05, 32.81, 29.37, 29.33, 29.28, 28.71, 28.15, 24.39

Data consistent with reported values.[16]

6 4-Bromo-4'-(ω-bromoalkyl)-1,1'-biphenyls

To a pre-dried flask flushed with argon, compound **5** (1 eq) was added. The flask was placed into an ice bath in order to maintain the temperature at 0 °C. The solid was solubilised using trifluoroacetic acid and dry dichloromethane (40 mL), along with stirring. Finally, triethylsilane was added to the flask and the ice bath was removed. The quantities of the reagents used in each reaction are listed in **Table S6**. The reaction was left for 24 h and the extent of the reaction was monitored by TLC using dichloromethane as the solvent system (RF values quoted in the product data). Once complete, the mixture was added to a beaker with dichloromethane (100 mL) and water (300 mL). The organic layer was separated and washed with water (3 × 50 mL). This was dried using anhydrous magnesium sulfate, which was removed by vacuum filtration, and the solvent evaporated under vacuum to leave a white solid which was recrystallised using hot ethanol (150 mL).

Table S6. Quantities of reagents used in the preparation of 4-bromo-4'-(ω-bromoalkyl)-1,1'-biphenyls (**6**).

n	(**5**)	Trifluoroacetic acid	Triethylsilane
2	6.00 g, 0.0169 mol	70.0 mL, 104 g, 0.914 mol	14.0 mL, 10.2 g, 0.0877 mol
4	6.51 g, 0.0170 mol	71.0 mL, 106 g, 0.927 mol	14.2 mL, 10.3 g, 0.0889 mol
5	5.00 g, 0.0126 mol	55.0 mL, 81.9 g, 0.713 mol	11.0 mL, 8.01 g, 0.0689 mol
6	10.0 g, 0.0244 mol	100 mL, 149 g, 1.31 mol	20.0 mL, 14.6 g, 0.125 mol
8	2.40 g, 5.48×10^{-3} mol	7.67 mL, 11.4 g, 0.100 mol	4.0 mL, 2.91 g, 0.0250 mol
10	2.80 g, 6.01×10^{-3} mol	15.0 mL, 22.3 g, 0.196 mol	9.0 mL, 6.55 g, 0.0563 mol

6.1 4-Bromo-4'-(2-bromoethyl)-1,1'-biphenyl

Yield: 4.34 g, 75.5 %. RF: 0.81. MP: 125 °C

ν_{max}/cm^{-1}: 1479, 1446, 1387, 1258, 1212, 1068, 1002, 804, 749, 652, 583, 506

δ_H/ppm (400 MHz, $CDCl_3$): 7.56 (2 H, d, J 7.9 Hz, Ar-H), 7.52 (2 H, d, J 7.6 Hz, Ar-H), 7.45 (2 H, d, J 7.9 Hz, Ar-H), 7.28 (2 H, d, J 7.6 Hz, Ar-H), 3.61 (2 H, t, J 7.4 Hz, Br-$\underline{CH_2}$-CH_2-), 3.21 (2 H, t, J 7.4 Hz, Ar-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 139.69, 138.66, 138.38, 131.89, 129.24, 128.62, 127.14, 121.54, 38.97, 32.79

6.2 4-Bromo-4'-(4-bromobutyl)-1,1'-biphenyl

Yield: 4.63 g, 74.0 %. RF: 0.78. MP: 98 °C

ν_{max}/cm^{-1}: 2938, 2863, 1479, 1461, 1390, 1255, 1202, 1075, 999, 805, 762, 731, 647, 495

δ_H/ppm (400 MHz, $CDCl_3$): 7.55 (2 H, d, J 8.0 Hz, Ar-H), 7.48 (2 H, d, J 7.7 Hz, Ar-H), 7.44 (2 H, d, J 8.0 Hz, Ar-H), 7.25 (2 H, d, J 7.7 Hz, Ar-H), 3.43 (2 H, t, J 6.5 Hz, Br-$\underline{CH_2}$-CH_2-), 2.69 (2 H, t, J 7.3 Hz, Ar-$\underline{CH_2}$-CH_2-), 1.92 (2 H, tt, J 7.3 Hz, 6.5 Hz, Br-CH_2-$\underline{CH_2}$-CH_2-), 1.82 (2 H, quin, J 7.3 Hz, Ar-CH_2-$\underline{CH_2}$-CH_2-),

δ_C/ppm (100 MHz, $CDCl_3$): 141.40, 139.94, 137.67, 131.83, 128.96, 128.58, 126.93, 121.29, 34.62, 33.62, 32.24, 29.80

Data consistent with reported values.[16]

6.3 4-Bromo-4'-(5-bromopentyl)-1,1'-biphenyl

Yield: 2.96 g, 61.5 %. RF: 0.85. MP: 78 °C

ν_{max}/cm^{-1}: 2932, 2851, 1479, 1428, 1389, 1260, 1210, 1077, 1000, 803, 768, 731, 558, 509, 482

δ_H/ppm (400 MHz, $CDCl_3$): 7.55 (2 H, d, J 8.0 Hz, Ar-H), 7.48 (2 H, d, J 7.8 Hz, Ar-H), 7.44 (2 H, d, J 8.0 Hz, Ar-H), 7.25 (2 H, d, J 7.8 Hz, Ar-H), 3.42 (2 H, t, J 6.7 Hz, Br-$\underline{CH_2}$-CH_2-), 2.67 (2 H, t, J 7.5 Hz, Ar-$\underline{CH_2}$-CH_2-), 1.91 (2 H, tt, J 7.5 Hz, 6.7 Hz, Br-CH_2-$\underline{CH_2}$-CH_2-), 1.70 (2 H, quin, J 7.5 Hz, Ar-CH_2-$\underline{CH_2}$-CH_2-), 1.53 (2 H, quin, J 7.5 Hz, Br-CH_2-CH_2-$\underline{CH_2}$-CH_2-),

δ_C/ppm (100 MHz, $CDCl_3$): 141.92, 139.99, 137.51, 131.82, 128.95, 128.57, 126.86, 121.24, 35.37, 33.77, 32.69, 30.58, 27.86

Data consistent with reported values.[1]

6.4 4-Bromo-4'-(6-bromohexyl)-1,1'-biphenyl

Yield: 6.77 g, 70.8 %. RF: 0.67. MP: 76 °C

ν_{max}/cm^{-1}: 2931, 2856, 1479, 1454, 1390, 1235, 1189, 1077, 1000, 804, 726, 646, 503

δ_H/ppm (400 MHz, $CDCl_3$): 7.55 (2 H, d, J 8.2 Hz, Ar-H), 7.46 (4 H, m, Ar-H), 7.24 (2 H, d, J 8.2 Hz, Ar-H), 3.41 (2 H, t, J 6.8 Hz, Br-$\underline{CH_2}$-CH_2-), 2.66 (2 H, t, J 7.3 Hz, Ar-$\underline{CH_2}$-CH_2-), 1.87 (2 H, tt, J 7.3 Hz, 6.8 Hz, Br-CH_2-$\underline{CH_2}$-CH_2-), 1.67 (2 H, quin, J 7.3 Hz, Ar-CH_2-$\underline{CH_2}$-CH_2-), 1.48 (2 H, quin, J 7.3 Hz, Br-CH_2-CH_2-$\underline{CH_2}$-CH_2-), 1.40 (2 H, quin, J 7.3 Hz, Ar-CH_2-CH_2-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$) 142.18, 140.03, 137.42, 131.81, 128.96, 128.57, 126.82, 121.21, 35.44, 33.95, 32.73, 31.21, 28.40, 28.03

Data consistent with reported values.[14]

6.5 4-Bromo-4'-(8-bromooctyl)-1,1'-biphenyl

Yield: 0.837 g, 36.0 %. RF: 0.75. MP: 62 °C

ν_{max}/cm^{-1}: 2925, 2853, 148, 1389, 1221, 1075, 1000, 805, 724, 644, 557, 504

δ_H/ppm (400 MHz, $CDCl_3$): 7.54 (2 H, d, J 8.5 Hz, Ar-H), 7.47 (4 H, m, Ar-H), 7.25 (2 H, d, J 8.3 Hz, Ar-H), 3.39 (2 H, t, J 6.8 Hz, Br-$\underline{CH_2}$-CH_2-), 2.63 (2 H, t, J 7.5 Hz, Ar-$\underline{CH_2}$-CH_2-), 1.82 (2 H, tt, J 7.5 Hz, 6.8 Hz, Br-CH_2-$\underline{CH_2}$-CH_2-), 1.65 (2 H, quin, J 7.5 Hz, Ar-CH_2-$\underline{CH_2}$-CH_2-), 1.36 (8 H, m, Br-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 142.45, 140.06, 137.34, 131.80, 128.96, 128.56, 126.79, 121.18, 35.58, 34.03, 32.81, 31.40, 29.31, 29.20, 28.70, 28.16

Data consistent with reported values.[16]

6.6 4-Bromo-4'-(10-bromodecyl)-1,1'-biphenyl

Yield: 0.880 g, 32.3 %. RF: 0.70. MP: 57 °C

ν_{max}/cm^{-1}: 2924, 2850, 1477, 1464, 1391, 1181, 1075, 1002, 827, 805, 723, 644, 491

δ_H/ppm (400 MHz, $CDCl_3$): 7.54 (2 H, d, J 7.8 Hz, Ar-H), 7.44 (4 H, dd, J 8.1 Hz, 7.8 Hz, Ar-H), 7.25 (2 H, d, J 8.1 Hz, Ar-H), 3.40 (2 H, t, J 6.7 Hz, Br-$\underline{CH_2}$-CH_2-), 2.63 (2 H, t, J 7.4 Hz, Ar-$\underline{CH_2}$-CH_2-), 1.85 (2 H, tt, J 7.4 Hz, 6.7 Hz, Br-CH_2-$\underline{CH_2}$-CH_2-), 1.63 (2 H, quin, J 7.4 Hz, Ar-CH_2-$\underline{CH_2}$-CH_2-), 1.33 (12 H, m, Br-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 142.54, 140.07, 137.29, 131.78, 128.95, 128.55, 126.76, 121.15, 35.59, 34.07, 32.83, 31.45, 29.45 (2 × C), 29.42, 29.30, 28.75, 28.17

Data consistent with reported values.[16]

7 4-Bromo-4'-{ω-[(4-bromophenyl)thio]alkyl}-1,1'-biphenyls

To a pre-dried flask flushed with argon, 4-bromothiophenol (1.1 eq) was added. Sodium hydroxide (1.32 eq) dissolved in ethanol (20 mL), sonicated to ensure all the solid was in solution, was added. The mixture was stirred for 2 h at room temperature. Compound **6** (1 eq) in tetrahydrofuran (5 mL) was

added and the reaction mixture was stirred at room temperature for 24 h. The quantities of the reagents used in each reaction are listed in **Table S7**. The extent of the reaction was monitored by TLC using dichloromethane as the solvent system (RF values quoted in the product data). The resulting white precipitate was collected and recrystallised from hot ethanol (75 mL).

Table S7. Quantities of reagents used in the syntheses of 4-bromo-4'-{ω-[(4-bromophenyl)thio]alkyl}-1,1'-biphenyls (**7**).

n	(**6**)	4-Bromothiophenol	Sodium hydroxide
2	1.30 g, 3.82×10^{-3} mol	0.796 g, 4.21×10^{-3} mol	0.202 g, 5.05×10^{-3} mol
4	1.50 g, 4.07×10^{-3} mol	0.847 g, 4.48×10^{-3} mol	0.215 g, 5.37×10^{-3} mol
5	1.00 g, 2.62×10^{-3} mol	0.545 g, 2.88×10^{-3} mol	0.138 g, 3.45×10^{-3} mol
6	2.50 g, 6.31×10^{-3} mol	1.31 g, 6.94×10^{-3} mol	0.333 g, 8.33×10^{-3} mol
8	0.800 g, 1.89×10^{-3} mol	0.393 g, 2.08×10^{-3} mol	0.100 g, 2.49×10^{-3} mol
10	0.750 g, 1.66×10^{-3} mol	0.345 g, 1.82×10^{-3} mol	0.088 g, 2.19×10^{-3} mol

7.1 4-Bromo-4'-{2-[(4-bromophenyl)thio]ethyl}-1,1'-biphenyl

Yield: 1.45 g, 84.6 %. RF: 0.82. MP: 102 °C

ν_{max}/cm^{-1}: 2913, 1472, 1432, 1388, 1091, 1073, 1001, 807, 749, 584, 454, 490, 477

δ_H/ppm (400 MHz, $CDCl_3$): 7.55 (2 H, d, J 7.7 Hz, Ar-H), 7.49 (2 H, d, J 7.8 Hz, Ar-H), 7.42 (4 H, m, Ar-H), 7.22 (4 H, m, Ar-H), 3.18 (2 H, t, J 7.5 Hz, S-$\underline{CH_2}$-CH_2-), 2.95 (2 H, t, J 7.5 Hz, Ar-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 139.76, 139.40, 138.32, 135.51, 131.99, 131.87, 130.83, 129.10, 128.60, 127.07, 121.46, 119.89, 35.18, 35.13

7.2 4-Bromo-4'-{4-[(4-bromophenyl)thio]butyl}-1,1'-biphenyl

Yield: 1.10 g, 56.7 %. RF: 0.75. MP: 96 °C

ν_{max}/cm^{-1}: 2934, 2854, 1480, 1472, 1389, 1256, 1092, 1077, 1000, 805, 729, 647, 623, 512, 499, 479

δ_H/ppm (400 MHz, $CDCl_3$): 7.54 (2 H, d, J 8.3 Hz, Ar-H), 7.45 (4 H, dd, J 8.4 Hz, 8.3 Hz, Ar-H), 7.38 (2 H, d, J 8.1 Hz Ar-H), 7.22 (2 H, d, J 8.1 Hz, Ar-H), 7.16 (2 H, d, J 8.4 Hz, Ar-H), 2.92 (2 H, t, J 7.4 Hz, S-$\underline{CH_2}$-CH_2-), 2.66 (2 H, t, J 7.4 Hz, Ar-$\underline{CH_2}$-CH_2-), 1.79 (2 H, quin, J 7.4 Hz, S-CH_2-$\underline{CH_2}$-CH_2-), 1.69 (2 H, quin, J 7.4 Hz, Ar-CH_2-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 141.55, 139.94, 137.60, 135.95, 131.87, 131.83, 130.62, 128.94, 128.57, 126.87, 121.26, 119.58, 34.95, 33.62, 30.26, 28.44

7.3 4-Bromo-4'-{5-[(4-bromophenyl)thio]pentyl}-1,1'-biphenyl

Yield: 1.13 g, 88.0 %. RF: 0.80. MP: 120 °C

ν_{max}/cm^{-1}: 2929, 2856, 1480, 1389, 1247, 1093, 1077, 1001, 805, 766, 730, 558, 482

δ_H/ppm (400 MHz, $CDCl_3$):): 7.54 (2 H, d, J 8.0 Hz, Ar-H), 7.45 (4 H, dd, J 8.0 Hz, 8.0 Hz, Ar-H), 7.39 (2 H, d, J 7.9 Hz, Ar-H), 7.23 (2 H, d, J 7.9 Hz, Ar-H), 7.17 (2 H, d, J 8.0 Hz, Ar-H), 2.89 (2 H, t, J 7.4 Hz, S-$\underline{CH_2}$-CH_2-), 2.64 (2 H, t, J 7.4 Hz, Ar-$\underline{CH_2}$-CH_2-), 1.66 (4 H, m, S-CH_2-$\underline{CH_2}$-CH_2-$\underline{CH_2}$-CH_2-), 1.48 (2 H, m, S-CH_2-CH_2-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 141.98, 139.99, 137.47, 136.13, 131.86, 131.81, 130.45, 128.95, 128.55, 126.83, 121.23, 119.48, 35.38, 33.62, 30.91, 28.91, 28.38

7.4 4-Bromo-4'-{6-[(4-bromophenyl)thio]hexyl}-1,1'-biphenyl

Yield: 2.24 g, 70.4 %. RF: 0.72. MP: 97 °C

ν_{max}/cm^{-1}: 2926, 2852, 1482, 1472, 1465, 1385, 1095, 1076, 1008, 1000, 801, 724, 508, 478

δ_H/ppm (400 MHz, $CDCl_3$): 7.54 (2 H, d, J 8.4 Hz, Ar-H), 7.45 (4 H, dd, J 8.5 Hz, 8.4 Hz, Ar-H), 7.38 (2 H, d, J 8.0 Hz, Ar-H), 7.23 (2 H, d, J 8.0 Hz, Ar-H), 7.17 (2 H, d, J 8.5 Hz, Ar-H), 2.89 (2 H, t, J 7.3 Hz, S-$\underline{CH_2}$-CH_2-), 2.64 (2 H, t, J 7.5 Hz, Ar-$\underline{CH_2}$-CH_2-), 1.64 (4 H, m, S-CH_2-$\underline{CH_2}$-CH_2-CH_2-$\underline{CH_2}$-CH_2-), 1.47 (2 H, quin, J 7.3 Hz, Ar-CH_2-CH_2-$\underline{CH_2}$-CH_2-), 1.37 (2 H, quin, J 7.3 Hz, S-CH_2-CH_2-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 142.23, 140.02, 137.40, 136.20, 131.85, 131.81, 130.38, 128.95, 128.56, 126.81, 121.21, 119.42, 35.45, 33.63, 31.23, 28.88, 28.75, 28.58

Data consistent with reported values.[1]

7.5 4-Bromo-4'-{8-[(4-bromophenyl)thio]octyl}-1,1'-biphenyl

Yield: 0.711 g, 71.9 %. RF: 0.87. MP: 93 °C

ν_{max}/cm^{-1}: 2924, 2851, 1481, 1388, 1094, 1077, 1001, 805, 723, 624, 507, 479

δ_H/ppm (400 MHz, $CDCl_3$): 7.54 (2 H, d, J 8.5 Hz, Ar-H), 7.45 (4 H, dd, J 8.5 Hz, 8.5 Hz, Ar-H), 7.36 (2 H, d Hz, J 8.2, Ar-H), 7.22 (2 H, d, J 8.2 Hz, Ar-H), 7.15 (2 H, d, J 8.5 Hz, Ar-H), 2.86 (2 H, t, J 7.3 Hz, S-$\underline{CH_2}$-CH_2-), 2.61 (2 H, t, J 7.3 Hz, Ar-$\underline{CH_2}$-CH_2-), 1.60 (4 H, m, S-CH_2-$\underline{CH_2}$-CH_2-CH_2-CH_2-CH_2-$\underline{CH_2}$-CH_2-), 1.35 (8 H, m, S-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 140.04, 137.30, 142.45, 136.23, 131.81, 131.77, 130.33, 128.93, 128.53, 126.75, 121.14, 119.35, 35.55, 33.63, 31.37, 29.30, 29.18, 29.02, 28.93, 28.71

7.6 4-Bromo-4'-{10-[(4-bromophenyl)thio]decyl}-1,1'-biphenyl

Yield: 0.611 g, 65.7 %. RF: 0.84. MP: 79 °C

ν_{max}/cm^{-1}: 2921, 2850, 1474, 1466, 1388, 1094, 1076, 1001, 805, 721, 623, 509, 478

δ_H/ppm (400 MHz, $CDCl_3$): 7.54 (2 H, d, J 8.0 Hz, Ar-H), 7.46 (4 H, dd, J 8.0 Hz, 7.9 Hz, Ar-H), 7.38 (2 H, d Hz, J 8.1, Ar-H), 7.24 (2 H, d, J 8.1 Hz, Ar-H), 7.17 (2 H, d, J 7.9 Hz, Ar-H), 2.88 (2 H, t, J 7.3 Hz, S-$\underline{CH_2}$-CH_2-), 2.63 (2 H, t, J 7.4 Hz, Ar-$\underline{CH_2}$-CH_2-), 1.63 (4 H, m, S-CH_2-$\underline{CH_2}$-CH_2-CH_2-CH_2-CH_2-CH_2-$\underline{CH_2}$-CH_2-), 1.30 (12 H, m, S-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 142.55, 140.07, 137.30, 136.30, 131.82, 131.79, 130.33, 128.96, 128.55, 126.76, 121.16, 119.35, 35.61, 33.66, 31.45, 29.47 (2 × C), 29.45, 29.31, 29.12, 28.98, 28.77

8 3^4-{ω-[(4'-Cyano-[1,1'-biphenyl]-4-yl)thio]alkyl}-[1^1,2^1:2^4,3^1-terphenyl]-1^4-carbonitriles (CBS*n*CT)

To a pre-dried flask flushed with argon and fitted with a condenser, compound **7** (1 eq) was added. 4-Cyanophenylboronic acid (2.5 eq) and tetrakis(triphenylphosphine)palladium(0) (0.025 eq) were added. A mixture of an aqueous solution of sodium carbonate (2 M, 10 mL), ethanol (5 mL) and toluene (40 mL) were added, and the reaction mixture was heated to 85 °C for 24 h with stirring. The quantities of the reagents used in each reaction are listed in **Table S8**. The reaction mixture was cooled to room temperature, before 32 % hydrochloric acid (5 mL) was added dropwise until effervescence was no longer observed. The mixture was filtered to remove the palladium catalyst, and the solvents were removed under vacuum. Water (100 mL) and dichloromethane (100 mL) were added to the solid obtained. The organic layer was washed with water (2 × 50 mL), dried over anhydrous magnesium sulfate and the solvent removed under vacuum. The crude brown solid was purified using a silica gel column with the eluent being 10 % 40:60 petroleum ether and 90 % dichloromethane (RF values quoted in product data). The eluent fractions of interest were evaporated under vacuum to leave a white solid which was recrystallised from hot toluene (40 mL).

Table S8. Quantities of reagents used in the syntheses of 3^4-{ω-[(4'-cyano-[1,1'-biphenyl]-4-yl)thio]alkyl}-[1^1,2^1:2^4,3^1-terphenyl]-1^4-carbonitriles (**8**).

n	(**7**)	4-Cyanophenylboronic acid	Tetrakis(triphenylphosphine)

			palladium(0)
2	1.20 g, 2.68×10^{-3} mol	0.984 g, 6.70×10^{-3} mol	0.077 g, 6.70×10^{-5} mol
4	0.900 g, 1.89×10^{-3} mol	0.695 g, 4.73×10^{-3} mol	0.055 g, 4.73×10^{-5} mol
5	0.900 g, 1.84×10^{-3} mol	0.676 g, 4.60×10^{-3} mol	0.053 g, 4.60×10^{-5} mol
6	1.50 g, 2.97×10^{-3} mol	1.09 g, 7.43×10^{-3} mol	0.086 g, 7.43×10^{-5} mol
8	0.600 g, 1.13×10^{-3} mol	0.416 g, 2.83×10^{-3} mol	0.033 g, 2.83×10^{-5} mol
10	0.600 g, 1.07×10^{-3} mol	0.394 g, 2.68×10^{-3} mol	0.031 g, 2.68×10^{-5} mol

8.1 3^4-{2-[(4'-Cyano-[1,1'-biphenyl]-4-yl)thio]ethyl}-[1^1,2^1:2^4,3^1-terphenyl]-1^4-carbonitrile (CBS2CT)

Yield: 0.462 g, 35.0 %. RF: 0.42

T_{CrN} 164 °C $T_{N_{TB}N}$ (148 °C) T_{NI} 201 °C

ν_{max}/cm^{-1}: 2970, 2224, 1605, 1489, 1392, 1094, 1002, 836, 808, 565, 526, 513

δ_H/ppm (400 MHz, $CDCl_3$): 7.69 (12 H, m, Ar-H), 7.59 (2 H, d, J 7.8 Hz, Ar-H), 7.53 (2 H, d, J 7.9 Hz, Ar-H), 7.45 (2 H, d, J 7.9 Hz, Ar-H), 7.33 (2 H, d, J 7.8 Hz, Ar-H), 3.29 (2 H, t, J 7.6 Hz, S-$\underline{CH_2}$-CH_2-), 3.04 (2 H, t, J 7.6 Hz, Ar-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 145.11, 144.84, 141.17, 139.57, 138.53, 137.92, 137.76, 136.54, 132.67, 132.66, 129.15, 129.09, 127.65, 127.64, 127.56, 127.55, 127.38, 127.22, 118.94, 118.90, 110.96, 110.90, 35.18, 34.62

EA: Calculated for $C_{34}H_{24}N_2S$: C = 82.90 %, H = 4.91 %, N = 5.69 %, S = 6.51 %; Found: C = 82.49 %, H = 4.82 %, N = 5.28 %, S = 6.49 %

8.2 3^4-{4-[(4'-Cyano-[1,1'-biphenyl]-4-yl)thio]butyl}-[1^1,2^1:2^4,3^1-terphenyl]-1^4-carbonitrile (CBS4CT)

Yield: 0.257 g, 26.1 %. RF: 0.35

T_{CrN} 169 °C $T_{N_{TB}N}$ (153 °C) T_{NI} 237 °C

ν_{max}/cm^{-1}: 2936, 2861, 2227, 1591, 1481, 1391, 1180, 1095, 1001, 806, 648, 557, 514

δ_H/ppm (400 MHz, $CDCl_3$): 7.69 (12 H, m, Ar-H), 7.56 (2 H, d, J 7.8 Hz, Ar-H), 7.49 (2 H, d, J 8.1 Hz, Ar-H), 7.38 (2 H, d, J 8.1 Hz, Ar-H), 7.27 (2 H, d, J 7.8 Hz, Ar-H), 3.02 (2 H, t, J 7.1 Hz, S-$\underline{CH_2}$-CH_2-), 2.71 (2 H, t, J 7.4 Hz, Ar-$\underline{CH_2}$-CH_2-), 1.81 (4 H, m, S-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 145.13, 144.88, 141.68, 141.35, 138.24, 137.75, 137.74, 136.23, 132.68, 132.64, 129.00, 128.86, 127.59, 127.58, 127.53, 127.52, 127.33, 127.00, 118.96, 118.91, 110.92, 110.80, 35.00, 33.01, 30.32, 28.46

EA: Calculated for $C_{36}H_{28}N_2S$: C = 83.04 %, H = 5.42 %, N = 5.38 %, S = 6.16 %; Found: C = 83.15 %, H = 5.39 %, N = 5.23 %, S = 6.02 %

8.3 3^4-{5-[(4'-Cyano-[1,1'-biphenyl]-4-yl)thio]pentyl}-[1^1,2^1:2^4,3^1-terphenyl]-1^4-carbonitrile (CBS5CT)

Yield: 0.204 g, 20.7 %. RF: 0.39

T_{CrN} 224 °C T_{NI} 297 °C

ν_{max}/cm^{-1}: 2930, 2856, 2227, 1604, 1486, 1394, 1182, 1097, 1002, 809, 560, 520

δ_H/ppm (400 MHz, $CDCl_3$): 7.69 (12 H, m, Ar-H), 7.55 (2 H, d, J 7.9 Hz, Ar-H), 7.51 (2 H, d, J 8.0 Hz, Ar-H), 7.39 (2 H, d, J 8.0 Hz, Ar-H), 7.27 (2 H, d, J 7.9 Hz, Ar-H), 2.99 (2 H, t, J 7.4 Hz, S-$\underline{CH_2}$-CH_2-), 2.67 (2 H, t, J 7.4 Hz, Ar-$\underline{CH_2}$-CH_2-), 1.74 (4 H, m, S-CH_2-$\underline{CH_2}$-CH_2-$\underline{CH_2}$-CH_2-), 1.55 (2 H, m, S-CH_2-CH_2-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 145.16, 144.91, 142.12, 141.41, 138.45, 137.70, 137.66, 136.16, 132.66, 132.65, 128.99, 128.69, 127.60, 127.58, 127.53, 127.52, 127.33, 126.97, 118.97, 118.93, 110.89, 110.81, 35.44, 33.02, 30.96, 28.95, 28.50

EA: Calculated for $C_{37}H_{30}N_2S$: C = 83.11 %, H = 5.66 %, N = 5.24 %, S = 6.00 %; Found: C = 82.72 %, H = 5.57 %, N = 4.76 %, S = 6.21 %

8.4 3^4-{6-[(4'-Cyano-[1,1'-biphenyl]-4-yl)thio]hexyl}-[1^1,2^1:2^4,3^1-terphenyl]-1^4-carbonitrile (CBS6CT)

Yield: 0.335 g, 20.5 %. RF: 0.43

$T_{CrN_{TB}}$ 131 °C $T_{N_{TB}N}$ 144 °C T_{NI} 238 °C

ν_{max}/cm^{-1}: 2927, 2851, 2228, 1604, 1486, 1394, 1260, 1181, 1096, 1002, 808, 560, 519

δ_H/ppm (400 MHz, $CDCl_3$): 7.69 (12 H, m, Ar-H), 7.55 (2 H, d, J 8.0 Hz, Ar-H), 7.50 (2 H, d, J 8.2 Hz, Ar-H), 7.39 (2 H, d, J 8.2 Hz, Ar-H), 7.27 (2 H, d, J 8.0 Hz, Ar-H), 2.98 (2 H, t, J 7.2 Hz, S-$\underline{CH_2}$-CH_2-), 2.66 (2 H, t, J 7.5 Hz, Ar-$\underline{CH_2}$-CH_2-), 1.69 (4 H, m, S-CH_2-$\underline{CH_2}$-CH_2-CH_2-$\underline{CH_2}$-CH_2-), 1.50 (2 H, quin, J 7.4, S-CH_2-CH_2-$\underline{CH_2}$-CH_2-), 1.42 (2 H, quin, J 7.4, Ar-CH_2-CH_2-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 145.16, 144.91, 142.37, 141.43, 138.51, 137.68, 137.57, 136.11, 132.66, 132.65, 128.99, 128.65, 127.58, 127.57, 127.53, 127.52, 127.32, 126.94, 118.98, 118.94, 110.88, 110.78, 35.49, 33.03, 31.25, 28.90, 28.79, 28.65

EA: Calculated for $C_{38}H_{32}N_2S$: C = 83.17 %, H = 5.88 %, N = 5.11 %, S = 5.84 %; Found: C = 82.90 %, H = 5.77 %, N = 5.21 %, S = 5.74 %

8.5 3^4-{8-[(4'-Cyano-[1,1'-biphenyl]-4-yl)thio]octyl}-[1^1,2^1:2^4,3^1-terphenyl]-1^4-carbonitrile (CBS8CT)

Yield: 0.155 g, 23.8 %. RF: 0.38

$T_{CrN_{TB}}$ 116 °C $T_{N_{TB}N}$ 145 °C T_{NI} 234 °C

ν_{max}/cm^{-1}: 2923, 2851, 2225, 1604, 1485, 1466, 1396, 1181, 1096, 1002, 805, 725, 538, 518

δ_H/ppm (400 MHz, CDCl3): 7.70 (12 H, m, Ar-H), 7.56 (2 H, d, J 8.2 Hz, Ar-H), 7.50 (2 H, d, J 8.4 Hz, Ar-H), 7.39 (2 H, d, J 8.4 Hz, Ar-H), 7.27 (2 H, d, J 8.2 Hz, Ar-H), 2.97 (2 H, t, J 7.4 Hz, S-$\underline{CH_2}$-CH_2-), 2.66 (2 H, t, J 7.4 Hz, Ar-$\underline{CH_2}$-CH_2-), 1.67 (4 H, m, S-CH_2-$\underline{CH_2}$-CH_2-CH_2-CH_2-CH_2-$\underline{CH_2}$-CH_2-), 1.41 (8 H, m, S-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 145.19, 144.93, 142.58, 141.48, 138.59, 137.65, 137.52, 136.08, 132.65, 132.64, 128.98, 128.60, 127.60, 127.57, 127.53, 127.50, 127.32, 126.91, 118.98, 118.93, 110.87, 110.78, 35.61, 33.05, 31.43, 29.34, 29.25, 29.07, 28.98, 28.82

EA: Calculated for $C_{40}H_{36}N_2S$: C = 83.29 %, H = 6.29 %, N = 4.86 %, S = 5.56 %; Found: C = 83.54 %, H = 6.26 %, N = 4.68 %, S = 5.20 %

8.6 3^4-{10-[(4'-Cyano-[1,1'-biphenyl]-4-yl)thio]decyl}-[1^1,2^1:2^4,3^1-terphenyl]-1^4-carbonitrile (CBS10CT)

Yield: 0.108 g, 16.7 %. RF: 0.47.

$T_{CrN_{TB}}$ 114 °C $T_{N_{TB}N}$ 139 °C T_{NI} 224 °C

ν_{max}/cm^{-1}: 2921, 2850, 2228, 1598, 1485, 1467, 1397, 1183, 1099, 1002, 806, 724 558, 517

δ_H/ppm (400 MHz, $CDCl_3$): 7.70 (12 H, m, Ar-H), 7.56 (2 H, d, J 7.9 Hz, Ar-H), 7.50 (2 H, d, J 8.2 Hz, Ar-H), 7.39 (2 H, d, J 8.2 Hz, Ar-H), 7.27 (2 H, d, J 7.9 Hz, Ar-H), 2.97 (2 H, t, J 7.4 Hz, S-$\underline{CH_2}$-CH_2-), 2.65 (2 H, t, J 7.5 Hz, Ar-$\underline{CH_2}$-CH_2-), 1.67 (4 H, m, S-CH_2-$\underline{CH_2}$-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$\underline{CH_2}$-CH_2-), 1.36 (12 H, m, S-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 145.21, 144.94, 142.66, 141.51, 138.63, 137.64, 137.50, 136.06, 132.65, 132.64, 128.98, 128.57, 127.60, 127.56, 127.53, 127.49, 127.32, 126.91, 118.97, 118.94, 110.86, 110.77, 35.64, 33.06, 31.48, 29.48, 29.47, 29.46, 29.35, 29.15, 29.01, 28.85

EA: Calculated for $C_{42}H_{40}N_2S$: C = 83.40 %, H = 6.67 %, N = 4.63 %, S = 5.30 %; Found: C = 83.35 %, H = 6.89 %, N = 4.65 %, S = 5.06 %

Additional Data

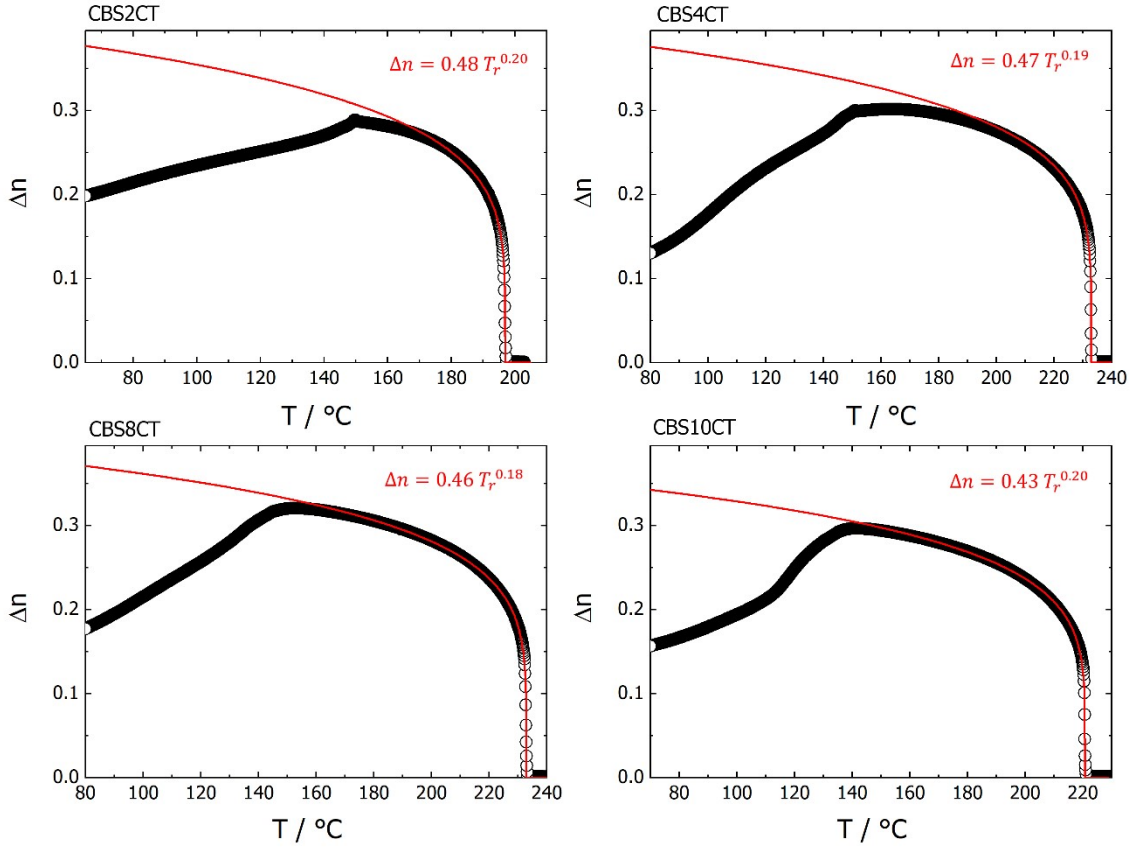


Figure S1. Optical birefringence (Δn, circles) of selected CBS*n*CT homologues. Data recorded in nematic phase were fitted to power law dependence, $\Delta n = \Delta n_0(\frac{T_c - T}{T_c})^{\beta}$, with parameters indicated on the graphs. Value of parameter Δn_0, which shows extrapolated birefringence of the perfectly ordered nematic phase, clearly decreases with elongation of the spacer length.

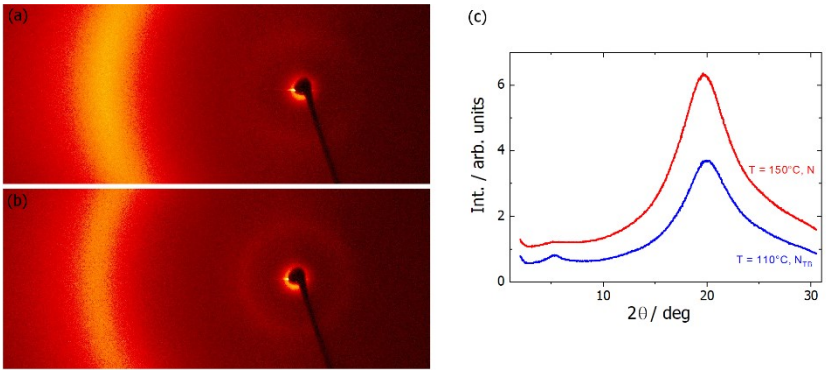


Figure S2. 2D X-ray diffraction patterns for CBS10CT in (a) N phase (T = 150 °C) and (b) NTB phase (T = 110 °C). (c) Diffracted intensity vs. diffraction angle obtained from the 2D pattern by integration over azimuthal angle, red curve is vertically shifted for clarity of presentation. Note, that the change of absolute value of intensity reflects mainly the change of sample alignment between N and N_{TB} phases.

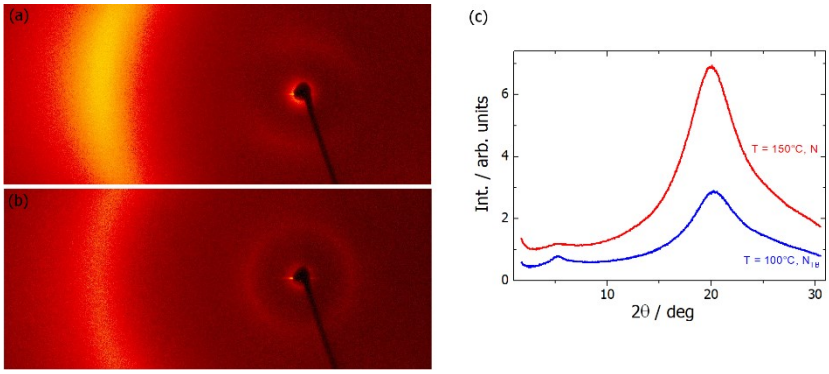


Figure S3. 2D X-ray diffraction patterns for CBS9OCT in (a) N phase (T = 150 °C) and (b) NTB phase (T = 110 °C). (c) Diffracted intensity vs. diffraction angle obtained from the 2D pattern by integration over azimuthal angle, red curve is vertically shifted for clarity of presentation. Note, that the change of absolute value of intensity reflects mainly the change of sample alignment between N and N_{TB} phases.

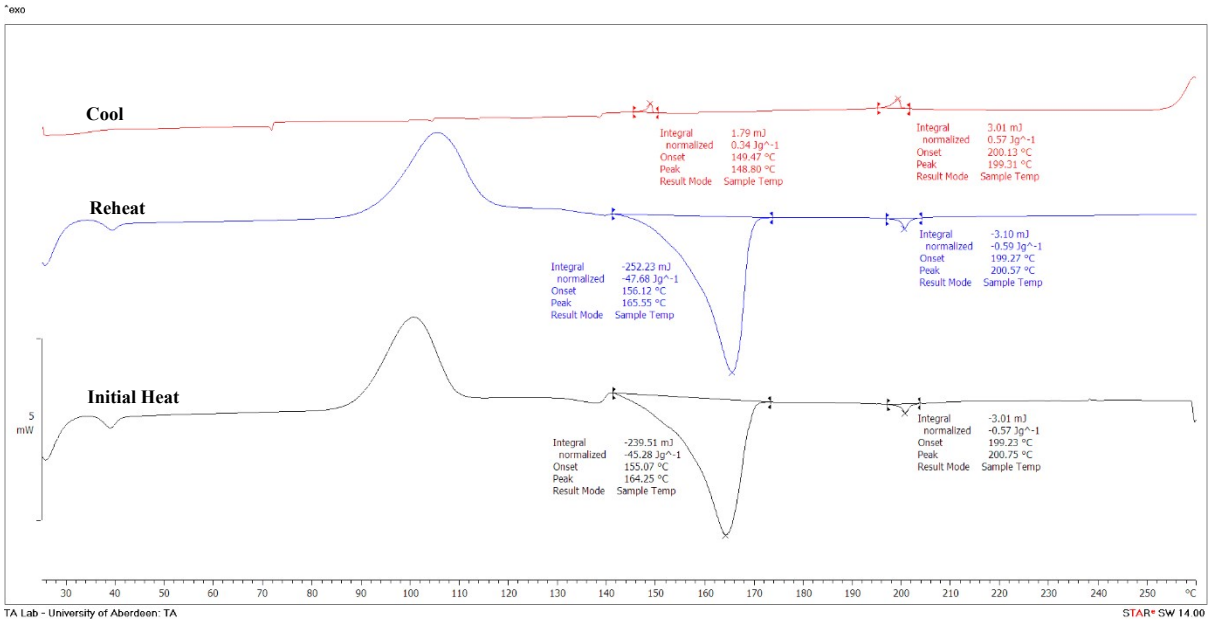


Figure S4. DSC trace of CBS2CT.

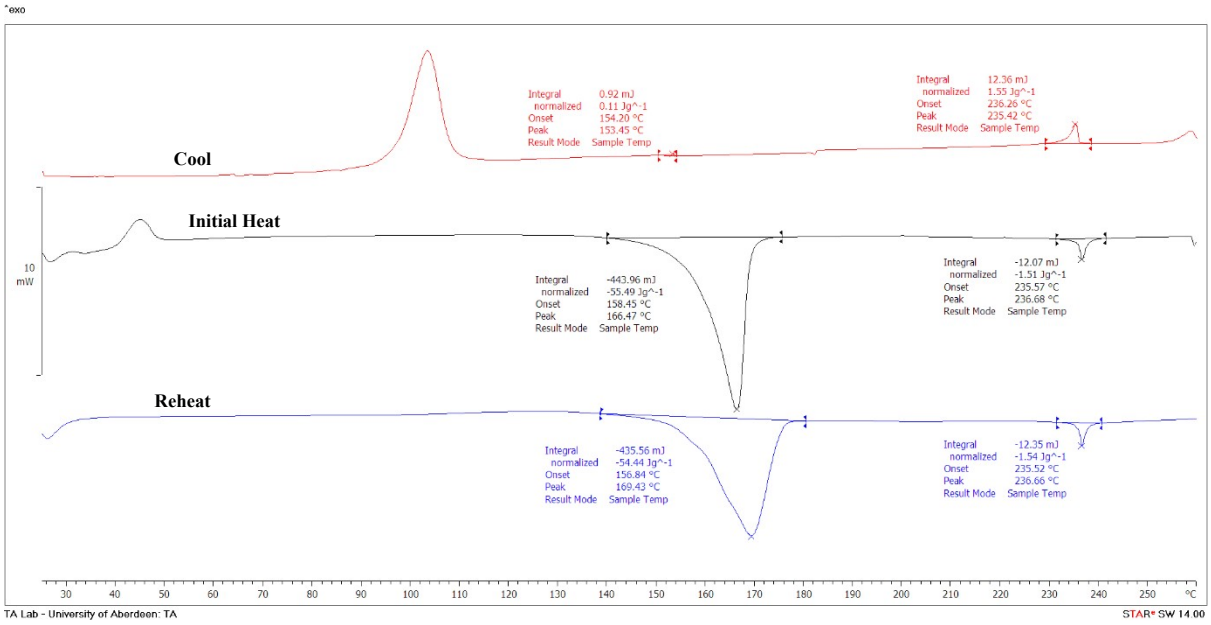


Figure S5. DSC trace of CBS4CT.

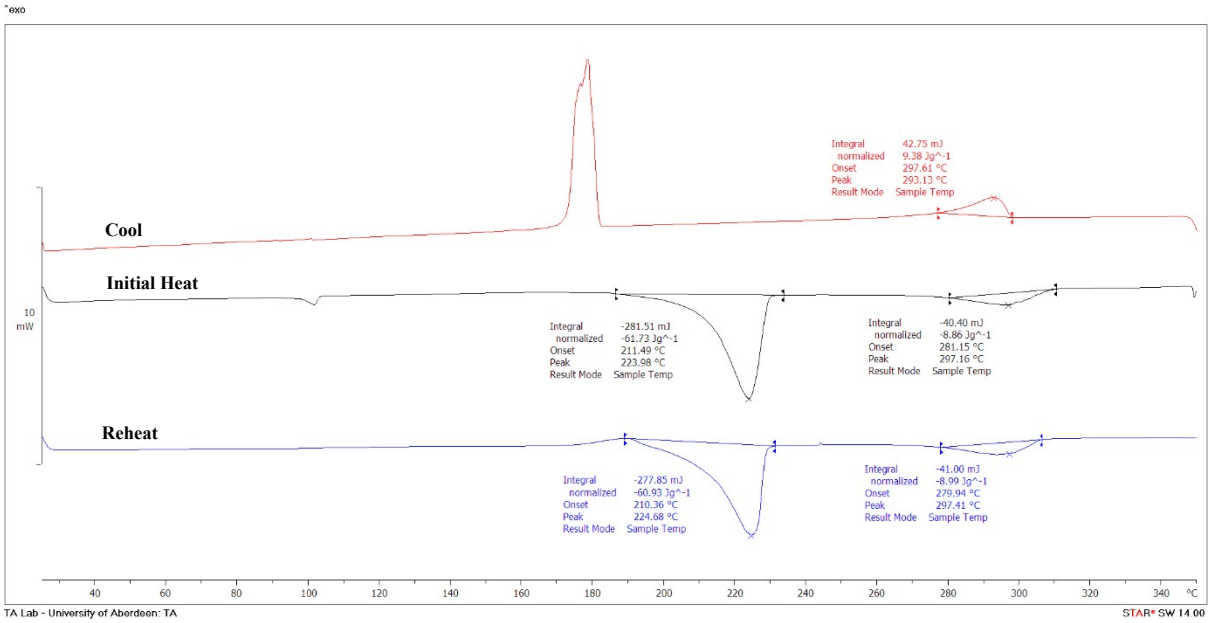


Figure S6. DSC trace of CBS5CT.

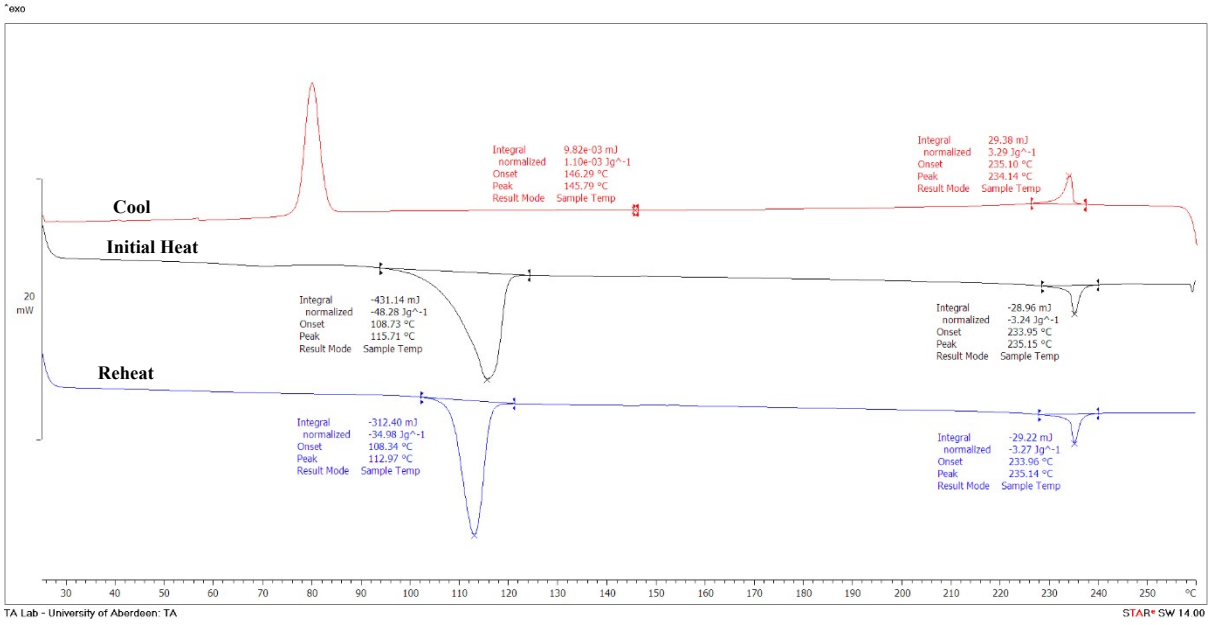


Figure S7. DSC trace of CBS8CT.

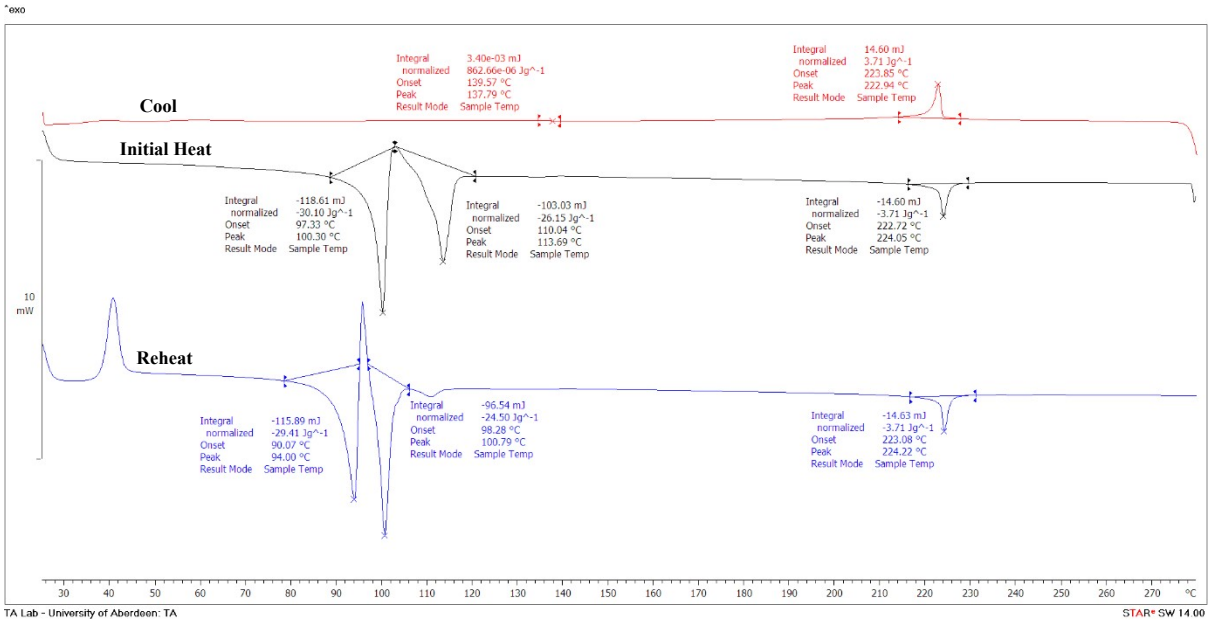


Figure S8. DSC trace of CBS10CT.

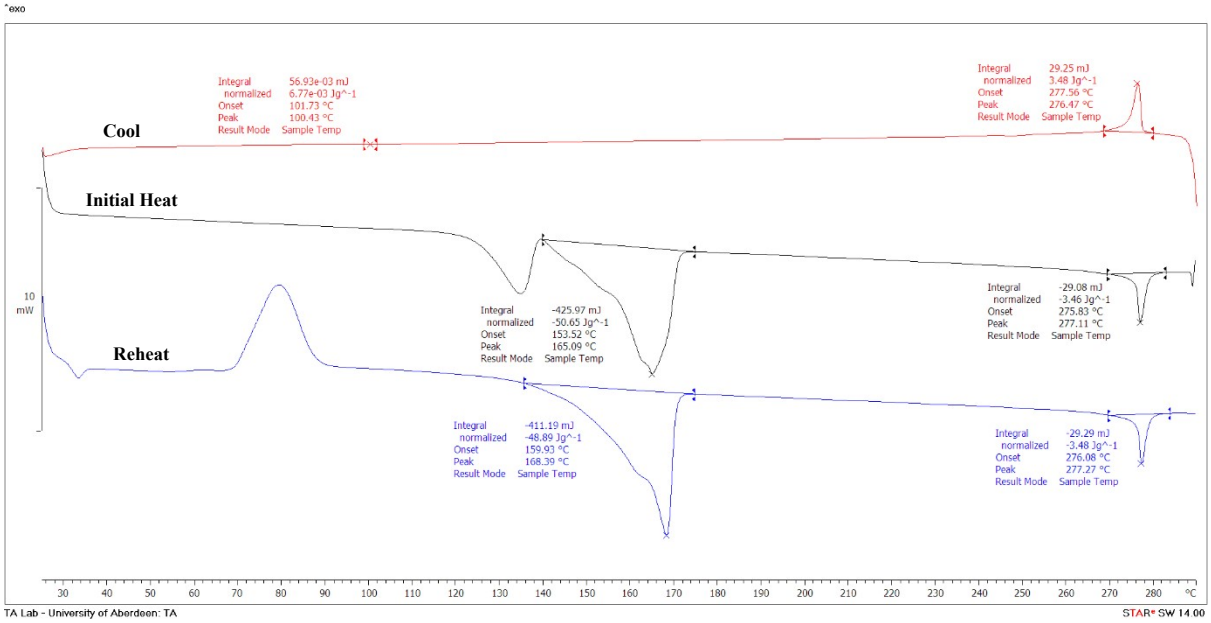


Figure S9. DSC trace of CBS3OCT.

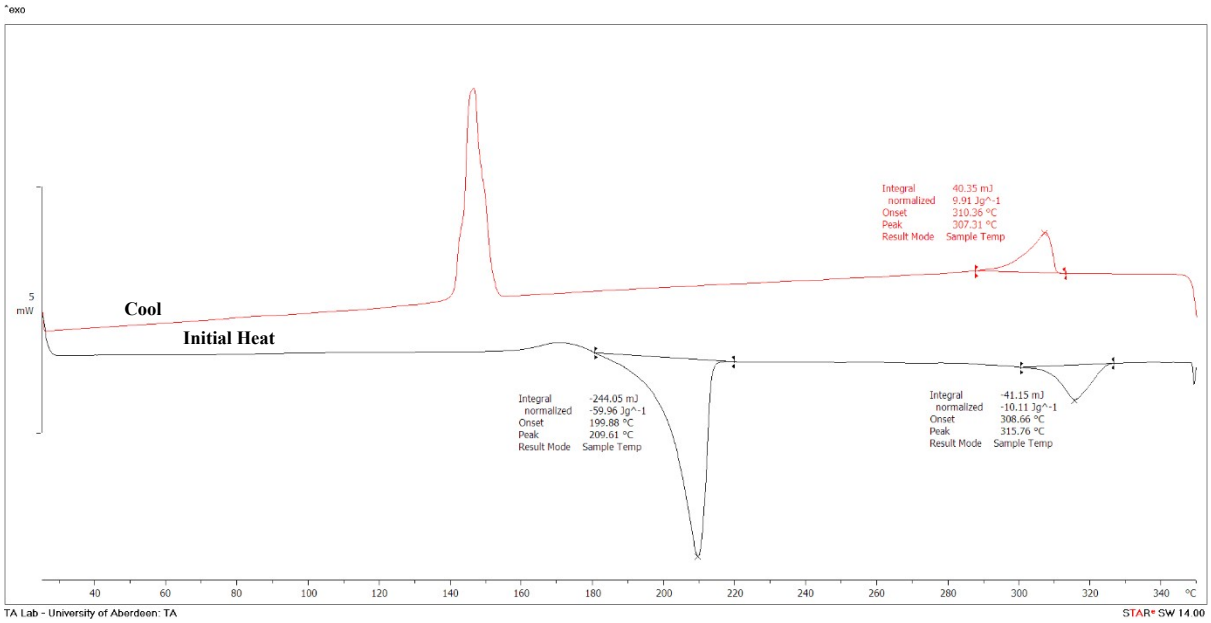


Figure S10. DSC trace of CBS4OCT.

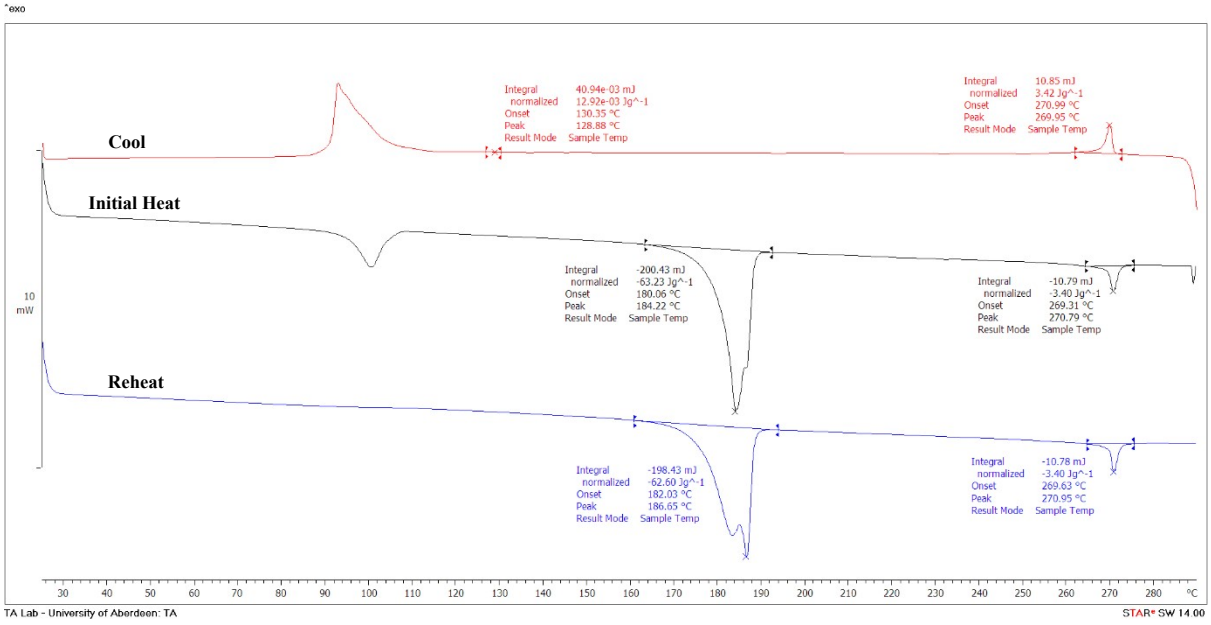


Figure S11. DSC trace of CBS5OCT.

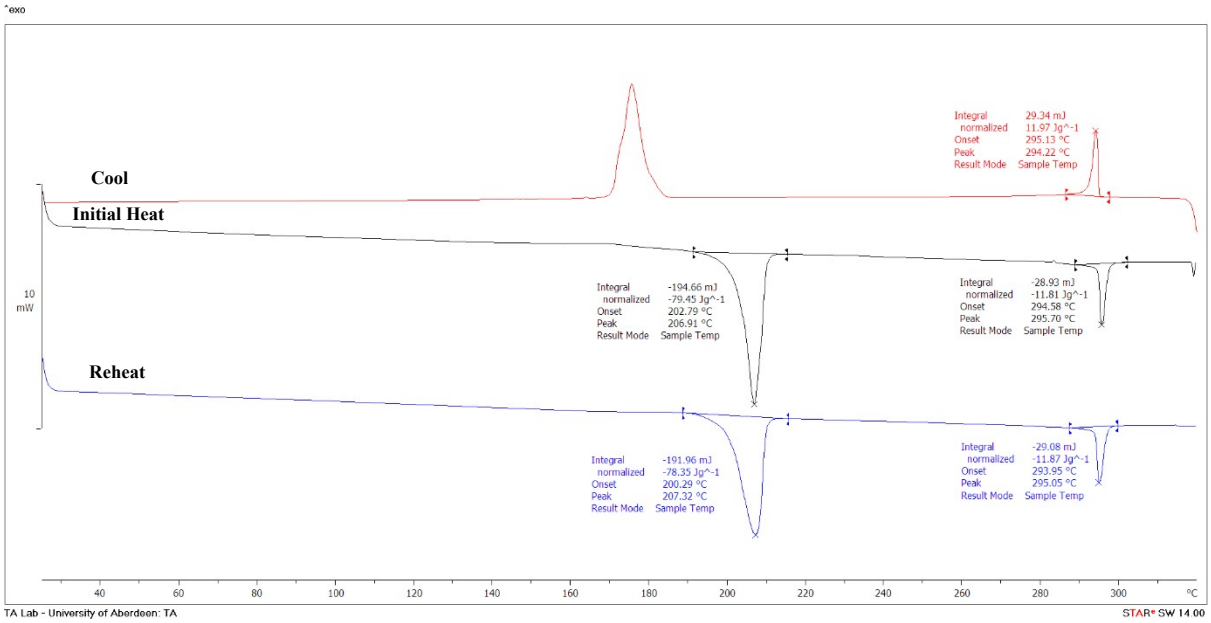


Figure S12. DSC trace of CBS6OCT.

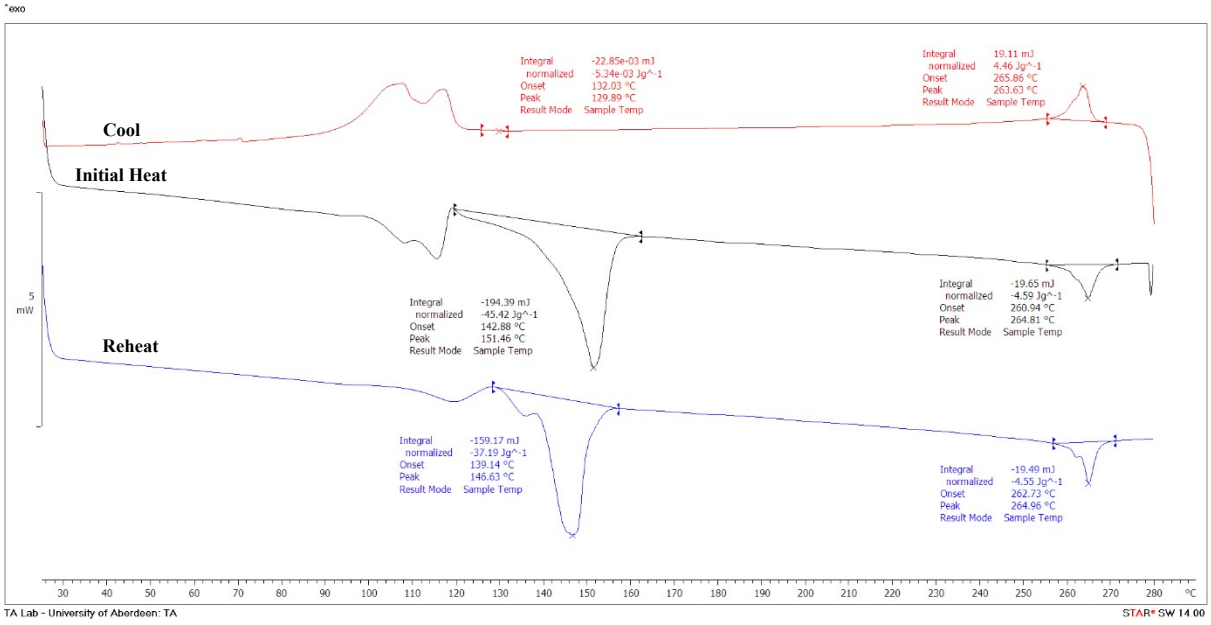


Figure S13. DSC trace of CBS7OCT.

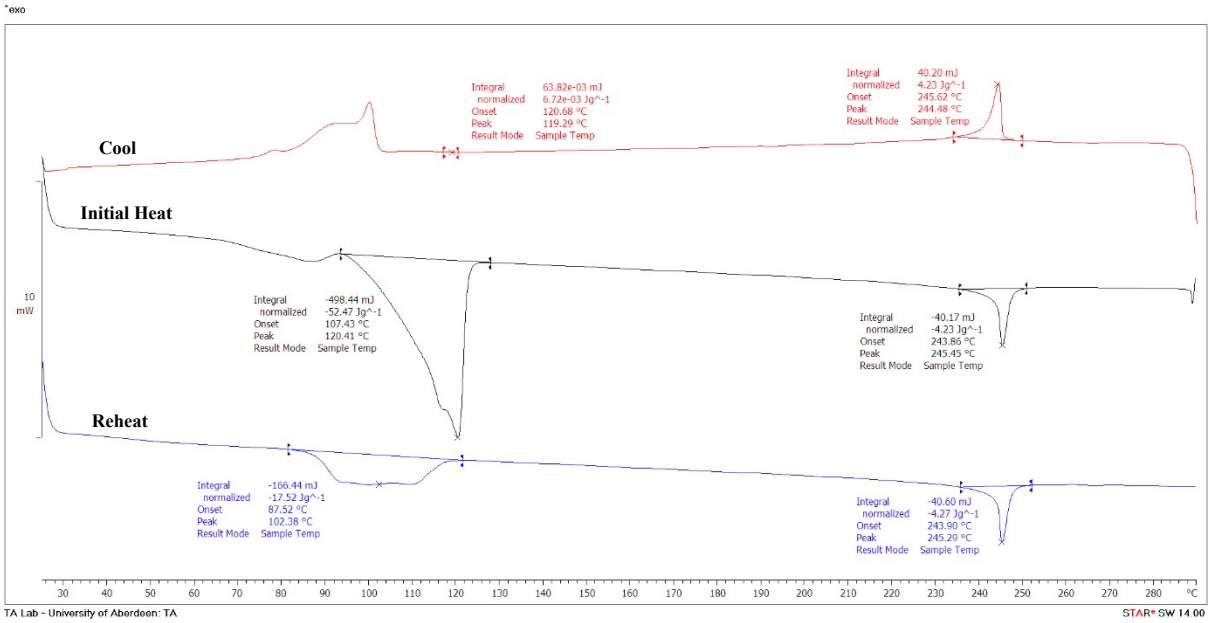


Figure S14. DSC trace of CBS9OCT.

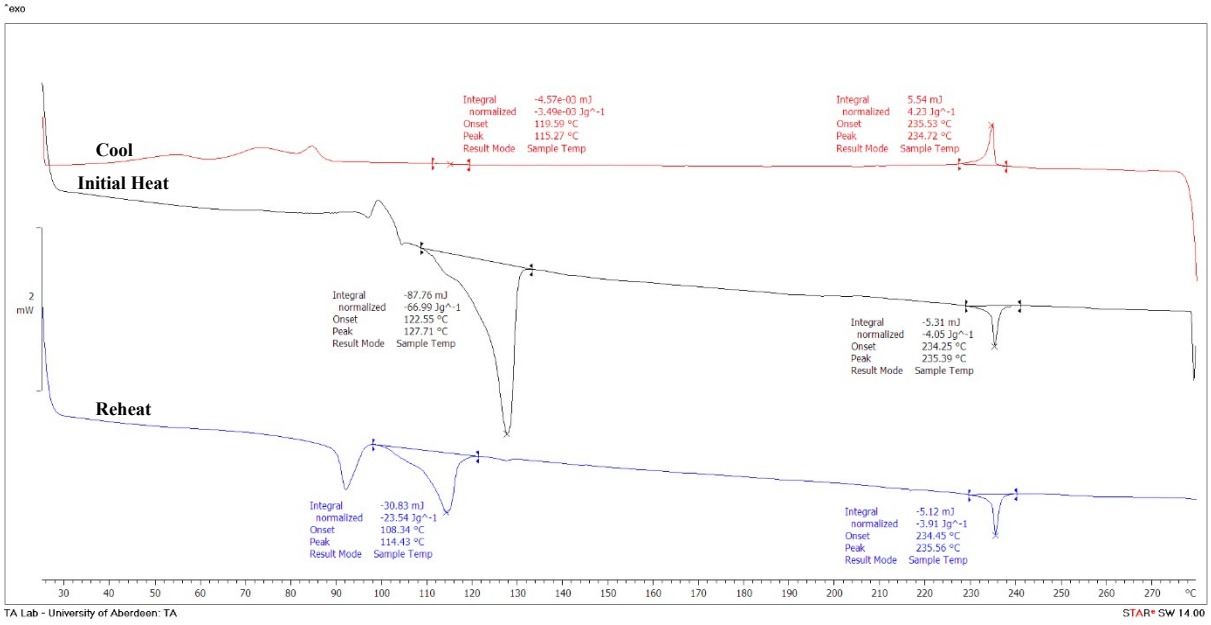


Figure S15. DSC trace of CBS11OCT.