Electronic Supplementary Information

New patterns of twist-bend liquid crystal phase behaviour: the synthesis and characterisation of the 1-(4-cyanobiphenyl-4'-yl)-10-(4-alkylaniline-benzylidene-4'-oxy)decanes (CB10O.*m*)

Ahlam F Alshammari,[a,c] Damian Pociecha,[b] Rebecca Walker,[a] John MD Storey,[a] Ewa Gorecka[b] and Corrie T Imrie[a*]

[a] Department of Chemistry, School of Natural and Computing Sciences, University of Aberdeen, AB24 3UE Scotland, United Kingdom.

[b] University of Warsaw, Faculty of Chemistry, ul. Zwirki i Wigury 101, 02-089 ˙ Warsaw, Poland

[c] Permanent address: Department of Chemistry, University of Hail, Hail, Saudi Arabia

*email: c.t.imrie@abdn.ac.uk

Materials & Methods

Reagents

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

Structure Characterisation

The proposed structures of all final products and intermediates that were synthesised were characterised using 1H NMR, 13C NMR and infrared spectroscopies. The NMR spectra were recorded on either a 400 MHz Bruker Avance III HD NMR spectrometer or a 300 MHz Bruker Ultrashield NMR spectrometer. The infrared spectra were recorded on a Thermal Scientific Nicolet IR100 FTIR spectrometer with an ATR diamond cell**.**

TLC and Column Chromatography

Using aluminium-backed plates with a coating of Merck Kieselgel 60 F254 silica obtained from Merck KGaA, reactions were monitored using thin layer chromatography and the appropriate solvent system. UV light (254 nm) or oxidation with a potassium permanganate stain or an iodine dip were used to see the spots on the plate.

Biotage Selekt system with 50 g or 100 g load capacity Biotage Sfar Silica High-Capacity Duo Columns. A UV detector tuned to 254 nm was used to identify the desired spots, and the equipment collected them when a threshold of 250 mAU was reached.

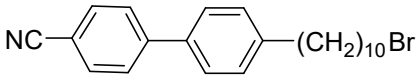
Purity Analysis

High-resolution mass spectrometry was carried out using a Waters XEVO G2 Q-Tof mass spectrometer by Dr. Morag Douglas at the University of Aberdeen.

The purities of the final products were verified using C, H, N microanalysis performed by Analytical Laboratory in the School of Chemistry at the University of London Metropolitan University Analytical and University of Strathclyde External CHN Analysis.

Synthetic & Analytical Data

4'-(10-bromodecyl)-[1,1'-biphenyl]-4-carbonitrile (1)

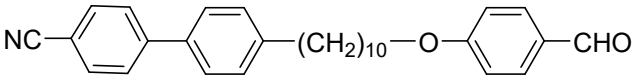


Sodium (s) (0.71 g, 31.0 mol) was added to a stirred suspension of dinitrile benzene (1.92 g, 15.0 mol) in 50 ml NH_3 (l) at -33 ˚c and then turned brown. After 5 minutes, benzonitrile (2.3 g, 2.32 ml, 22.51 mol) was added and left to stir for 30 min. Dibromodecane (5.39 g, 4.03 ml, 18 mol) was added dropwise and left to stir for 1.5 h. Et_2O (30 ml) was added and the flask left open to remove NH_3 (l). The mixture was added to a mixture of Et_2O (30 ml) and water (30 ml). The layers were separated, and the aqueous layer washed with Et_2O (60 ml). The organic layers were combined, washed with water (3 x 50 ml) and dried over anhydrous $MgSO_4$.The solvent was removed under vacuum and the yellow liquid was purified by column chromatography [9:1 Hexane, Ether]. Yield: 0.786 g, 13%. MP: 59 ˚C.

IR ν (cm^{-1}): 2848-2914 (C-H, alkane), 2223.37 (CN), 1605.1 (C-H, aromatic), 1470.29 (C-H, alkyl), 567 (C-Br).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.77 – 7.66 (m, 4H, Ar), 7.54 (d, *J* = 8.2 Hz, 2H, Ar), 7.32 (d, *J* = 8.1 Hz, 2H, Ar), 3.43 (t, *J* = 6.8 Hz, 2H, $ArCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2\underline{CH_2}Br$), 2.66 (t, *J* = 7.8 Hz, 2H, $Ar\underline{CH_2}CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2Br$), 1.88 (p, *J* = 6.9 Hz, 2H, $Ar(CH_2)_8\underline{CH_2}CH_2Br$), 1.67 (p, *J* = 7.4 Hz, 2H, $ArCH_2\underline{CH_2}CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2Br$),1.55 – 1.22 (m, 12H, $ArCH_2CH_2\underline{CH_2CH_2CH_2CH_2CH_2CH_2}CH_2CH_2Br$)^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 28.17, 28.76, 29.29, 29.42, 29.45, 31.39, 32.83, 34.07, 35.64, 110.55, 119.06, 127.09, 127.49, 129.20, 132.58, 136.48, 143.78, 145.64.

4'-(10-(4-formylphenoxy) decy)-[1,1'-biphenyl]-4-carbonitrile (2)



A mixture of 4-(10-bromodecyl)-[1,1bipheny]-4carbonitrile (0.29 g, 0.75 mol), 4- hydroxybenzaldehyde (0.10 g, 0.81 mol), and potassium carbonate (0.20 g, 1.44mol) in dry DMF (10 ml) was heated to 90 ˚C for 24 h. The reaction mixture was added to water (30 ml). The precipitate was collected by vacuum filtration and washed with DCM (15 ml) and water (15 ml). The layers were separated, and the organic layer was washed with water (3 x 10 ml). The organic layers were combined and dried over anhydrous $MgSO_4$, and the solvent was removed *in vacuo*. Yield: 0.17 g, 51 %. MP: 98 ˚C

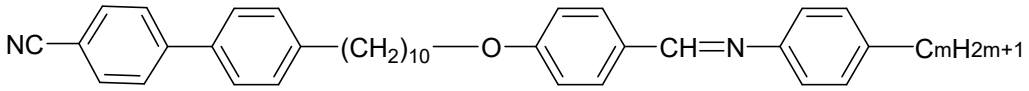
IR ν (cm^{-1}): 2921.01, 2222.13 (C≡N stretch), 1683.80 (C=O aldehyde), 1598.81, 1468.68 1258.48 1157.67, 812.54.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 9.90 (s, 1H, $ArCO\underline{H}$), 7.85 (d, *J* = 8.7 Hz, 2H, Ar), 7.76 – 7.62 (m, 4H, Ar), 7.53 (d, *J* = 8.2 Hz, 2H, Ar), 7.31 (d, *J* = 8.2 Hz, 2H, Ar), 7.01 (d, *J* = 8.7 Hz, 2H, Ar), 4.06 (t, *J* = 6.5 Hz, 2H, $ArCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2\underline{CH_2}OAr$), 2.67 (t, *J* = 7.8 Hz, 2H, Ar-$\underline{CH_2}CH_2CH_2CH_2CH_2CH_2CH_2CH_2$ CH_2OAr), 1.89 – 1.78 (p, *J* = 7.2 Hz, 2H, $ArCH_2CH_2CH_2CH_2CH_2$-

$CH_2CH_2CH_2\underline{CH_2}CH_2OAr$), 1.67 (p, *J* = 7.2 Hz, 2H, Ar $CH_2\underline{CH_2}CH_2CH_2CH_2$ CH_2 $CH_2CH_2CH_2CH_2OAr$), 1.53 – 1.30 (m, 12H. $ArCH_2CH_2\underline{CH_2CH_2CH_2}$ $\underline{CH_2CH_2CH_2}CH_2CH_2OAr$).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 25.97, 29.06, 29.33, 29.49, 29.53, 31.41, 35.65, 68.42, 110.56, 114.75, 119.05, 127.09, 127.49, 129.19, 129.78, 132.01, 132.58, 136.48, 143.77, 145.77, 145.62, 164.26, 190.83.

4'-(10-{4-[{[4-Alkylphenyl]imino}methyl]phenoxy} decyl)[1,1'-biphenyl]-4- carbonitrile, CB10O.*m* (3):



4'-[6-(4-Formylphenoxy) decyl][1,1'-biphenyl]-4-carbonitrile (1 eq.), the desired alkylaniline (1.1 eq.) and a crystal of *p*-toluenesulfonic acid were combined in EtOH (8 mL) and heated at reflux for 4-5 h. The mixture was cooled to room temperature and the resulting precipitate collected by vacuum filtration. The crude product was recrystallized from ethanol.

CB10O.1: IR ν (cm^{-1}): 2922, 2849, 2223 (C≡N stretch), 1627 (C=N), 1605 (para disubstituted benzene), 1512, 1255, 1165, 818, 540.

^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.41 (s, 1H, $\underline{CH}$=N), 7.84 (d, *J* = 8.7 Hz, 2H, Ar), 7.80 – 7.59 (q, *J* = 8.5 Hz , 4H, Ar), 7.53 (d, *J* = 8.1 Hz, 2H, Ar), 7.31 (d, *J* = 8.0 Hz, 2H, Ar), 7.21 (d, *J* = 8.1 Hz, 2H, Ar), 7.14 (d, *J* = 8.1 Hz, 2H, Ar), 6.98 (d, *J* = 8.7 Hz, 2H, Ar), 4.04 (t, *J* = 6.5 Hz, 2H, $ArCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2$ $\underline{CH_2}OAr$), 2.68 (t, *J* = 7.7 Hz, 2H, $Ar\underline{CH_2}CH_2CH_2CH_2CH_2$- $CH_2CH_2CH_2CH_2CH_2OAr$), 2.39 (s, 3H, $Ar\underline{CH_3}$), 1.83 (p, *J* = 6.7 Hz, 2H, Ar $CH_2CH_2CH_2CH_2CH_2$ CH_2- $CH_2CH_2\underline{CH_2}CH_2OAr$), 1.67 (p, *J* = 7.4 Hz, 2H, Ar $CH_2\underline{CH_2}CH_2CH_2CH_2$ CH_2 $CH_2CH_2CH_2CH_2OAr$), 1.54 – 0.88 (m, 12H, $ArCH_2CH_2\underline{CH_2CH_2CH_2CH_2CH_2CH_2}CH_2CH_2OAr$). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 161.73, 159.01, 149.81, 145.64, 143.80, 136.47, 135.33, 132.57, 130.37, 129.73, 129.20, 127.49, 127.08, 120.78, 119.06, 114.66, 110.54, 68.17, 35.65, 31.40, 29.52, 29.47, 29.34, 29.31, 29.31, 29.18, 26.00, 20.99.

Elemental Analysis: Calculated for $C_{37}H_{40}N_2O$: C 84.05%, H 7.63%, N 5.30 %, Found: C 84.00 %, H 7.59 %, N 5.19 %.

CB10O.2: IR ν (cm^{-1}): 2921, 2850, 2224 (C≡N stretch), 1624 (C=N), 1605 (para disubstituted benzene), 1511, 1255, 1164, 815, 544.

^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.41 (s, 1H, $\underline{CH}$=N), 7.85 (d, *J* = 8.6 Hz, 2H, Ar), 7.78 – 7.64 (q, *J* = 8.5 Hz, 4H, Ar), 7.53 (d, *J* = 8.1 Hz, 2H, Ar), 7.31 (d, *J* = 8.0 Hz, 2H, Ar), 7.24 (d, *J* = 8.1 Hz, 2H, Ar), 7.16 (d, *J* = 8.2 Hz, 2H, Ar), 6.98 (d, *J* = 8.6 Hz, 2H, Ar), 4.04 (t, *J* = 6.5 Hz, 2H, $ArCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2\underline{CH_2}OAr$), 2.68 (m, 4H, Ar $\underline{CH_2}(CH_2)_9OAr$, $Ar\underline{CH_2}CH_3$), 1.83 (p, *J* = 6.8 Hz, 2H, $ArCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2\underline{CH_2}CH_2OAr$), 1.67 (p, *J* = 7.3 Hz, 2H, Ar $CH_2\underline{CH_2}CH_2CH_2CH_2$ CH_2 $CH_2CH_2CH_2CH_2OAr$), 1.52 – 1.31 (m, 12H, Ar $CH_2CH_2\underline{CH_2CH_2CH_2}$ $\underline{CH_2}$ $\underline{CH_2CH_2}CH_2CH_2OAr$), 1.28 (t, *J* = 7.6 Hz, 3H, $ArCH_2\underline{CH_3}$).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 161.73, 159.03, 150.00, 145.64, 143,80, 141.76, 136.47, 132.57, 130.38, 129.20, 128.53, 127.49, 127.08, 120.84, 114.66, 110.55, 68.18, 35.64, 31.41, 29.52, 29.47, 29.35,29.31, 29.18, 28.42, 26.00, 15.68.

Elemental Analysis: Calculated for $C_{38}H_{42}N_2O$: C 84.09%, H 7.80%, N 5.16 %, Found: C 83.85%, H 7.77 %, N 5.07 %.

CB10O.3: IR ν (cm^{-1}): 2921, 2849, 2220 (C≡N stretch), 1624 (C=N), 1605 (para disubstituted benzene), 1510, 1252, 1163, 812, 540.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.42 (s, 1H, $\underline{CH}$=N), 7.85 (d, *J* = 8.7 Hz, 2H, Ar), 7.78 – 7.61 (q, *J* = 8.5 Hz, 4H, Ar), 7.53 (d, *J* = 8.2 Hz, 2H, Ar), 7.31 (d, *J* = 8.0 Hz, 2H, Ar), 7.21 (d, *J* = 8.2 Hz, 2H, Ar), 7.15 (d, *J* = 8.3 Hz, 2H, Ar), 6.98 (d, *J* = 8.7 Hz, 2H, Ar), 4.04 (t, *J* = 6.5 Hz, 2H, $ArCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2\underline{CH_2}OAr$), 2.73 – 2.58 (m, 4H, $Ar\underline{CH_2}CH_2CH_2CH_2CH_2\,CH_2\,CH_2CH_2CH_2\,CH_2OAr$), 1.83 (p, *J* = 6.7 Hz, 2H, $Ar\,CH_2CH_2CH_2CH_2CH_2\,CH_2\,CH_2CH_2\underline{CH_2}\,CH_2OAr$), 1.76 – 1.60 (m, 4H, $Ar\,CH_2\underline{CH_2}CH_2CH_2CH_2\,CH_2\,CH_2CH_2CH_2CH_2OAr$, $ArCH_2\underline{CH_2}CH_3$), 1.53 – 1.22 (m, 12H, $Ar\,CH_2CH_2\underline{CH_2CH_2CH_2}\,\underline{CH_2}\,\underline{CH_2CH_2}CH_2CH_2OAr$), 0.98 (t, *J* = 7.3 Hz, 3H, $Ar(CH_2)_2\underline{CH_3}$).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 160.5, 159.0, 149.6, 145.64, 143.80, 140.26 ,136.57, 132.57, 130.37,129.14, 129.20, 127.49, 127.08, 123.31, 120.75, 119, 114.66, 110.70, 68.17, 37.6, 35.65, 31.41, 29.53, 29.48, 29.31, 29.18, 26.00, 24.64, 13.83.

HR-MS: (TOF ESI+) (m/z): [M+H]+ calculated for $C_{39}H_{45}N_2O$ = 557.3515; found = 557.3532 (-3.1 ppm difference)

CB10O.4: IR (ATR) ν (cm^{-1}): 2921, 2849, 2224 (C≡N stretch), 1627 (C=N), 1606 (para disubstituted benzene), 1513, 1254, 1164, 812, 554.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.42 (s, 1H, $\underline{CH}$=N), 7.84 (d, *J* = 8.7 Hz, 2H, Ar), 7.80 – 7.56 (q, *J*=8.7 Hz, 4H, Ar), 7.53 (d, *J* = 8.2 Hz, 2H, Ar), 7.31 (d, *J* = 8.1 Hz, 2H, Ar), 7.21 (d, *J* = 8.3 Hz, 2H, Ar), 7.15 (d, *J* = 8.3 Hz, 2H, Ar), 6.98 (d, *J* = 8.7 Hz, 2H, Ar), 4.04 (t, *J* = 6.5 Hz, 2H, $Ar(CH_2)_9\underline{CH_2}OAr$), 2.67(m, 4H, $Ar\underline{CH_2}CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2OAr$, $Ar\underline{CH_2}CH_2\ \ CH_2CH_3$), 1.83 (p, *J* = 6.7 Hz, 2H, $ArCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2\underline{CH_2}CH_2OAr$), 1.72 – 1.60 (m, 4H, $ArCH_2\underline{CH_2}CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2OAr$, $ArCH_2\underline{CH_2}CH_2CH_3$), 1.51 – 1.33 (m, 14H, $ArCH_2CH_2\underline{CH_2CH_2CH_2CH_2CH_2CH_2}CH_2CH_2OAr$, $ArCH_2CH_2\underline{CH_2}CH_3$), 0.96 (t, *J* = 7.3 Hz, 3H, $Ar\text{-}(CH_2)_3\underline{CH_3}$).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 161.70, 158.97, 149.94, 145.62, 143.79, 140.43, 136.46, 132.56, 130.36, 129.19, 129.07, 127.48, 127.07, 120.75, 114.65, 110.53, 68.16, 35.65, 35.19, 33.73, 31.41, 29.53, 29.47, 29.35, 29.31, 29.17, 26.00, 22.37, 13.99.

HR-MS: (TOF ESI+) (m/z): [M+H]+ calculated for $C_{40}H_{47}N_2O$ = 571.3662; found = 571.3688 (-4.6 ppm difference)

CB10O.5: IR ν (cm^{-1}): 2921, 2850, 2225 (C≡N stretch), 1606 (C=N), 1573 (para disubstituted benzene), 1513, 1254, 1163, 812, 554.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.42 (s, 1H, $\underline{CH}$=N), 7.84 (d, *J* = 8.7 Hz, 2H, Ar), 7.71 (q, *J* = 8.7 Hz, 4H, Ar), 7.53 (d, *J* = 8.3 Hz, 2H, Ar), 7.31 (d, *J* = 8.2 Hz, 2H, Ar), 7.21 (d, *J* = 8.3 Hz, 2H, Ar), 7.15 (d, *J* = 8.3 Hz, 2H, Ar), 6.98 (d, *J* = 8.7 Hz, 2H, Ar), 4.04 (t, *J* = 6.5 Hz, 2H, $Ar(CH_2)_9\underline{CH_2}OAr$), 3.27 – 2.26 (m, 4H, $Ar\underline{CH_2}(CH_2)_9OAr$, $Ar\underline{CH2}(CH_2)_3CH_3$), 1.82 (p, *J* = 7.0 Hz, 2H, $Ar.(CH_2)_8\underline{CH_2}CH_2OAr$),

1.78 – 1.60 (m, 4H, $ArCH_2\underline{CH_2}CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2OAr$, $ArCH_2\underline{CH_2}$-$CH_2CH_2CH_3$), 1.54 – 1.12 (m, 16H, $ArCH_2CH_2\underline{CH_2CH_2CH_2CH_2CH_2CH_2}CH_2CH_2OAr$, $ArCH_2$- $CH_2\underline{CH_2CH_2}CH_3$), 0.92 (t, *J* = 7.0 Hz, 3H, $ArCH_2CH_2CH_2CH_2\underline{CH_3}$).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 160.70, 158.97, 149.94, 145.62, 143.79, 140.43, 136.46, 132.56, 130.36, 129.19, 129.08, 127.49, 127.07, 120.76, 114.66, 111.93, 68.17, 35.65, 35.19, 33.73, 31.41, 29.53, 29.47, 29.35, 29.31, 29.17, 26.00, 22.57, 14.06.

HR-MS: (TOF ESI+) (m/z): [M+H]+ calculated for $C_{41}H_{49}N_2O$ = 585.3844; found = 585.3845 (-0.2 ppm difference)

CB10O.6: IR ν (cm^{-1}): 2918, 2848, 2225 (C≡N stretch), 1606 (C=N), 1570 (para disubstituted benzene), 1511, 1256, 1165, 816, 539.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.42 (s, 1H, $\underline{CH}$=N), 7.85 (d, *J* = 8.4 Hz, 2H, Ar), 7.71 (q, *J* = 8.5 Hz, 4H, Ar), 7.53 (d, *J* = 8.2 Hz, 2H, Ar), 7.31 (d, *J* = 8.2 Hz, 2H, Ar), 7.21 (d, *J* = 8.3, Hz, 2H, Ar), 7.15 (d, *J* = 8.1 Hz, 2H, Ar), 6.98 (d, *J* = 8.7 Hz, 2H, Ar), 4.04 (t, *J* = 6.5 Hz, 2H, $Ar(CH_2)_9\underline{CH_2}OAr$), 2.92 – 2.27 (m, 4H, $Ar\underline{CH_2}(CH_2)_9OAr$, $Ar\underline{CH_2}(CH_2)_4CH_3$), 1.83 (p, *J* = 6.7 Hz, 2H, $Ar(CH_2)_8\underline{CH_2}CH_2OAr$) 1.71 – 1.59 (m, 4H, $ArCH_2\underline{CH_2}(CH_2)_8OAr$, $ArCH_2\underline{CH_2}(CH_2)_3CH_3$), 1.55 – 1.10 (m, 18H, $ArCH_2CH_2\underline{CH_2CH_2CH_2CH_2CH_2CH_2}CH_2CH_2OAr$, $ArCH_2CH_2\underline{CH_2CH_2CH_2}CH_3$), 0.91 (t, *J* = 6.5 Hz, 3H, $ArCH_2CH_2CH_2CH_2CH_2\underline{CH_3}$).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 160.07, 159.56, 149.6, 145.64, 143.80, 141.60 ,133.6, 132.57, 130.37,129.20, 129.07, 127.49, 127.08, 123.5, 120.76, 119.06, 114.66, 110.51 ,68.17, 35.65, 35.51, 31.75, 31.54, 31.41, 29.53, 29.47, 29.35, 29.31, 29.18, 29.00, 26.00, 22.63, 14.12.

Elemental Analysis: Calculated for $C_{42}H_{50}N_2O$: C 84.23%, H 8.42%, N 4.68 %, Found: C 83.73 %, H 8.38 %, N 4.72 %.

CB10O.7: IR ν (cm^{-1}): 2919, 2848, 2225 (C≡N stretch), 1607 (C=N), 1570 (para disubstituted benzene), 1511, 1255, 1165, 811, 539.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.42 (s, 1H, $\underline{CH}$=N), 7.84 (d, *J* = 8.3 Hz, 2H, Ar), 7.71 (q, *J* = 8.4 Hz, 4H, Ar), 7.53 (d, *J* = 8.2 Hz, 2H, Ar), 7.31 (d, *J* = 8.0 Hz, 2H, Ar), 7.21 (d, *J* = 8.1, Hz, 2H, Ar), 7.15 (d, *J* = 8.1 Hz, 2H, Ar) , 6.98 (d, *J* = 8.6 Hz, 2H, Ar), 4.04 (t, *J* = 6.5 Hz, 2H, $Ar(CH_2)_9\underline{CH_2}OAr$), 2.73 – 2.60 (m, 4H, $Ar\underline{CH_2}(CH_2)_9OAr$, $Ar\underline{CH_2}(CH_2)_5CH_3$), 1.83 (p, *J* = 6.7 Hz, 2H, $Ar(CH_2)_8\underline{CH_2}CH_2OAr$), 1.71 – 1.61 (m, 4H, $ArCH_2\underline{CH_2}(CH_2)_8OAr$, $ArCH_2\underline{CH_2}(CH_2)_4CH_3$), 1.54 – 1.21 (m, 20H, $ArCH_2CH_2\underline{CH_2CH_2CH_2CH_2CH_2CH_2}CH_2CH_2OAr$, $ArCH_2CH_2\underline{CH_2CH_2CH_2CH_2}CH_3$), 0.91 (t, *J* = 7.0 Hz, 3H, $ArCH_2CH_2CH_2CH_2CH_2CH_2\underline{CH_3}$).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 161.72, 158.98, 149.93, 145.64, 143.80, 140.50, 136.47, 132.57, 130.38, 129.20, 129.07, 127.49, 127.09, 120.76, 119.06, 114.66, 110.55, 68.18, 35.65, 35.51, 31.85, 31.59, 31.41, 29.53, 29.48, 29.35, 29.32, 29.29, 29.21, 29.18, 26.01, 22.68, 14.12.

HR-MS: (TOF ESI+) (m/z): [M+H]+ calculated for $C_{43}H_{53}N_2O$ = 613.4138; found, 613.4158 (-3.3 ppm difference)

CB10O.8: IR ν (cm^{-1}): 2919, 2849, 2233 (C≡N stretch), 1606 (C=N), 1571 (para disubstituted benzene), 1510, 1253, 1164, 816, 538.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.32 (s, 1H, $\underline{CH}$=N), 7.75 (d, *J* = 8.5 Hz, 2H, Ar), 7.62 (q, *J* = 8.7 Hz, 4H, Ar), 7.44 (d, *J* = 8.2 Hz, 2H, Ar), 7.22 (d, *J* = 8.0 Hz, 2H, Ar), 7.12 (d, *J* = 8.2, Hz, 2H, Ar), 7.1 (d, *J* = 8.1 Hz, 2H, Ar) , 6.89 (d, *J* = 8.6 Hz, 2H, Ar), 3.94 (t, *J* = 6.5 Hz, 2H, $Ar(CH_2)_9\underline{CH_2}OAr$), 2.63 – 2.50 (m, 4H, $Ar\underline{CH_2}(CH_2)_9OAr$, $Ar\underline{CH_2}(CH_2)_6CH_3$), 1.73 (p, *J* = 6.7 Hz, 2H, $Ar(CH_2)_8\underline{CH_2}CH_2OAr$), 1.59 – 1.51 (m, 4H, $ArCH_2\underline{CH_2}(CH_2)_8OAr$, $ArCH_2\underline{CH_2}(CH_2)_5CH_3$), 1.44 – 1.22 (m, 22H,

$ArCH_2CH_2\underline{CH_2}CH_2CH_2CH_2CH_2CH_2CH_2CH_2OAr$, $ArCH_2CH_2\underline{CH_2}CH_2CH_2CH_2CH_2CH_3$), 0.81 (t, *J* = 6.9 Hz, 3H, $ArCH_2CH_2CH_2CH_2CH_2CH_2\underline{CH_3}$).
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 158.98, 145.64, 143.80, 136.46, 132.57, 130.38, 129.20, 129.08, 127.49, 127.09, 120.76, 114.67, 110.55, 68.18, 35.65, 35.52, 31.91, 31.59, 31.41, 29.53, 29.51, 29.48, 29.34, 29.31, 29.29, 29.18, 26.01, 22.69, 14.13.

Elemental Analysis: Calculated for $C_{44}H_{54}N_2O$: C 84.30%, H 8.68%, N 4.47 %, Found: C 84.07 %, H 8.63 %, N 4.59 %.

CB10O.9: IR ν (cm^{-1}): 2917, 2849, 2233 (C≡N stretch), 1622 (C=N), 1605 (para disubstituted benzene), 1511, 1251, 1162, 810, 539.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.42 (s, 1H, $\underline{CH}$=N), 7.84 (d, *J* = 8.6 Hz, 2H, Ar), 7.71 (q, *J* = 8.3 Hz, 4H, Ar), 7.53 (d, *J* = 8.2 Hz, 2H, Ar), 7.31 (d, *J* = 8.1 Hz, 2H, Ar), 7.21 (d, *J* = 8.2 Hz, 2H, Ar), 7.15 (d, *J* = 8.2 Hz, 2H, Ar), 6.98 (d, *J* = 8.7 Hz, 2H, Ar), 4.04 (t, *J* = 6.5 Hz, 2H, $Ar(CH_2)_9\underline{CH_2}OAr$), 2.73 – 2.59 (m, 4H, $Ar\underline{CH_2}(CH_2)_9OAr$, $Ar\underline{CH_2}(CH_2)_7CH_3$), 1.83 (p, *J* = 6.7 Hz, 2H, $Ar(CH_2)_8\underline{CH_2}CH_2OAr$), 1.68 – 1.64 (m, 4H, $ArCH_2\underline{CH_2}(CH_2)_8OAr$, $ArCH_2\underline{CH_2}(CH_2)_6CH_3$), 1.52 – 1.19 (m, 24H, $ArCH_2CH_2\underline{CH_2}CH_2CH_2CH_2CH_2CH_2CH_2CH_2OAr$, $ArCH_2CH_2\underline{CH_2}CH_2CH_2CH_2CH_2CH_2CH_3$), 0.91 (t, *J* = 6.7 Hz, 3H $Ar(CH_2)_8\underline{CH_3}$).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 161.10, 158.98, 149.91, 145.6, 143.80, 140.5, 136.5, 132.57, 130.37, 129.20, 129.07, 127.49, 127.09, 120.76, 118.6, 114.66, 110.6, 68.18, 35.65, 35.51, 31.92, 31.59, 31.41, 29.58, 29.54, 29.48, 29.35, 29.18, 26.01, 22.70, 14.13.

Elemental Analysis: Calculated for $C_{45}H_{56}N_2O$: C 84.33 %, H 8.81 %, N 4.37%, Found: C 83.90%, H 8.73 %, N 4.40 %.

CB10O.10: IR ν (cm^{-1}): 2920, 2894, 2220 (C≡N stretch), 1606 (C=N), 1596 (para disubstituted benzene), 1511, 1252, 1165, 812, 540.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.42 (s, 1H, $\underline{CH}$=N), 7.84 (d, *J* = 8.7 Hz, 2H, Ar), 7.71 (q, *J* = 8.5 Hz, 4H, Ar), 7.57 – 7.50 (d, *J* = 8.2 Hz, 2H, Ar), 7.31 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.2, Hz, 2H, Ar), 7.15 (d, *J* = 8.1 Hz, 2H, Ar), 6.98 (d, *J* = 8.7 Hz, 2H, Ar), 4.04 (t, *J* = 6.5 Hz, 2H, $Ar(CH_2)_9\underline{CH_2}OAr$), 2.73 – 2.59 (m, 4H, $Ar\underline{CH_2}(CH_2)_9OAr$, $Ar\underline{CH_2}(CH_2)_8CH_3$), 1.83 (p, *J* = 6.7 Hz, 2H, $Ar(CH_2)_8\underline{CH_2}CH_2OAr$), 1.70 – 1.59 (m, 4H, $ArCH_2\underline{CH_2}(CH_2)_8OAr$, $ArCH_2\underline{CH_2}(CH_2)_7CH_3$), 1.54 – 1.13 (m, 26H, $ArCH_2CH_2\underline{CH_2}CH_2CH_2CH_2CH_2CH_2CH_2CH_2OAr$, $ArCH_2CH_2\underline{(CH_2)_7}CH_3$), 0.91 (t, *J* = 6.7 Hz, 3H, $ArCH_2CH_2(CH_2)_7\underline{CH_3}$).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 160.00, 158.98, 149.93, 145.64, 143.80, 140.51, 133.6, 136.47, 132.57, 130.38, 129.14 ,129.20, 129.07, 127.49, 127.08, 120.76, 119.06, 115.21 ,114.66, 68.18, 35.65, 35.51 ,31.92, 31.59, 31.41, 29.64, 29.54, 29.48, 29.4, 29.35, 29.31, 29.18, 26.01, 22.70, 14.14.

Elemental Analysis: Calculated for $C_{46}H_{58}N_2O$: C 84.35%, H 8.93%, N 4.28 %, Found: C 84.45 %, H 8.95 %, N 4.41%.

CB10O.12: IR ν (cm^{-1}): 2915, 2848, 2233 (C≡N stretch), 1622 (C=N), 1606 (para disubstituted benzene), 1510, 1249, 1169, 812, 546.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.42 (s, 1H, CH=N), 7.84 (d, *J* = 8.7 Hz, 2H, Ar), 7.71 (q, *J* = 8.5 Hz, 4H, Ar), 7.53 (d, *J* = 8.2 Hz, 2H, Ar), 7.31 (d, *J* = 8.0 Hz, 2H, Ar), 7.21 (d, *J* = 8.2, Hz, 2H, Ar), 7.15 (d, *J* = 8.3, Hz, 2H, Ar) , 6.98 (d, *J* = 8.7 Hz, 2H, Ar), 4.04 (t, *J* = 6.5 Hz, 2H, $Ar(CH_2)_9CH_2OAr$), 2.84 – 2.42 (m, 4H, $ArCH_2(CH_2)_9OAr$, $ArCH_2(CH_2)_{10}CH_3$), 1.83 (p, *J* = 6.7 Hz, 2H, $Ar(CH_2)_8CH_2CH_2OAr$), 1.72 – 1.60 (m, 4H, $ArCH_2CH_2(CH_2)_8OAr$, $ArCH_2CH_2(CH_2)_9CH_3$), 1.53 – 1.06 (m, 30H, $Ar(CH_2)_2(CH_2)_6CH_2CH_2OAr$, $ArCH_2CH_2(CH_2)_9CH_3$), 0.90 (t, *J* = 6.7 Hz, 3H, $ArCH_2CH_2(CH_2)_9CH_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 161.71, 158.97, 149.96, 145.21, 143.79, 140.49, 136.57, 130.37, 129.25, 129.20, 129.07, 127.49, 127.08, 120.76, 114.66, 110.55, 68.17, 35.56, 35.51, 31.41, 29.70, 29.62, 29.54, 29.48, 29.38, 29.33, 29.18, 28.01, 26.01, 22.71, 14.14.

Elemental Analysis: Calculated for $C_{48}H_{62}N_2O$: C 84.41%, H 9.15 %, N 4.10 %, Found: C 84.12%, H 9.43%, N 4.00 %.

CB10O.14: IR ν (cm^{-1}): 2916, 2848, 2231 (C≡N stretch), 1622 (C=N), 1608 (para disubstituted benzene), 1511, 1249, 1171, 813, 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* = 8.6 Hz, 4H, Ar), 7.53 (d, *J* = 8.2 Hz, 2H, Ar), 7.31 (d, *J* = 8.1 Hz, 2H, Ar), 7.21(d, *J*= 8.3 Hz, 2H, Ar), 7.16 (d, *J*= 8.1 Hz, 2H, Ar), 6.98 (d, *J* = 8.7 Hz, 2H, Ar), 4.04 (t, *J* = 6.5 Hz, 2H, $Ar(CH_2)_9CH_2OAr$), 2.73 – 2.59 (m, 4H, $ArCH_2(CH_2)_9OAr$, $ArCH_2(CH_2)_{12}CH_3$), 1.83 (p, *J* = 6.7 Hz, 2H, $Ar(CH_2)_8CH_2CH_2OAr$), 1.74 – 1.58 (m, 4H, $ArCH_2CH_2(CH_2)_8OAr$, $ArCH_2CH_2(CH_2)_{11}CH_3$), 1.32 (m, 34H, $Ar(CH_2)_2(CH_2)_6CH_2CH_2OAr$, $ArCH_2CH_2(CH_2)_{11}CH_3$), 0.91 (t, *J* = 6.7 Hz, 3H, $ArCH_2CH_2(CH_2)_{11}CH_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 161.73, 158.97, 149.62, 145.64, 143.80, 140.51, 136.47, 132.57, 130.39, 129.20, 129.08, 127.49, 127.08, 120.76, 119.06, 114.66, 110.55, 68.18, 35.65, 35.51, 31.94, 31.59, 31.41, 29.72, 29.70, 29.68, 29.63, 29.54, 29.48, 29.38, 29.35, 29.33, 29.32, 29.18, 26.01, 22.71, 14.14.

Elemental Analysis: Calculated for $C_{50}H_{66}N_2O$: C 84.45 %, H 9.36 %, N 3.94 %, Found: C 84.43 %, H 9.40 %, N 3.91%.

CB10O.16: IR ν (cm^{-1}): 2914, 2847, 2232 (C≡N stretch), 1621 (C=N), 1606 (para disubstituted benzene), 1510, 1249, 1169, 812, 545.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.42 (s, 1H, CH=N), 7.84 (d, *J* = 8.7 Hz, 2H, Ar), 7.71 (q, *J* = 8.3 Hz, 4H, Ar), 7.53 (d, *J* = 8.2 Hz, 2H, Ar), 7.31 (d, *J* = 8.0 Hz, 2H, Ar), 7.21(d, *J*= 8.2, Hz, 2H, Ar) – 7.15 (d, *J*= 8.2 Hz, 2H, Ar) , 6.98 (d, *J* = 8.7 Hz, 2H, Ar), 4.04 (t, *J* = 6.5 Hz, 2H, $Ar(CH_2)_9CH_2OAr$), 2.73 – 2.59 (m, 4H, $ArCH_2(CH_2)_9OAr$, $ArCH_2(CH_2)_{14}CH_3$), 1.83 (p, *J* = 6.6 Hz, 2H, $Ar(CH_2)_8CH_2CH_2OAr$), 1.60 (m, 4H, $ArCH_2CH_2(CH_2)_8OAr$, $ArCH_2CH_2(CH_2)_{13}CH_3$), 1.54 – 1.06 (m, 38H, $Ar(CH_2)_2(CH_2)_6CH_2CH_2OAr$, $ArCH_2CH_2(CH_2)_{13}CH_3$), 0.90 (t, *J* = 6.7 Hz, 3H, $ArCH_2CH_2(CH_2)_{13}CH_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 161.71, 158.97, 149.94, 145.64, 143.80, 140.49, 136.47,132.57, 130.37, 129.25, 129.20, 129.07, 127.49. 127.08, 120.76, 119.06, 114.66, 110.55, 68.17, 35.65, 35.51, 31.94, 31.41, 29.72, 29.63, 29.63, 29.54, 29.48, 29.38, 29.34, 29.18, 26.01, 22.71, 14.14.

Elemental Analysis: Calculated for $C_{52}H_{70}N_2O$: C 84.50%, H 9.55 %, N 3.79%, Found: C 84.28 %, H 9.65%, N 3.74%.

CB10O.18: IR ν (cm^{-1}): 2914, 2847, 2231 (C≡N stretch), 1622 (C=N), 1606 (para disubstituted benzene), 1510, 1248, 1168, 812, 544.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.42 (s, 1H, CH=N), 7.84 (d, *J* = 8.7 Hz, 2H, Ar), 7.71 (q, *J* = 8.4 Hz, 4H, Ar), 7.53 (d, *J* = 8.2 Hz, 2H, Ar), 7.31 (d, *J* = 8.1 Hz, 2H, Ar), 7.21(d, *J*= 8.3 Hz, 2H, Ar) – 7.15 (d, *J*= 8.3 Hz, 2H, Ar), 6.98 (d, *J* = 8.8 Hz, 2H, Ar), 4.04 (t, *J* = 6.5 Hz, 2H, $Ar(CH_2)_9\underline{CH_2}OAr$), 2.73 – 2.59 (m, 4H, $ArCH_2\underline{CH_2}(CH_2)_8OAr$, $ArCH_2\underline{CH_2}(CH_2)_{15}CH_3$), 1.83 (p, *J* = 6.7 Hz, 2H, $Ar(CH_2)_8\underline{CH_2}CH_2OAr$), 1.72- 1.58 (m, 4H, $ArCH_2\underline{CH_2}(CH_2)_8OAr$, $ArCH_2\underline{CH_2}(CH_2)_{15}CH_3$), 1.53 – 1.21 (m, 42H, $Ar(CH_2)_2\underline{(CH_2)_6}CH_2CH_2OAr$, $ArCH_2CH_2\underline{(CH_2)_{15}}CH_3$), 0.90 (t, *J* = 6.7 Hz, 3H, $ArCH_2CH_2(CH_2)_{15}\underline{CH_3}$).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 161.79, 158.98, 149.93, 140.56, 132.57, 130.37, 129.20, 129.07, 127.49, 127.08, 120.76, 114.66,110.58, 68.17, 35.65, 35.51, 31.94, 31.59, 31.41, 29.72, 29.63, 29.54, 29.48, 29.38, 29.35, 29.18, 26.01, 22.71, 14.14

Elemental Analysis: Calculated for $C_{35}H_{36}N_2O$: C 84.54%, H 9.72%, N 3.65%, Found: C 84.64 %, H 9.73%, N 3.61 %

Thermal Data

Table S1. The transitional properties of the CB10O.*m* series.

n	T_{Cr-}/˚C ΔH/kJmol^{-1} ΔS/R	$T_{SmYSmC_{TB-DH}}$/˚C $^{g}T_{SmYSmC_{TB-SH}}$/˚C	T_{SmXSm1}/˚C $^{d}T_{Sm\ C_{TB-DH}Sm C_{TBSH}}$ /˚C ΔH/kJmol^{-1} ΔS/R	$T_{SmXN_{TB}}$/˚C $^{a}T_{Sm1N_{TB}}$/˚C $^{c}T_{SmC\ TB-SH}N_{TB}$/˚C $^{e}T_{SmC\ TB-SH}SmA$/˚C ΔH/kJmol^{-1} ΔS/R	$T_{N_{TB}N}$/˚C $^{b}T_{Sm1N}$/˚C $^{f}T_{SmAN}$/˚C	T_{NI}/˚C ΔH/kJmol^{-1} ΔS/R
1	115.2 41.50 12.86				95.3* ≈ 0	133.4 1.28 0.38
2	105.4 29.22 9.29			79.4* 4.07 1.39	90.0* ≈ 0	130.1 1.67 0.50
3	94.6 44.67 14.62		75.9* 1.82 0.63	^{a}87.5* 1.78 0.59	95.5* ≈ 0	135.2 1.65 0.49
4	98.3 20.56 6.66		77.7* 0.02 0.01		^{b}90.5* 0.58 0.19	123.1 0.78 0.24
5	97.8 26.35 8.55		68.0* 1.66 0.59		^{b}93.5* 1.86 0.61	129.5 1.42 0.42
6	86.8 23.26 7.78		62.6* 1.82 0.65		^{b}94.5 2.79 0.91	121.0 1.40 0.43
7	90.3 18.05 5.98			^{a}80.9* 1.66 0.57	82.3* 0.02 0.01	119.6 1.47 0.45
8	95.9 30.55 9.96			^{a}74.2* 1.51 0.52	78.5* ≈ 0	114.2 1.21 0.38
9	92.8 32.03 10.54				80.4* ≈ 0	113.6 1.42 0.44
10	79.4 49.71 16.98				77.0* ≈ 0	108.2 1.19 0.38
12	87.3 61.31 20.48	61.3*†	^{d}75.4* 0.06 0.02	^{C}80.0* ≈ 0	81.2* ≈ 0	107.7 1.82 0.57
14	87.5 70.98 23.69	61.6*†	^{d} 73.9* ≈ 0	^{C}79.1* 0.11 0.04	80.9* ≈ 0	106.1 1.65 0.53
16	81.8 76.01 25.78	71.4* 8.79 3.07	^{d} 76.7* ≈ 0	^{e}88.1* 0.52 0.17	^{f}91.7* 0.12 0.04	104.8 2.14 0.68
18	85.4 63.39 21.28	^{g}75.9*†		^{e} 89.3* 0.79 0.26	^{f}97.6 0.07 0.02	102.7 1.92 0.61

*Data extracted from cooling trace. †Overlapping peaks preclude enthalpy change measurement

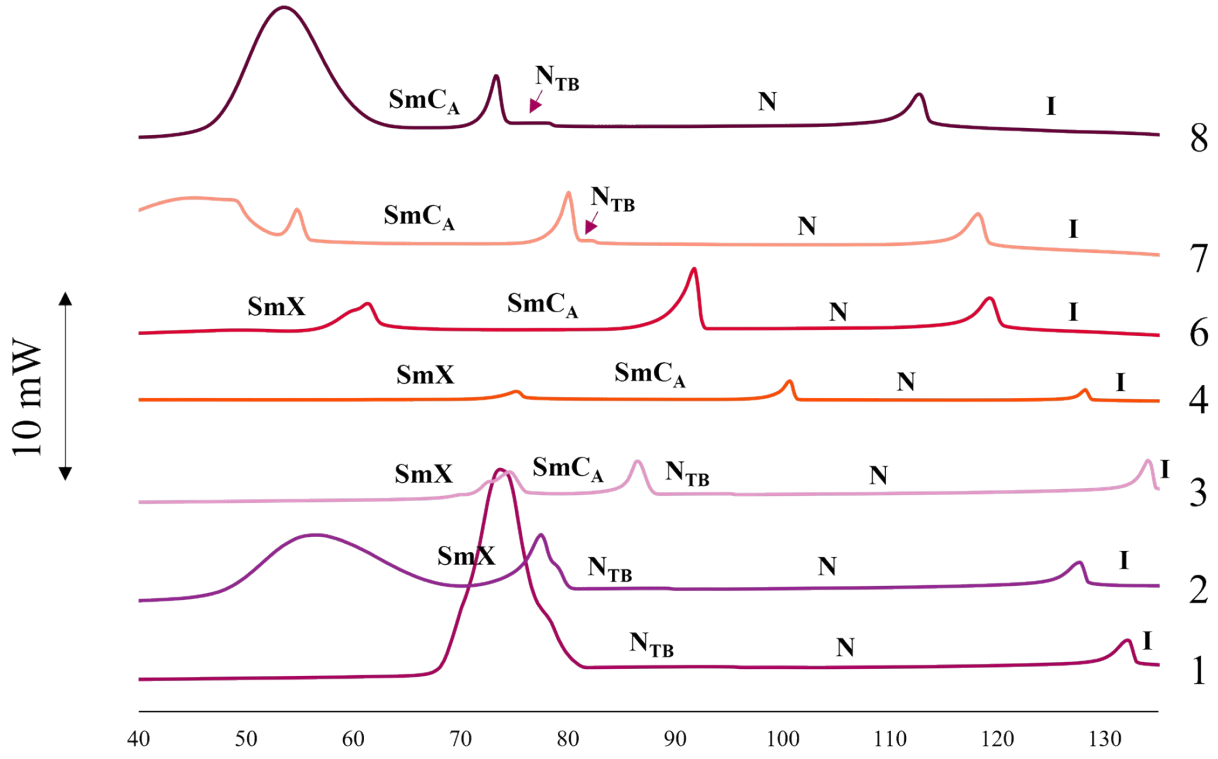


Figure S1. Representative DSC traces for CB10O.*m* series for *m* = 1-8 obtained on the first cooling of the sample from the isotropic phase.

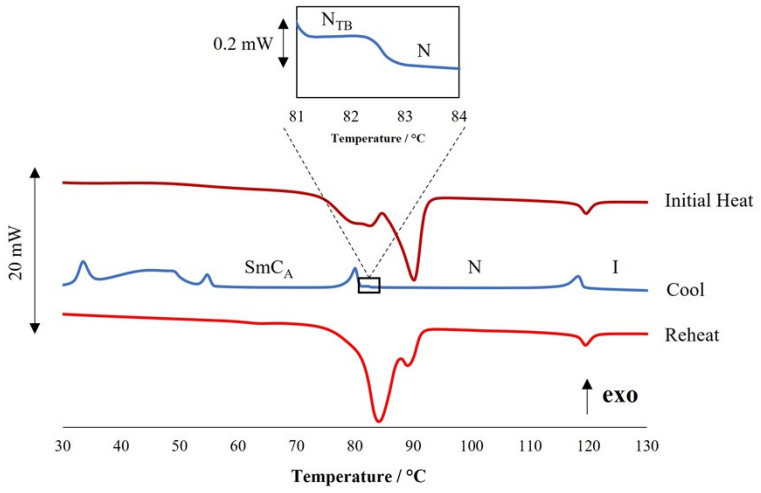


Figure S2. The DSC traces obtained for CB10O.7 on initial heat, first cooling, and subsequent reheating of the sample, revealing that there is no detectable decomposition of the sample during this thermal cycle. The inset shows the N_{TB}-N transition.