Electronic Supplementary Information (ESI)

Twist-bend nematic liquid crystals based on thioether linkage

Yuki Arakawa,* Kenta Komatsu and Hideto Tsuji

Department of Applied Chemistry and Life Science, Graduate School of Engineering, Toyohashi University of Technology, 1-1 Hibarigaoka, Tempaku-cho, Toyohashi, Aichi 441-8580, Japan. E-mail: arakawa@tut.jp

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1. Chemicals

4-Bromobenzenethiol, 4-bromophenol, 4-cyanophenylboronic acid pinacol ester, corresponding *α,ω*-dibromoalkanes, 18-crown 6-ether, tetrakis(triphenylphosphine)palladium (0) [$Pd(PPh_3)_4$] and triphenylphosphine (PPh_3) were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan), whilst acetone, tetrahydrofuran (THF) and 1,4-dioxane for reaction solvent were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). Acetonitrile for reaction solvent, potassium carbonate (K_2CO_3) and cesium carbonate (Cs_2CO_3) were purchased from Nacalai Tesque Inc. (Kyoto, Japan).

2. Synthesis and characterization of CBS*n*SCB

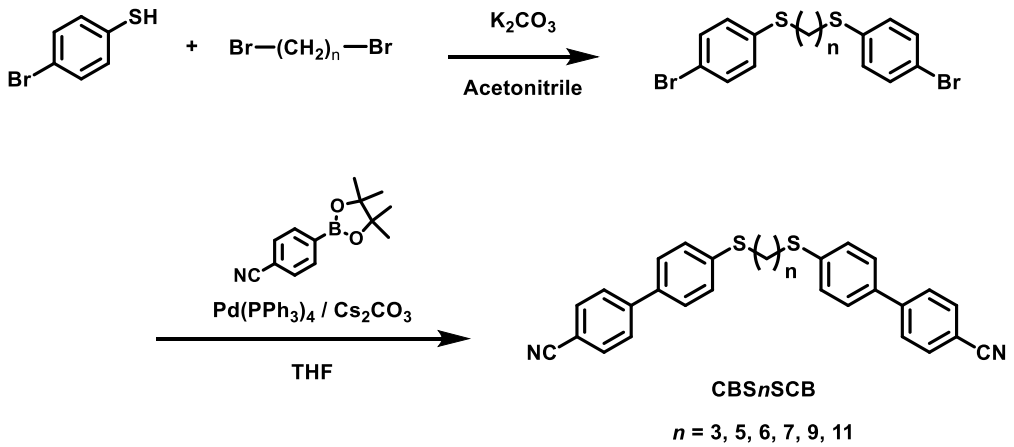

Fig. S1. Synthetic route of CBS*n*SCB.

Synthesis of 1,3-bis[(4-bromophenyl)thio]propane (General procedure)
A mixture of 1,3-dibromopropane (0.17 mL, 1.67 mmol), 4-bromobenzenethiol (0.653 g, 3.46 mmol), potassium carbonate (0.947 g, 6.85 mmol) and acetonitrile (12 mL) was stirred at reflux temperature. After 18h, the mixture was extracted with dichloromethane, washed with water and brine, and dried over $MgSO_4$. After removing the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (eluent: dichloromethane/hexane = 1/5), to afford a colorless solid (0.663 g, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.4 Hz, Ar–*H*, 4H), 7.16 (d, J = 8.4 Hz, Ar–*H*, 4H), 3.01 (t, J = 7.0 Hz, S–C*H*$_2$, 4H), 1.92 (tt, J = 7.0 and 7.0 Hz, S–CH$_2$–C*H*$_2$, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.1, 132.0, 131.0, 120.1, 32.5, 28.1 ppm.

1,5-bis[(4-bromophenyl)thio]pentane
A colorless solid (0.703 g, 72%). ^{1}H NMR (400 MHz) δ 7.39 (d, J = 8.4 Hz, Ar–*H*, 4H), 7.17 (d, J = 8.4 Hz, Ar–*H*, 4H), 2.88 (t, J = 7.2 Hz, S–C*H*$_2$, 4H), 1.64 (tt, J = 6.8 and 7.2 Hz, S–CH$_2$–C*H*$_2$, 4H), 1.59–1.50 (m, S–(CH$_2$)$_2$–C*H*$_2$, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.9, 135.9, 131.9, 131.9, 131.9, 131.9, 130.6, 130.6, 130.6, 130.6, 119.6, 119.6, 33.6, 33.6, 28.5, 28.5, 27.7 ppm.

1,7-bis[(4-bromophenyl)thio]heptane
A colorless solid (0.979 g, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.8 Hz, Ar–*H*, 4H), 7.17 (d, J = 8.8 Hz, Ar–*H*, 4H), 2.88 (t, J = 7.4 Hz, S–C*H*$_2$, 4H), 1.62 (tt, J = 7.4 and 7.4 Hz, S–CH$_2$–C*H*$_2$, 4H), 1.41 (tt, J = 7.2 and 7.4 Hz, S–(CH$_2$)$_2$–C*H*$_2$, 4H), 1.36–

1.24 (m, S–$(CH_2)_3$–CH_2, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.2, 136.2, 131.9, 131.9, 131.9, 131.9, 130.4, 130.4, 130.4, 130.4, 119.5, 33.6, 33.6, 28.9, 28.9, 28.62, 28.55, 28.55 ppm.

1,9-bis[(4-bromophenyl)thio]nonane

A colorless solid (1.007 g, 96%). ^{1}H NMR (400 MHz) δ 7.39 (d, J = 8.4 Hz, Ar–*H*, 4H), 7.17 (d, J = 8.4 Hz, Ar–*H*, 4H), 2.88 (t, J = 7.4 Hz, S–CH_2, 4H), 1.62 (tt, J = 7.4 and 7.4 Hz, S–CH_2–CH_2, 4H), 1.40 (tt, J = 6.6 and 7.4 Hz, S–$(CH_2)_2$–CH_2, 4H), 1.32–1.22 (m, S–$(CH_2)_3$–$(CH_2)_2$, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.3, 136.3, 131.8, 131.8, 131.8, 131.8, 130.4, 130.4, 130.4, 130.4, 119.4, 119.4, 33.7, 33.7, 29.3, 29.01, 29.01, 28.96, 28.96, 28.7, 28.7 ppm.

1,11-bis[(4-bromophenyl)thio]undecane

A colorless solid (0.766 g, 76%). ^{1}H NMR (400 MHz) δ 7.38 (d, J = 8.4 MHz, Ar–*H*, 4H), 7.17 (d, J = 8.4 Hz, Ar–*H*, 4H), 2.88 (t, J = 7.4 Hz, S–CH_2, 4H), 1.62 (tt, J = 7.0 and 7.4 Hz, S–CH_2–CH_2, 4H), 1.40 (tt, J = 6.8 and 7.0 Hz, S–$(CH_2)_2$–CH_2, 4H), 1.33–1.21 (m, S–$(CH_2)_3$–CH_2, S–$(CH_2)_4$–CH_2 and S–$(CH_2)_5$–CH_2, 10H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.3, 136.3, 131.8, 131.8, 131.8, 131.8, 130.4, 130.4, 130.4, 130.4, 119.4, 119.4, 33.7, 29.4, 29.4, 29.4, 29.4, 29.1, 29.1, 29.0, 29.0, 28.8, 28.8 ppm.

4',4'''-[1,3-propanediylbis(thio)]bis(1,1'-Biphenyl)-4-carbonitrile (CBS3SCB)
(General procedure)

THF (12 mL) degassed bubbling argon and 4-cyanophenylboronic acid pinacol ester 0.115 g, 0.504 mmol) added to 1,3-bis[(4-bromophenyl)thio]propane (99.6 mg, 0.238 mmol), Cs_2CO_3 (0.312 g, 0.95 mmol), $Pd(PPh_3)_4$ (27.7 mg, 24.0 μmol) under argon. After stirring at reflux temperature for 18h, the reaction mixture was extracted with dichloromethane, washed with water and brine, and the organic layer was dried over $MgSO_4$. After removing the solvent under reduced pressure, the crude product was purified by silica gel column (eluent: dichloromethane/hexane = 5/1) and recrystallized from hexane and dichloromethane, to afford a colorless solid (68.1 g, 62%). ^{1}H NMR (400 MHz) δ 7.71 (d, J = 8.4 Hz, Ar–*H*, 4H), 7.63 (d, J = 8.4 Hz, Ar–*H*, 4H), 7.50 (d, J = 8.4 Hz, Ar–*H*, 4H), 7.40 (d, J = 8.4 Hz, Ar–*H*, 4H), 3.14 (t, J = 7.0 Hz, S–CH_2, 4H), 2.06 (tt, J = 7.0 and 7.0 Hz, S–CH_2–CH_2, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 137.4, 136.6, 132.6, 132.6, 129.2, 129.2, 127.6, 127.6, 127.3, 127.3, 118.8, 111.0, 31.9, 31.9, 28.1 ppm.

4',4'''-[1,5-pentanediylbis(thio)]bis(1,1'-Biphenyl)-4-carbonitrile (CBS5SCB)
A colorless solid (0.104 g, 32%). ^{1}H NMR (400 MHz) δ 7.71 (d, J = 8.4 Hz, Ar–*H*, 4H), 7.65 (d, J = 8.4 Hz, Ar–*H*, 4H), 7.50 (d, J = 8.4 Hz, Ar–*H*, 4H), 7.39 (d, J = 7.39 Hz, Ar–*H*, 4H), 2.98 (t, J = 6.8 Hz, S–CH_2, 4H), 1.73 (tt, J = 6.8 and 7.2 Hz, S–CH_2–CH_2, 4H), 1.68–1.59 (m, S–$(CH_2)_2$–CH_2, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 144.9, 138.2, 138.2, 136.3, 136.3, 132.7, 132.7, 132.7, 132.7, 128.9, 128.9, 128.9, 128.9, 127.6, 127.6, 127.6, 127.6, 127.3, 127.3, 127.3, 127.3, 118.9, 118.9, 110.9, 110.9, 33.0, 33.0, 28.5, 28.5, 27.9 ppm.

4',4'''-[1,7-heptanediylbis(thio)]bis(1,1'-Biphenyl)-4-carbonitrile (CBS7SCB)
A colorless solid (0.184 g, 56 %). ^{1}H NMR (400 MHz) δ 7.71 (d, J = 8.4 Hz, Ar–*H*, 4H), 7.65 (d, J = 8.4 Hz, Ar–*H*, 4H), 7.51 (d, J = 8.4 Hz, Ar–*H*, 4H), 7.38 (d, J = 8.4 Hz, Ar–*H*, 4H), 2.97 (t, J = 7.4 Hz, S–CH_2, 4H), 1.70 (tt, J = 7.4 and 7.4 Hz, S–CH_2–CH_2, 4H), 1.47 (tt, J = 7.2 and 7.4 Hz, S–$(CH_2)_2$–CH_2, 4H), 1.32 (tt, J = 7.2 and 7.4 Hz, S–$(CH_2)_3$–CH_2, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 144.9, 138.5, 138.5, 136.2, 136.2, 132.6, 132.6, 132.6, 132.6, 128.7, 128.7, 128.7, 128.7, 127.5, 127.5, 127.5, 127.5, 127.3, 127.3, 127.3, 127.3, 118.9, 118.9, 110.8, 110.8, 33.1, 33.1, 28.9, 28.9, 28.7, 28.6, 28.6 ppm.

4',4'''-[1,9-nonanediylbis(thio)]bis(1,1'-Biphenyl)-4-carbonitrile (CBS9SCB)
A colorless solid (0.238 g, 73%). ^{1}H NMR (400 MHz) δ 7.72 (d, J = 8.4 Hz, Ar–*H*, 4H), 7.66 (d, J = 8.4 Hz, Ar–*H*, 4H), 7.51 (d, J = 8.4 Hz, Ar–*H*, 4H), 7.38 (d, J = 8.4 Hz, Ar–*H*, 4H), 2.97 (t, J = 7.4 Hz, S–CH_2, 4H), 1.69 (tt, J = 7.4 and 7.4 Hz, S–CH_2–CH_2, 4H), 1.45 (tt, J = 7.2 and 7.4 Hz, S–$(CH_2)_2$–CH_2, 4H), 1.37–1.28 (m, S–$(CH_2)_3$–$(CH_2)_3$, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 144.9, 138.6, 138.6, 136.1, 136.1, 132.6, 132.6, 132.6, 132.6, 128.6, 128.6, 128.6, 128.6, 127.5, 127.5, 127.5, 127.5, 127.3, 127.3, 127.3, 127.3, 118.9, 118.9, 110.8, 110.8, 33.1, 33.1, 29.3, 29.04, 29.04, 28.97, 28.97, 28.8, 28.8 ppm

4',4'''-[1,11-undecanediylbis(thio)]bis(1,1'-Biphenyl)-4-carbonitrile (CBS11SCB)
A colorless solid (0.194 g, 60%). ^{1}H NMR (400 MHz) δ 7.72 (d, J = 8.8 Hz, Ar–*H*, 4H), 7.66 (d, J = 8.4 Hz, Ar–*H*, 4H), 7.51 (d, J = 8.8 Hz, Ar–*H*, 4H), 7.39 (d, J = 8.4 Hz, Ar–*H*, 4H), 2.97 (t, J = 7.4 Hz, S–CH_2, 4H), 1.69 (tt, J = 7.4 and 7.6 Hz, S–CH_2–CH_2, 4H), 1.45 (tt, J =6.8 and 7.6 Hz, S–$(CH_2)_2$–CH_2, 4H), 1.37–1.24 (m, S–$(CH_2)_3$–$(CH_2)_5$, 10H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 144.9, 138.6, 138.6, 136.1, 136.1, 132.6, 132.6, 132.6, 132.6, 128.6, 128.6, 128.6, 128.6, 127.5, 127.5, 127.5, 127.5, 127.3, 127.3,

127.3, 127.3, 118.9, 118.9, 110.8, 110.8, 33.1, 33.1, 29.4, 29.4, 29.4, 29.1, 29.1, 29.0, 29.0, 28.8, 28.8 ppm.

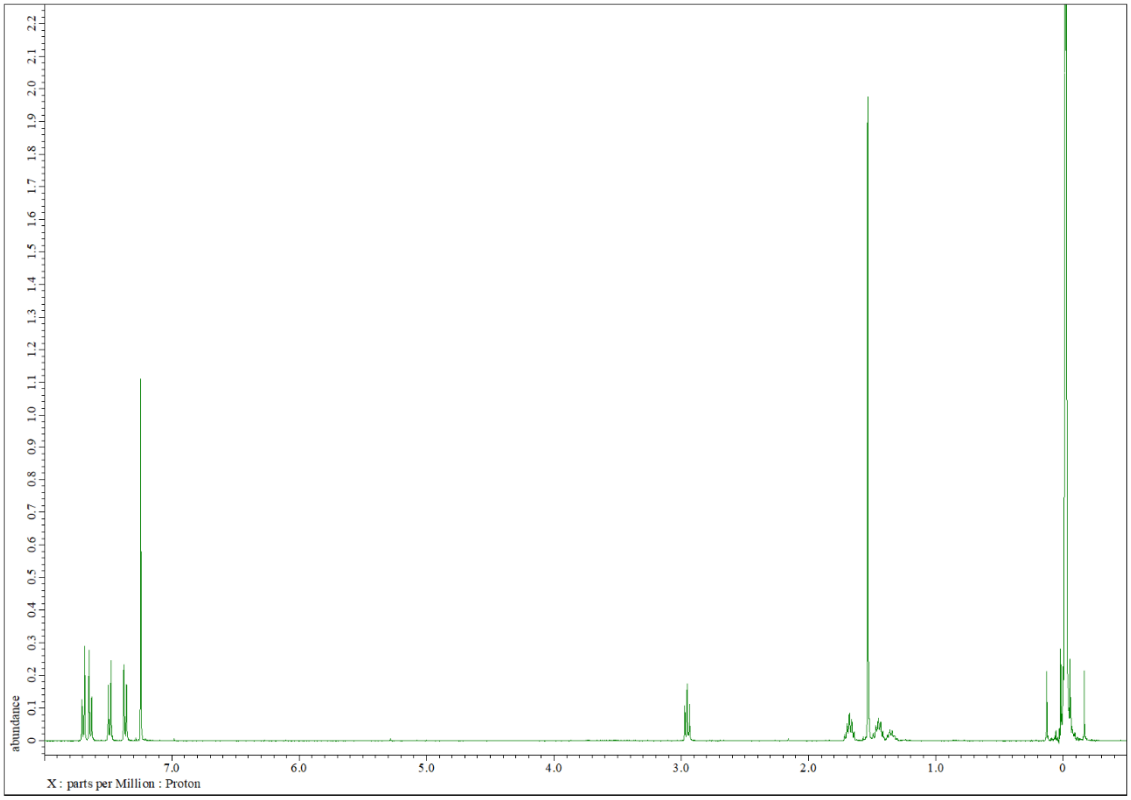

Fig. S2. Representative ^{1}H NMR spectrum for CBS7SCB in $CDCl_3$.

3. Synthesis and characterization of CBS*n*OCB

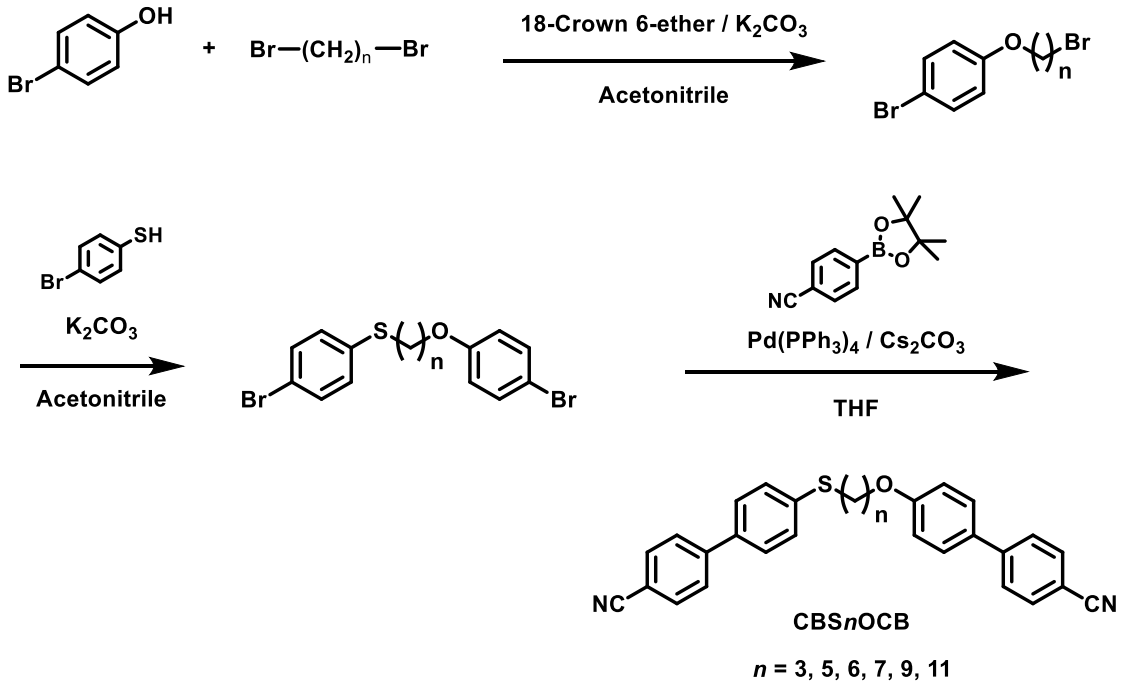

Fig. 3. Synthetic route of CBS*n*OCB.

Synthesis of 1-Bromo-4-(3-bromopropoxy)benzene (General procedure)

According to the literature [1], A mixture of 1,3-dibromopropane (1.00 g, 4.97 mmol), 4-bromophenol (0.430 g, 2.49 mmol), potassium carbonate (0.674 g, 4.88 mmol), 18-crown 6-ether (15.7 mg, 59.2 μmol) and acetone (12 mL) was stirred at reflux temperature. After 18h, the mixture was extracted with dichloromethane, washed with water and brine, and dried over $MgSO_4$. After removing the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (eluent: dichloromethane /hexane = 1/5), to afford a colorless liquid (0.324 g, 44%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.8 Hz, Ar–*H*, 2H), 6.79 (d, J = 8.8 Hz, Ar–*H*, 2H), 4.07 (t, J = 5.8 Hz, O–CH_2, 2H), 3.59 (t, J = 6.4 Hz, Br–CH_2, 2H), 2.31 (tt, J = 5.8 and 6.4 Hz, O–CH_2–CH_2, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 132.3, 116.4, 113.1, 65.6, 32.3, 29.8, 32.3, 29.8 ppm.

1-Bromo-4-(5-bromopentyloxy)benzene

A colorless solid (0.830 g, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.8 Hz, Ar–*H*, 2H), 6.77 (d, J = 8.8 Hz, Ar–*H*, 2H), 3.93 (t, J = 6.2 Hz, O–CH_2, 2H), 3.44 (t, J = 6.8 Hz, Br–CH_2, 2H), 1.94 (tt, J = 6.8 and 7.2 Hz, Br–CH_2–CH_2, 2H), 1.81 (tt, J = 6.2 and

7.0 Hz, O–CH_2–CH_2, 2H), 1.67–1.57 (m, S–$(CH_2)_2$–CH_2, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 132.3, 116.3, 112.8, 67.9, 33.5, 32.5, 28.4, 24.8 ppm.

Bromo-4-(7-bromoheptyloxy)benzene
A colorless solid (0.839 g, 41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.8 Hz, Ar–*H*, 2H), 6.77 (d, J = 8.8 Hz, Ar–*H*, 2H), 3.92 (t, J = 6.6 Hz, O–CH_2, 2H), 3.41 (t, J = 6.8 Hz, Br–CH_2, 2H), 1.87 (tt, J = 6.6 and 7.6, Hz, O–CH_2–CH_2, 2H), 1.78 (tt, J = 6.8 and 7.0 Hz, Br–CH_2–CH_2, 2H), 1.47 (tt, J = 7.0 and 7.6 Hz, S–$(CH_2)_2$–CH_2, 2H), 1.47 (tt, J = 7.0 and 7.6 Hz, Br–$(CH_2)_2$–CH_2, 4H), 1.43–1.34 (m, S–$(CH_2)_3$–CH_2, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 132.2, 132.2, 116.3, 116.3, 112.6, 112.6, 68.1, 33.8, 32.7, 29.1, 28.5, 28.1, 25.9 ppm.

1-Bromo-4-(9-bromononyloxy)benzene
A colorless solid (0.853 g, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.4 Hz, Ar–*H*, 2H), 6.77 (d, J = 8.4 Hz, Ar–*H*, 2H), 3.91 (t, J = 6.4 Hz, O–CH_2, 2H), 3.41 (t, J = 6.8 Hz, Br–CH_2, 2H), 1.86 (tt, J = 6.8 and 7.1 Hz, Br–CH_2–CH_2, 2H), 1.76 (tt, J = 6.4 and 6.9 Hz, O–CH_2–CH_2, 2H), 1.49–1.25 (m, J = 6.9 and 7.1 Hz, O–$(CH_2)_2$–(CH_2)$_5$, 10H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 132.2, 116.4, 112.6, 68.3, 34.0, 32.8, 29.3, 29.24, 29.16, 28.7, 28.2, 26.0 ppm.

1-Bromo-4-(11-bromoundecyloxy)benzene
A colorless solid (0.140 g, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 9.2 Hz, Ar–*H*, 2H), 6.77 (d, J = 9.2 Hz, Ar–*H*, 2H), 3.91 (t, J = 6.6 Hz, O–CH_2, 2H), 3.41 (t, J = 6.8 Hz, Br–CH_2, 2H), 1.85 (tt, J = 6.8 and 7.1 Hz, Br–CH_2–CH_2, 2H), 1.76 (tt, J = 6.6 and 7.1 Hz, O–$(CH_2)_2$–CH_2, 2H), 1.25–1.50 (m, O–$(CH_2)_3$–CH_2, 14H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.l, 132.2, 116.3, 112.6, 68.3, 32.0, 32.9, 29.5, 29.44, 29.41, 29.34, 29.2, 28.8, 28.2, 26.0 ppm.

1-Bromo-4-{[3-(4-bromophenoxy)propyl]thio}benzene (General procedure)
A mixture of 1-Bromo-4-(3-bromopropoxy)benzene (0.213 g, 0.725 mmol), 4-bromobenzenethiol (0.137 g, 0.723 mmol), potassium carbonate (0.198 g, 1.44 mmol) and acetonitrile (12 mL) was stirred at reflux temperature. After 18h, the mixture was extracted with ethylacetate, washed with water and brine, and dried over $MgSO_4$. After removing the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (eluent: dichloromethane/hexane = 1/5), to afford a colorless solid (0.230 g, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.8 Hz, Ar–*H*,

2H), 7.36 (d, *J* = 8.8 Hz, Ar–*H*, 2H), 7.20 (d, *J* = 8.8 Hz, Ar–*H*, 2H), 6.75 (d, *J* = 8.8 Hz, Ar–*H*, 2H), 4.02 (t, *J* = 6.0 Hz, O–CH_2, 2H), 3.09 (t, *J* = 7.2 Hz, S–CH_2, 2H), 2.08 (tt, *J* = 6.0 and 7.2 Hz, O–CH_2–CH_2, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 157.8, 135.4, 132.3, 132.0, 130.8, 119.9, 116.3, 113.0, 66.1, 30.3, 28,8 ppm.

1-Bromo-4-{[5-(4-bromophenoxy)pentyl]thio}benzene

A colorless solid (0.220 g, 81%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.36 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.18 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 6.75 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 3.91 (t, *J* = 6.2 Hz, O–CH_2, 2H), 2.91 (t, *J* = 7.2 Hz, S–CH_2, 2H), 1.78 (tt, *J* = 6.2 and 7.0 Hz, O–CH_2–CH_2, 2H), 1.70 (tt, *J* = 7.2 and 7.3 Hz, S–CH_2–CH_2, 2H), 1.65–1.57 (m, *J* = 7.0 and 7.3 Hz, S–$(CH_2)_2$–CH_2, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 158.1, 136.0, 132.2, 131.9, 130.6, 119.6, 116.3, 112.7, 67.9, 33.7, 28.7, 25.2 ppm.

1-Bromo-4-{[7-(4-bromophenoxy)heptyl]thio}benzene

A colorless solid (0.642 g, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.39 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.36 (d, *J* = 9.2 Hz, Ar–*H*, 2H), 7.17 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 6.76 (d, *J* = 9.2 Hz, Ar–*H*, 2H), 3.90 (t, *J* = 6.4 Hz, O–CH_2, 2H), 2.89 (t, *J* = 7.4 Hz, S–CH_2, 2H), 1.76 (tt, *J* = 6.4 and 7.6 Hz, O–CH_2–CH_2, 2H), 1.64 (tt, *J* = 7.4 and 7.4 Hz, S–CH_2–CH_2, 2H), 1.45 (tt, *J* = 7.2 and 7.6 Hz, O–CH_2–CH_2, 2H), 1.45 (tt, *J* = 7.4 and 7.4 Hz, S–CH_2–CH_2–CH_2, 2H), 1.40–1.31 (m, O–$(CH_2)_3$–CH_2, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 158.2, 136.2, 132.2, 132.2, 131.9, 131.9, 130.4, 130.4, 119.5, 116.3, 116.3, 112.6, 68.1, 33.7, 29.1, 28.9, 28.8, 28.6, 25.9 ppm.

1-Bromo-4-{[9-(4-bromophenoxy)nonyl]thio}benzene

A colorless solid (0.233 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.35 (d, *J* = 9.2 Hz, Ar–*H*, 2H), 7.17 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 6.77 (d, *J* = 9.2 Hz, Ar–*H*, 2H), 3.91 (t, *J* = 6.4 Hz, O–CH_2, 2H), 2.88 (t, *J* = 6.8 Hz, S–CH_2, 2H), 1.75 (tt, *J* = 6.4 and 7.0 Hz, O–CH_2–CH_2, 2H), 1.63 (tt, *J* = 7.2 and 7.5 Hz, S–CH_2–CH_2, 2H), 1.50–1.25 (m, O–$(CH_2)_2$–$(CH_2)_5$, 10H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 158.3, 136.3, 132.2, 131.9, 130.4, 119.4, 116.3, 112.6, 68.2, 33.7, 29.4, 29.3, 29.2, 29.04, 28.98, 28.7, 26.0 ppm.

1-Bromo-4-{[11-(4-bromophenoxy)undecyl]thio}benzene

A colorless solid (0.165 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.39 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.36 (d, *J* = 8.8 Hz, Ar–*H*, 2H), 7.17 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 6.77 (d, *J* = 8.8 Hz, Ar–*H*, 2H), 3.91 (t, *J* = 6.6 Hz, O–CH_2, 2H), 2.88 (t, *J* = 7.4 Hz, S–CH_2, 2H), 1.76

(tt, J = 6.6 and 7.0 Hz, O–CH_2–CH_2, 2H), 1.69 (tt, J = 7.4 and 7.4 Hz, S–CH_2–CH_2, 2H), 1.53–1.26 (m, O–$(CH_2)_2$–(CH_2)$_7$, 14H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 136.3, 132.2, 131.8, 130.4, 119.4, 116.3, 112.6, 68.3, 33.7, 29.50, 29.46, 29.44, 29.3, 29.2, 29.1, 29.0, 28.8, 26.0 ppm.

4'-[(3-{[4'-cyano-(1,1'-biphenyl)-4-yl]oxy}propyl)thio]-(1,1'-biphenyl)-4-carbonitrile (NCS3OCN)

A colorless solid (0.131 g, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.4 Hz, Ar–*H*, 2H), 7.70 (d, J = 8.8 Hz, Ar–*H*, 2H), 7.69 (d, J = 8.4 Hz, Ar–*H*, 2H), 7.63 (d, J = 8.8 Hz, Ar–*H*, 2H),7.53 (d, J = 8.4 Hz, Ar–*H*, 2H), 7.51 (d, J = 8.4 Hz, Ar–*H*, 2H), 7.44 (d, J = 8.4 Hz, Ar–*H*, 2H), 6.99 (d, J = 8.4 Hz, Ar–*H*, 2H), 4.15 (t, J = 5.8 Hz, O–CH_2, 2H), 3.21 (t, J = 7.2 Hz, S–CH_2, 2H), 2.20 (tt, J = 5.8 and 7.2 Hz, O–CH_2–CH_2, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 145.2, 144.9, 137.7, 136.6, 132.7, 132.6, 131.8, 129.2, 128.4, 127.7, 127.4, 127.1, 119.0, 118.8, 115.2, 111.0, 66.1, 29.8, 28.9 ppm.

4'-[(5-{[4'-cyano-(1,1'-biphenyl)-4-yl]oxy}pentyl)thio]-(1,1'-biphenyl)-4-carbonitrile (NCS5OCN)

A colorless solid (0.135 g, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.8 Hz, Ar–*H*, 2H), 7.70 (d, J = 8.8 Hz, Ar–*H*, 2H), 7.65 (d, J = 8.8 Hz, Ar–*H*, 2H), 7.63 (d, J = 8.8 Hz, Ar–*H*, 2H), 7.53 (d, J = 8.8 Hz, Ar–*H*, 2H), 7.51 (d, J = 8.4 Hz, Ar–*H*, 2H), 7.40 (d, J = 8.4 Hz, Ar–*H*, 2H), 6.98 (d, J = 8.8 Hz, Ar–*H*, 2H), 4.02 (t, J = 6.4 Hz, O–CH_2, 2H), 3.05 (t, J = 7.2 Hz, S–CH_2, 2H), 1.86 (tt, J = 6.4 and 6.8 Hz, O–CH_2–CH_2, 2H), 1.80 (tt, J = 7.2 and 7.2 Hz, S–CH_2–CH_2, 2H), 1.73–1.62 (m, J = 6.8 and 7.2 Hz, S–$(CH_2)_2$–CH_2, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 145.2, 144.9, 138.3, 136.3, 132.7, 132.6, 131.5, 128.9, 128.4, 127.6, 127.4, 127.1, 119.1, 118.9, 115.1, 110.9, 110.2, 67.8, 33.1, 28.81, 28.78, 25.4 ppm.

4'-[(7-{[4'-cyano-(1,1'-biphenyl)-4-yl]oxy}heptyl)thio]-(1,1'-biphenyl)-4-carbonitrile (NCS7OCN)

A colorless solid (0.226 g, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.4 Hz, Ar–*H*, 2H), 7.69 (d, J = 8.4 Hz, Ar–*H*, 2H), 7.66 (d, J = 8.4 Hz, Ar–*H*, 2H), 7.64 (d, J = 8.4 Hz, Ar–*H*, 2H), 7.52 (d, J = 8.8 Hz, Ar–*H*, 2H), 7.51 (d, J = 8.4 Hz, Ar–*H*, 2H), 7.39 (d, J = 8.4 Hz, Ar–*H*, 2H), 6.98 (d, J = 8.8 Hz, Ar–*H*, 2H), 4.02 (t, J = 6.6 Hz, O–CH_2, 2H), 2.97 (t, J = 7.2 Hz, S–CH_2, 2H), 1.82 (tt, J = 6.6 and 7.0 Hz, O–CH_2–CH_2, 2H), 1.72 (tt, J = 7.2 and 7.8 Hz, S–CH_2–CH_2, 2H), 1.54–1.36 (m, O–$(CH_2)_2$–(CH_2)$_3$, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 145.2, 144.9, 138.5, 136.2, 132.64, 132.64, 132.57,

132.57, 131.4, 128.7, 128.7, 128.3, 128.3, 127.5, 127.5, 127.3, 127.3, 127.1, 127.1, 119.1, 118.9, 115.1, 115.1, 110.8, 110.1, 68.1, 33.1, 29.1, 28.93, 28.90, 28.7, 25.9 ppm.

4'-[(9-{[4'-cyano-(1,1'-biphenyl)-4-yl]oxy}nonyl)thio]-(1,1'-biphenyl)-4-carbonitrile (NCS9OCN)

A colorless solid (75.9 mg, 38%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.4 Hz, Ar–*H*, 2H), 7.69 (d, J = 8.4 Hz, Ar–*H*, 2H), 7.66 (d, J = 8.4 Hz, Ar–*H*, 2H), 7.64 (d, J = 8.4 Hz, Ar–*H*, 2H), 7.52 (d, J = 8.4 Hz, Ar–*H*, 2H), 7.51 (d, J = 8.8 Hz, Ar–*H*, 2H), 7.39 (d, J = 8.4 Hz, Ar–*H*, 2H), 6.99 (d, J = 8.8 Hz, Ar–*H*, 2H), 4.00 (t, J = 6.6 Hz, O–CH_2, 2H), 2.98 (t, J = 7.4 Hz, S–CH_2, 2H), 1.80 (tt, J = 6.6 and 7.0 Hz, O–CH_2–CH_2, 2H), 1.70 (tt, J = 7.4 and 7.4 Hz, S–CH_2–CH_2, 2H), 1.53–1.26 (m, O–$(CH_2)_2$–$(CH_2)_5$, 10H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 145.3, 145.0, 138.6, 136.1, 132.7, 132.6, 131.3, 128.7, 128.3, 127.5, 127.3, 127.1, 119.1, 118.9, 115.1, 110.8, 110.1, 68.2, 33.1, 29.4, 29.3, 29.2, 29.1,29.0, 28.8, 26.0 ppm.

4'-[(11-{[4'-cyano-(1,1'-biphenyl)-4-yl]oxy}undecyl)thio]-(1,1'-biphenyl)-4-carbonitrile (NCS11OCN)

A colorless solid (62.1 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.8 Hz, Ar–*H*, 2H), 7.69 (d, J = 8.8 Hz, Ar–*H*, 2H), 7.66 (d, J = 8.8 Hz, Ar–*H*, 2H), 7.64 (d, J = 8.4 Hz, Ar–*H*, 2H), 7.53 (d, J = 8.8 Hz, Ar–*H*, 2H), 7.50 (d, J = 8.8 Hz, Ar–*H*, 2H), 7.39 (d, J = 8.8 Hz, Ar–*H*, 2H), 6.99 (d, J = 8.8 Hz, Ar–*H*, 2H), 4.00 (t, J = 6.4 Hz, O–CH_2, 2H), 2.97 (t, J = 7.4 Hz, S–CH_2, 2H), 1.80 (tt, J = 6.4 and 7.0 Hz, O–CH_2–CH_2, 2H), 1.69 (tt, J = 7.4 and 7.4 Hz, S–CH_2–CH_2, 2H), 1.53–1.26 (m, O–$(CH_2)_2$–$(CH_2)_7$, 14H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 150.0, 145.0, 138.7, 136.1, 132.7, 132.6, 131.3, 128.6, 128.3, 127.5, 127.3, 127.1, 119.1, 118.9, 115.1, 110.8, 110.1, 68.2, 33.1, 30.9, 29.54, 29.49, 29.4, 29.24, 29.16, 29.0, 28.9, 26.1 ppm.

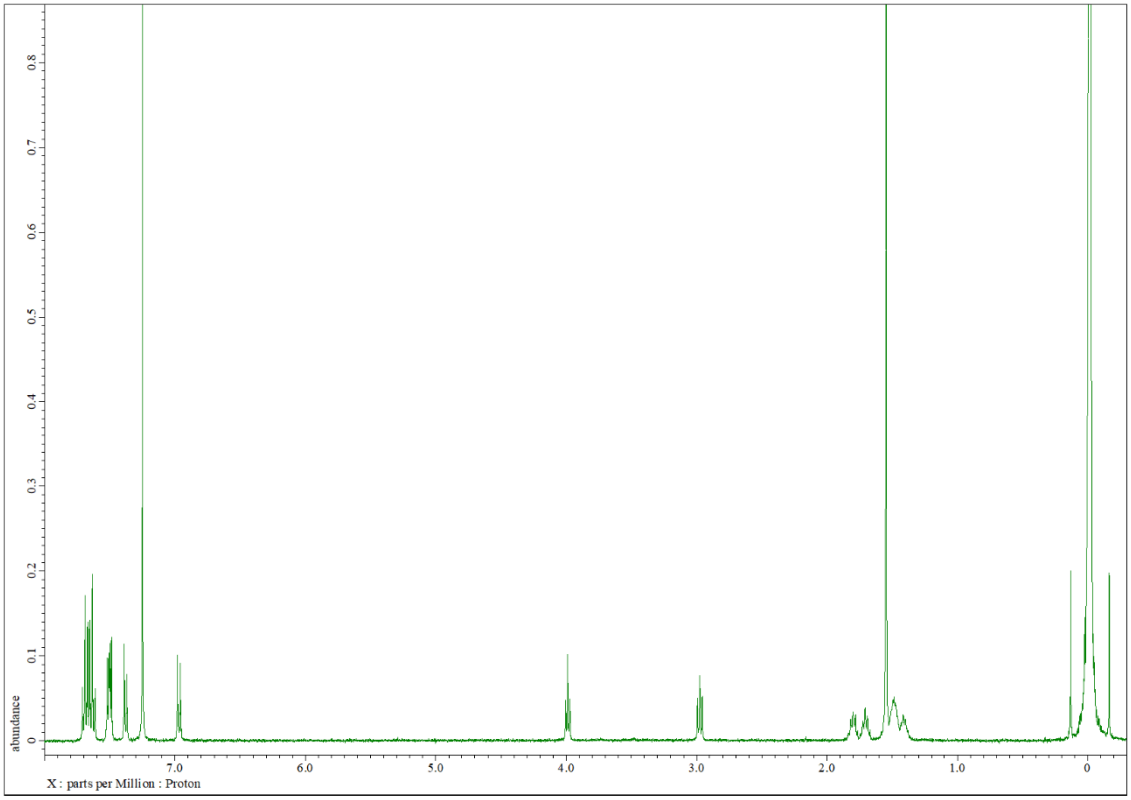

Fig. S4. Representative ^{1}H NMR spectrum for CBS7OCB in $CDCl_3$.

4. Phase transition behavior

Table S1. Phase transition temperature (°C) and enthalpy changes (kJ mol^{-1}) at a rate of 3 °C min^{-1} upon 2nd heating.

Sample	Phase sequence
CBS3SCB	Cr 141.2 (42.7) Iso
CBS5SCB	Cr 137.0 (32.9) Iso
CBS6SCB	Cr 196.6 (61.9) Iso
CBS7SCB	Cr 112.1 (37.1) N 115.9 (0.9) I
CBS9SCB	Cr 112.5 (35.2) N 117.5 (1.7) I
CBS11SCB	Cr 112.5 (40.0) N 115.4 (1.9) I
CBS3OCB	Cr 120.2 (27.3) N 138.2 (0.79) I
CBS5OCB	Cr 137.8 (29.5) N 145.1 (1.2) I
CBS6OCB	Cr 191.7 (-)[a] N 192.9 (-)[a] I
CBS7OCB	Cr_1 101.7 (22.1) Cr_2 122.4 (23.1) N 147.6 (1.9) I
CBS9OCB	Cr 109.9 (13.1) N 143.9 (0.82) I
CBS11OCB	Cr 115.2 (43.0) N 135.7 (3.06) I

[a] The accurate enthalpy changes could not be evaluated due to the peak overlap.

Table S2. Entropy changes (ΔS) scaled by gas constant (R) at N_{TB}-N transition [$\Delta S(N_{TB}N)/R$] and at N-I transition [$\Delta S(NI)/R$] at a rate of 3 °C min^{-1} upon 1st cooling.

Sample	$\Delta S(N_{TB}N)/R$	$\Delta S(NI)/R$
CBS3SCB	-	0.06
CBS5SCB	-	0.23
CBS6SCB	-	-
CBS7SCB	0.11	0.42
CBS9SCB	-	0.73
CBS11SCB	-	0.93
CBS3OCB	-	0.15
CBS5OCB	0.01	0.42
CBS6OCB	-	2.03
CBS7OCB	0.02	0.57
CBS9OCB	-	0.62
CBS11OCB	-	0.87

5. POM observation

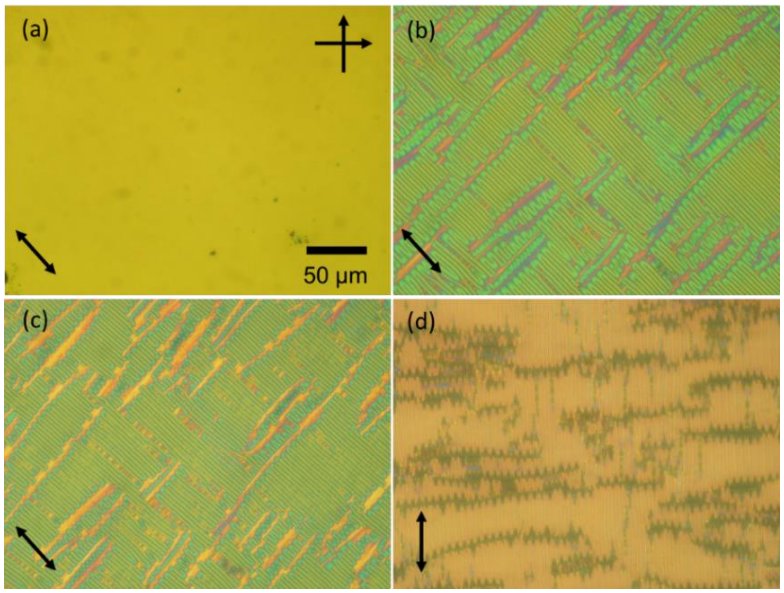

Fig. S5. Photomicrographs of CBS7OCB, in the uniaxially-planar aligned polyimide surface cells with a cell thickness of 3µm, for N phase at 100 °C (a) and N_{TB} phases at 70 °C (b) and 50 °C (c) and (d).

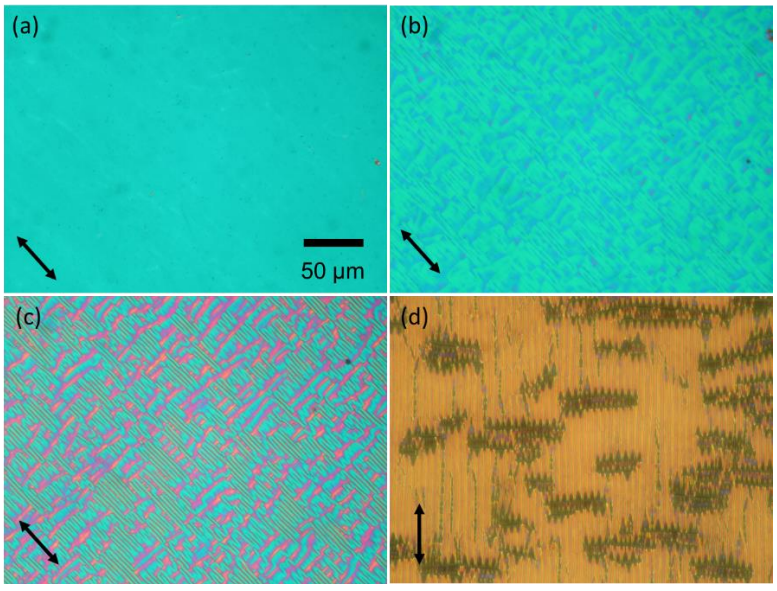

Fig. S6. Photomicrographs of CBS5SCB, in the uniaxially-planar aligned polyimide surface cells with a cell thickness of 3µm, for N phase at 90 °C (a) and N_{TB} phases at 75 °C (b) and 70 °C (c) and (d).

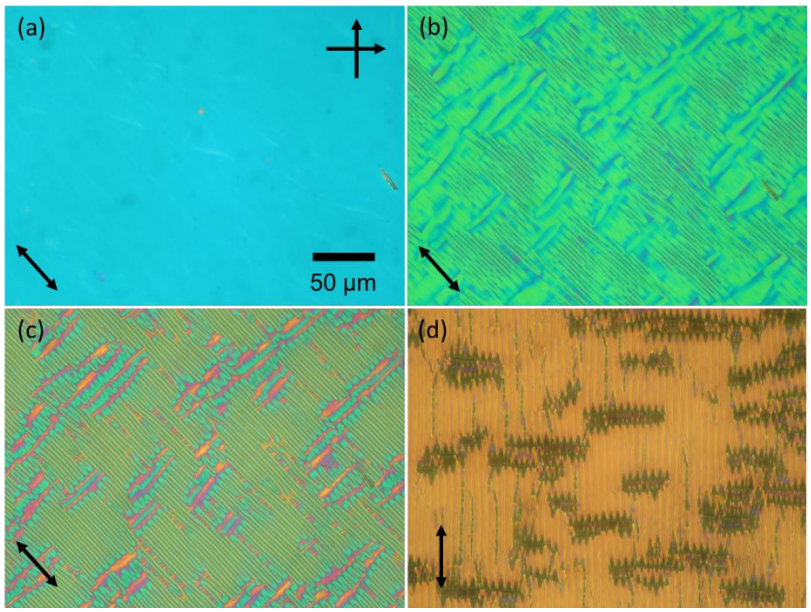

Fig. S7. Photomicrographs of CBS5OCB, in the uniaxially-planar aligned polyimide surface cells with a cell thickness of 3µm, for N phase at 130 °C (a) and N_{TB} phases at 85 °C (b), 70 °C (c) and (d).

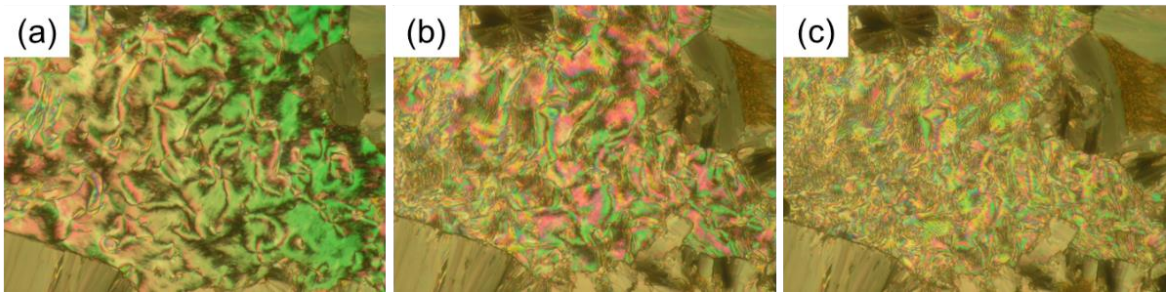

Fig. S8. Photomicrographs of CBS3SCB in a non-treated glass cell for N phase at 50 °C (a) N_{TB} phases at 38 °C (b) and at 25 °C (c) crystallized partially upon cooling.

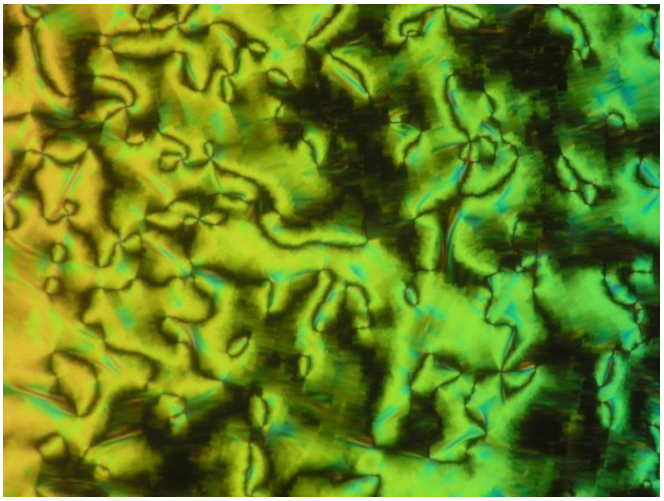

Fig. S9. Photomicrograph of CBS9OCB in a non-treated glass cell for N_{TB} phase at 92 °C upon cooling at a rate of 20 °C min^{-1}.

6. DSC measurements

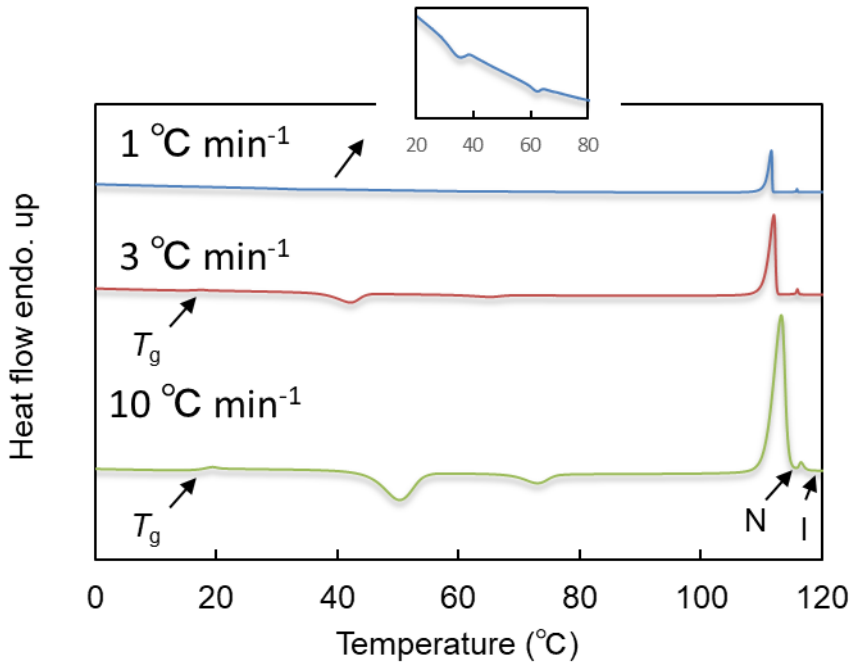

Fig. S10. DSC curves for CBS7SCB upon heating at different rates of 1, 3 and 10 °C min^{-1}.

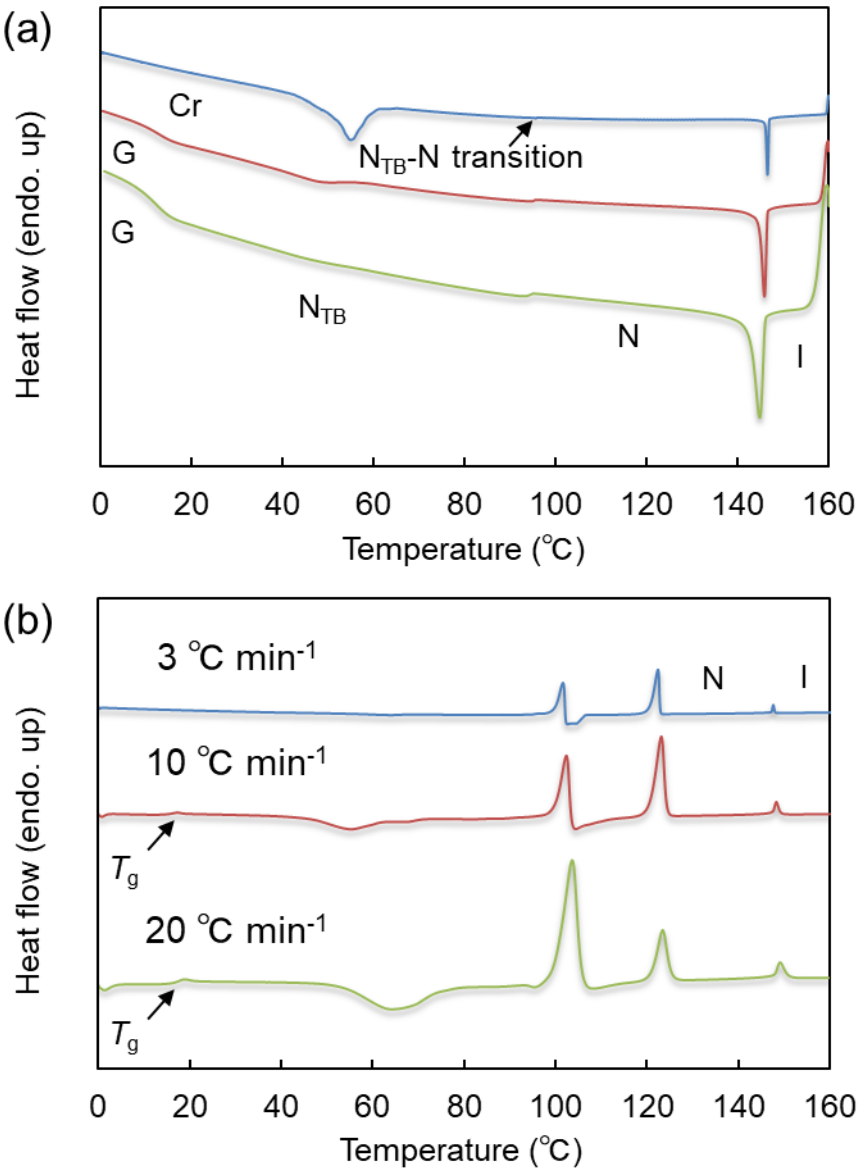

Fig. S11. DSC curves for CBS7OCB upon heating (a) and cooling (b) at different rates of 3, 10 and 20 °C min^{-1}.

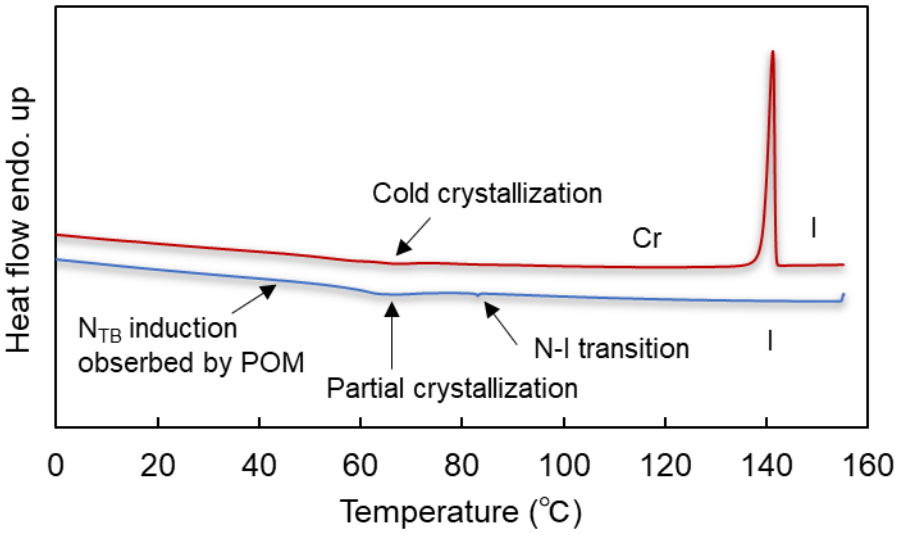

Fig. S12. DSC curves for CBS3SCB upon heating (a) and cooling (b) at a rate of 3 °C min^{-1}.

7. XRD measurements

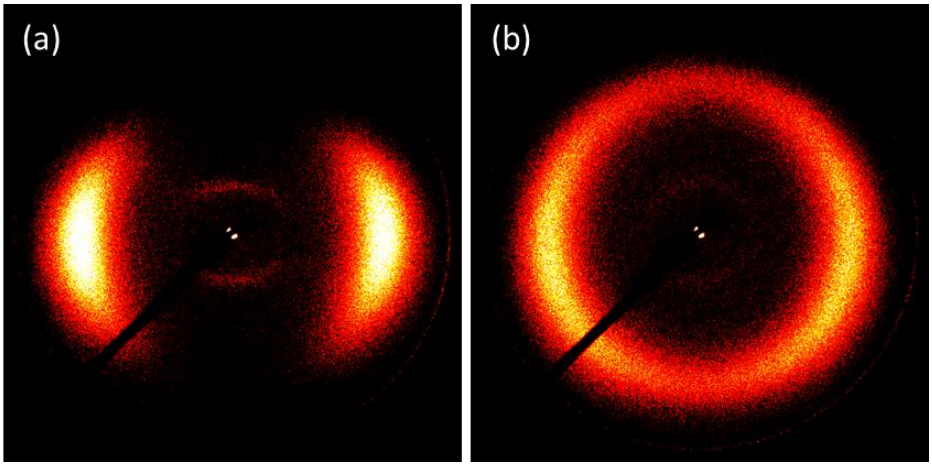

Fig. S13. 2D-XRD patterns of CBS7OCB for N phase at 100 °C (a) and N_{TB} phase at 90 °C (b).

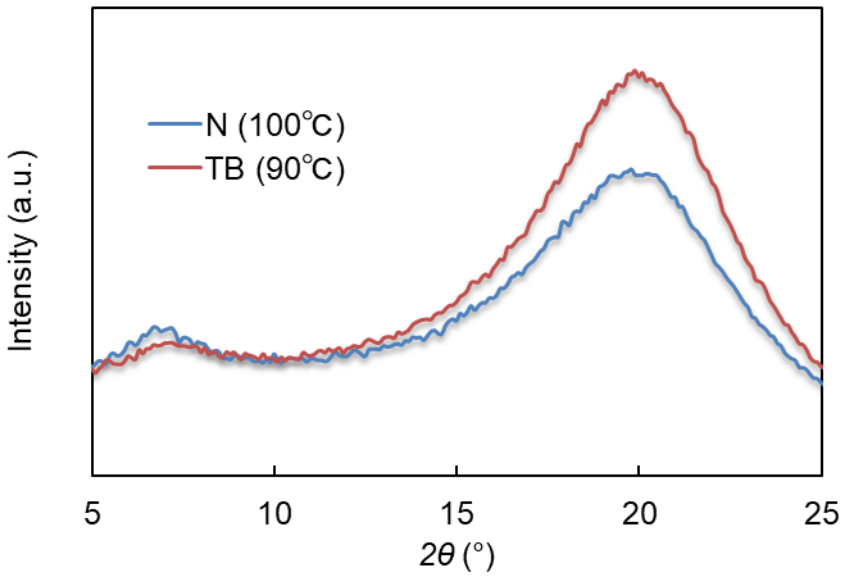

Fig. S14. 1D-XRD patterns of CBS7OCB for N phase at 100 °C and N_{TB} phase at 90 °C.

Table S3. *d*-spacings for diffractions in small-angle region (d_{SAX}) and wide-angle region (d_{WAX}) and orientational order parameters (S) based on XRD measurements.

	T (°C)	T_{NI}-T (°C)	d_{SAX} (Å)	d_{WAX} (Å)	S
N	110	5	11.5	4.6	0.36
N	105	10	12.5	4.5	0.43
N	100	15	12.8	4.5	0.43
N	95	20	13.0	4.5	0.48
N	90	25	12.8	4.5	0.46
N_{TB}	85	30	12.8	4.5	0.31 [a]
N_{TB}	80	35	12.3	4.4	0.15 [a]
N_{TB}	75	40	12.3	4.4	0.10 [a]
N	140	7	12.3	4.6	0.46
N	130	17	12.6	4.6	0.51
N	120	27	12.8	4.5	0.52
N	110	37	12.8	4.5	0.54
N	100	47	12.7	4.5	0.54
N_{TB}	90	57	12.4	4.4	0.20 [a]
N_{TB}	85	62	12.1	4.4	0.14 [a]
N_{TB}	80	67	12.6	4.4	0.13 [a]

[a] The S values in each N_{TB} phase are given for reference. Such a decrement in each N_{TB} phase is not consistent with the trend for N_{TB} phase and the reason is described in the manuscript.

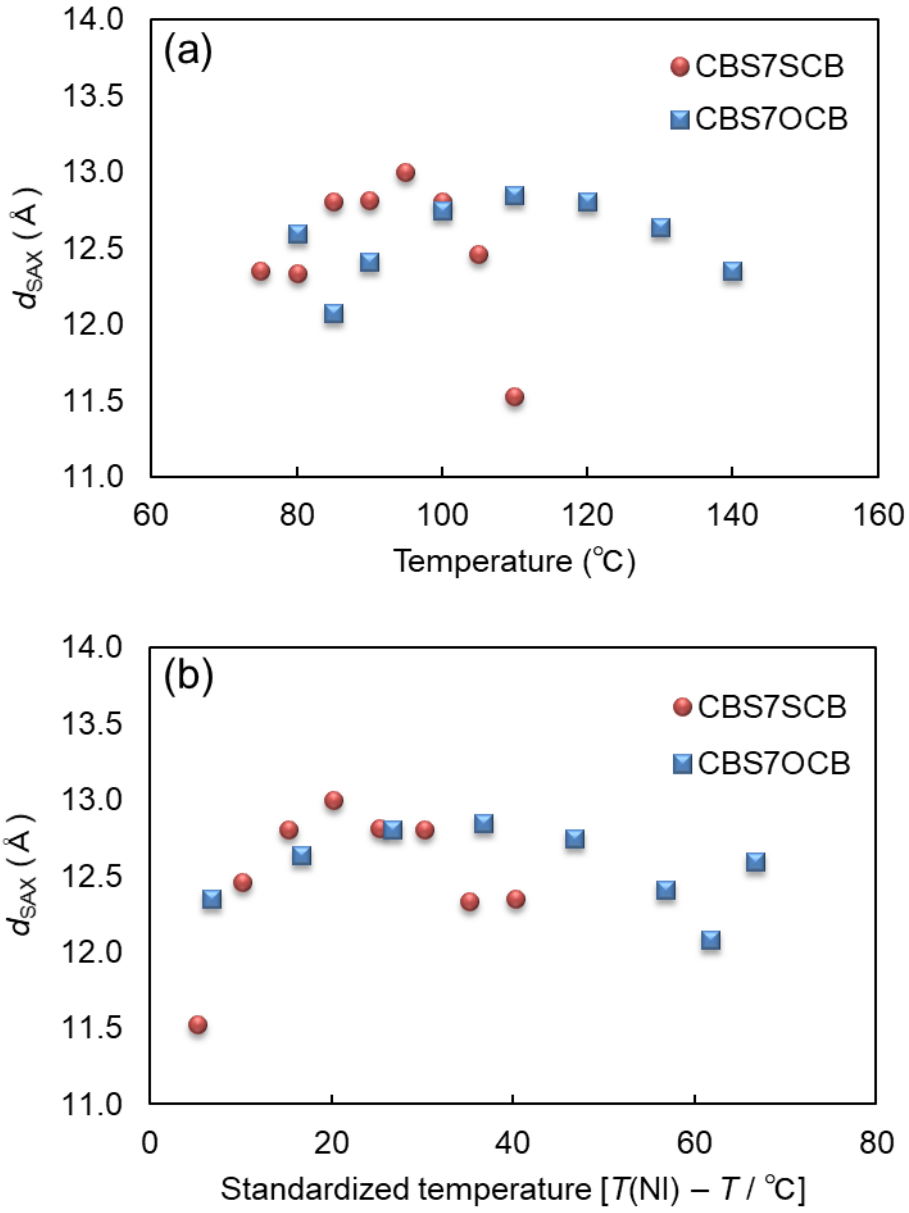

Fig. S15. The temperature dependence of the *d*-spacing values evaluated from each small-angle diffraction (d_{SAX}) for CBS7SCB and CBS7OCB at measurement temperature (a) and standardized temperature (b).

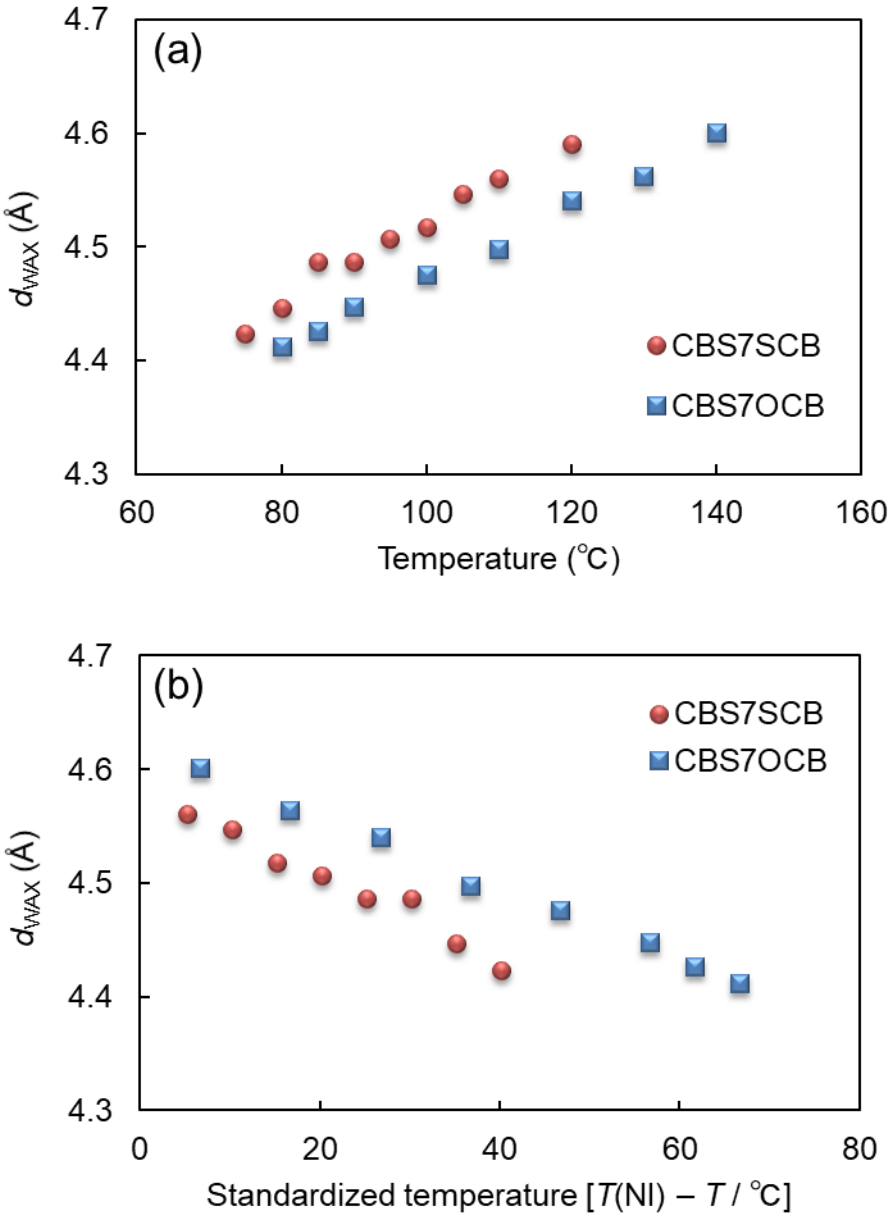

Fig. S16. The temperature dependence of the *d*-spacing values evaluated from each wide-angle diffraction (d_{WAX}) for CBS7SCB and CBS7OCB at measurement temperature (a) and standardized temperature (b).

8. Order parameter estimation

The order parameter (*S*) estimation was carried out corresponding to Ref. [2]. The (S) values were evaluated from the following equation [3].

$$\mathbf{S} = \frac{(\mathbf{3}\langle \boldsymbol{cos^2\beta} \rangle - \mathbf{1})}{\mathbf{2}}$$

$$\langle \boldsymbol{cos^2\beta} \rangle = \frac{\int_0^{\pi/2} \boldsymbol{I(\beta) cos^2\beta |sin\beta| d\beta}}{\int_0^{\pi/2} \boldsymbol{I(\beta) |sin\beta| d\beta}}$$

where, β and $I(\beta)$ are azimuthal angle and its corresponding intensity centered at 2θ = ca. 4.5 for wide-angle broadened diffractions.

9. Optimized geometries based on theoretical calculations

Table S4. Atom coordinates and absolute energy levels of CBS7SCB obtained from theoretical calculations.

E(RB3LYP) = -2181.46900331 hartree				
Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	-6.56879	-0.09681	-0.06309
2	6	-7.71327	0.69842	-0.03878
3	6	-8.99857	0.137472	-0.0056
4	6	-10.2098	0.989722	0.016205
5	6	-11.3817	0.60179	-0.65953
6	6	-12.5213	1.396139	-0.64277
7	6	-12.5185	2.615371	0.055424
8	6	-13.6897	3.440502	0.075153
9	7	-14.6406	4.111135	0.09115
10	6	-11.3561	3.017757	0.734334
11	6	-10.2244	2.212459	0.712766
12	6	-9.09363	-1.26635	0.005062
13	6	-7.95994	-2.06735	-0.01312
14	6	-6.677	-1.49386	-0.04901
15	16	-5.29982	-2.621	-0.07857
16	6	-3.82664	-1.52651	-0.04979
17	6	-2.55855	-2.38687	-0.03455
18	6	-1.28134	-1.53444	-0.01667
19	6	0.000002	-2.37846	0.000209
20	6	1.281347	-1.53444	0.017071
21	6	2.558555	-2.38687	0.034973
22	6	3.82664	-1.5265	0.050196
23	16	5.299825	-2.62099	0.079021
24	6	6.677002	-1.49385	0.049267
25	6	7.959942	-2.06735	0.013228
26	6	9.093629	-1.26635	-0.00509
27	6	8.998568	0.137471	0.005563
28	6	10.20975	0.989719	-0.0164
29	6	10.22427	2.212446	-0.71298

30	6	11.35602	3.017747	-0.7347
31	6	12.51854	2.615373	-0.05592
32	6	13.68967	3.440508	-0.07579
33	7	14.64061	4.111143	-0.09191
34	6	12.52136	1.396153	0.642294
35	6	11.38174	0.601802	0.659201
36	6	7.713275	0.698422	0.03888
37	6	6.568798	-0.09681	0.063333
38	1	-5.59855	0.385275	-0.10309
39	1	-7.59961	1.778292	-0.07772
40	1	-11.3899	-0.32308	-1.22813
41	1	-13.4141	1.085805	-1.17617
42	1	-11.3529	3.954054	1.283266
43	1	-9.34394	2.522289	1.267453
44	1	-10.0704	-1.73875	0.059948
45	1	-8.0666	-3.14867	0.010601
46	1	-3.83858	-0.88131	-0.93516
47	1	-3.86892	-0.89145	0.841933
48	1	-2.57448	-3.04443	0.84435
49	1	-2.55079	-3.04153	-0.91588
50	1	-1.27079	-0.87384	-0.89573
51	1	-1.29467	-0.87499	0.863231
52	1	-0.01158	-3.03917	0.878996
53	1	0.011587	-3.03918	-0.87857
54	1	1.29467	-0.875	-0.86284
55	1	1.270788	-0.87382	0.896122
56	1	2.550796	-3.04151	0.916313
57	1	2.57449	-3.04444	-0.84392
58	1	3.86893	-0.89147	-0.84155
59	1	3.838572	-0.88128	0.935544
60	1	8.066594	-3.14867	-0.0105
61	1	10.07035	-1.73875	-0.06009
62	1	9.343792	2.522267	-1.26757
63	1	11.35276	3.954036	-1.28364
64	1	13.41425	1.085832	1.175607
65	1	11.39008	-0.32305	1.227821

66	1	7.599621	1.778296	0.077805
67	1	5.598565	0.385283	0.10344

Table S5. Atom coordinates and absolute energy levels of CBS7OCB obtained from theoretical calculations.

E(RB3LYP) = -1858.49566404 hartree				
Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	0.004228	-0.004	-9.8E-05
2	6	-0.00426	0.000473	-0.00252
3	6	-0.01244	-0.01186	-5.4E-05
4	6	0.013198	0.01111	-0.00054
5	6	0.000731	0.00129	-0.00212
6	6	-0.00779	-0.00155	0.002023
7	6	-0.00543	-0.00442	0.000107
8	6	0.05365	0.042895	0.000215
9	7	-0.0557	-0.04462	-0.00016
10	6	-0.00337	-0.007	-0.0025
11	6	0.001784	-0.00012	0.003026
12	6	0.001139	-0.00169	0.002467
13	6	0.000168	0.008746	0.000321
14	6	0.011707	-0.00126	2.06E-05
15	16	-0.00169	0.014439	5.31E-05
16	6	0.00408	0.006994	-1.4E-05
17	6	-0.00668	-0.0149	-6.6E-05
18	6	-0.00107	0.022155	3.58E-06
19	6	-0.00118	-0.02404	-0.00011
20	6	0.004619	0.021366	6.27E-05
21	6	0.009163	-0.01591	3.34E-05
22	6	-0.00369	0.017893	1.61E-05
23	8	-0.00112	0.010572	-0.00013
24	6	-0.01527	-0.00535	0.000659
25	6	0.000385	0.013595	-0.00057
26	6	-0.00342	-0.00204	-0.00244
27	6	0.014947	-0.01142	-8.1E-05
28	6	-0.01588	0.008855	-0.00059

29	6	-0.00106	-9E-05	-0.00196
30	6	0.003829	-0.00679	0.002017
31	6	0.006379	-0.00361	5.09E-05
32	6	-0.05902	0.035194	7.95E-05
33	7	0.061317	-0.03651	6.68E-06
34	6	0.007499	-0.00053	-0.00245
35	6	-2.4E-05	0.001656	0.002817
36	6	0.004134	0.002025	0.002934
37	6	-0.00275	-0.00979	-0.00041
38	1	-0.00128	-0.00345	0.00015
39	1	0.000555	-0.00418	0.001312
40	1	0.000553	0.002362	0.003037
41	1	-0.0038	-0.00054	0.001984
42	1	-0.00138	-0.00355	-0.00204
43	1	0.002424	0.000101	-0.0031
44	1	-0.00358	0.001679	-0.00124
45	1	-0.00034	0.004993	-0.00033
46	1	-0.00026	-0.00293	0.001957
47	1	-0.00026	-0.00292	-0.00195
48	1	0.000249	0.005202	-0.00139
49	1	0.000239	0.00522	0.001446
50	1	-9.5E-05	-0.00577	0.002042
51	1	-8.1E-05	-0.00574	-0.00202
52	1	0.000351	0.005552	-0.00176
53	1	0.000352	0.005566	0.001823
54	1	-0.00091	-0.00594	0.002082
55	1	-0.0009	-0.00593	-0.00211
56	1	0.00165	0.004773	-0.00139
57	1	0.001637	0.004739	0.001374
58	1	-0.00048	-0.00459	0.003383
59	1	-0.00039	-0.0046	-0.00334
60	1	-0.0026	0.004439	0.000329
61	1	0.003038	0.002345	0.001288
62	1	-0.00238	-0.00023	0.00304
63	1	0.00185	-0.00341	0.002013
64	1	0.003886	-1.9E-05	-0.00207

65	1	-0.00092	0.002218	-0.00305
66	1	-0.00012	-0.00402	-0.00125
67	1	0.001886	-0.00314	-0.00032

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