Supporting information for

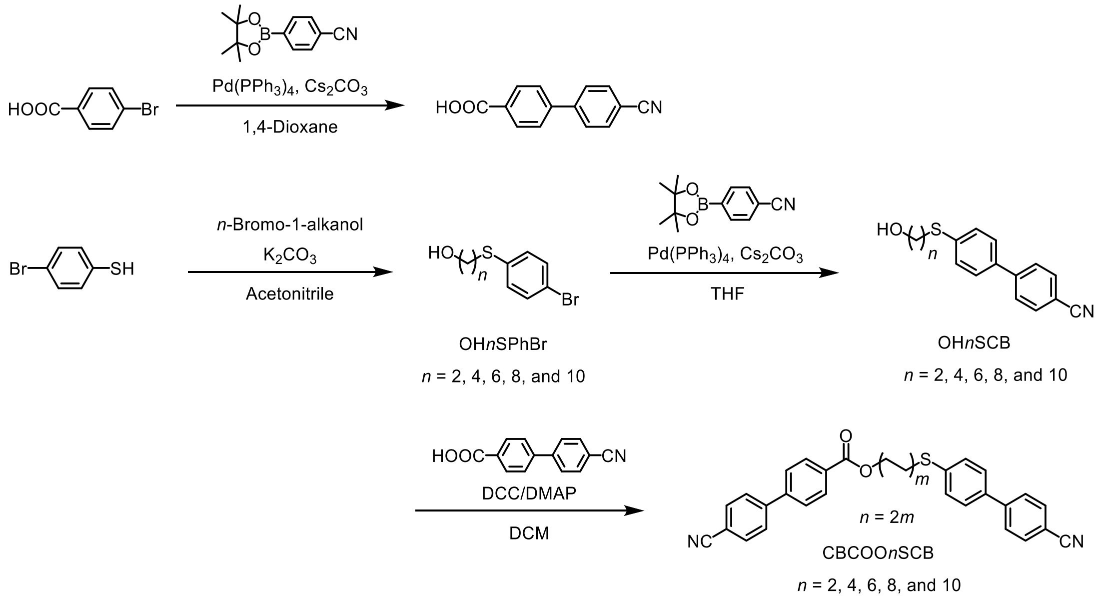
Distinct twist-bend nematic phase behaviors associated with the ester-linkage direction of thioether-linked liquid crystal dimers

Yuki Arakawa,[a]* Kenta Komatsu,[a] Jun Feng,[b] Chenhui Zhu,[b] and Hideto Tsuji[a]

[a] 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

[b] Advanced Light Source, Lawrence Berkeley National Lab, Berkeley, CA, 94720 USA

S1. Characterization data of CBCOO*n*SCB



Scheme S1. Synthetic routes of CBCOO*n*SCB.

Both series were synthesized referring to procedures in the literature [S1], for which the specific procedures for CBCOO6SCB and CBOCO6SCB were described in this ESI.

4'-Cyano-4-biphenylcarboxylic acid

4-Bromobenzoic acid (2.00 g, 9.95 mmol), 4-cyanophenylboronic acid pinacol ester (2.28 g, 9.95 mmol), Cs_2CO_3 (6.48 g, 19.9 mmol), and $Pd(PPh_3)_4$ (0.204 g, 0.236 μmol) were put in a two-necked flask purged with argon gas, and then 1,4-dioxane (20 mL) degassed by bubbling argon gas was added into the flask. The mixture was stirred at reflux temperature under an argon atmosphere for 8 h. The stirred mixture was cooled to ambient temperature and neutralized with 1M HCl aqueous. The mixture with precipitates was poured into an excess amount of distilled water and filtrated. The obtained filtrate was rinsed with acetone and purified by recrystallisation in a mixed solvent of chloroform/methanol. Yield: 36%. The NMR spectral data were similar to those described in ref. S1.

1-Bromo-4-(2'-hydroxyethylthio)benzene (OH2SPhBr)

A mixture of 4-Bromobenzenethiol (0.500 g, 2.64 mmol), 2-bromoethanol (1.18 mL, 8.86 mmol), K_2CO_3 (1.10 g, 7.93 mmol), and *N,N*-dimethylformamide (5 mL) in a round flask was stirred at ambient temperature for 12 h. The mixture was extracted with ethylacetate and washed with water and brine. The organic phase was dried over $MgSO_4$ and the volatiles were removed *in vacuo*. The obtained compound was used to the next step without further purification. Yield: >99%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.26 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 4.53 (s, C–O*H*, 2H), 3.75 (t, *J* = 5.8 and 6.0 Hz, HO–CH_2, 2H), 3.11 (t, *J* = 6.0 Hz, S–CH_2, 2H) ppm.

4'-(2-Hydroxyethylthio)-4-cyanobiphenyl (OH2SCB)

OH2SPhBr (0.604 g, 2.59 mmol), 4-cyanophenylboronic acid pinacol ester (0.594 g, 2.59 mmol), Cs_2CO_3 (1.69 g, 5.19 mmol), and $Pd(PPh_3)_4$ (0.150 g, 0.130 μmol) were put in a two-necked flask purged with argon gas, and then THF (8 mL) degassed by bubbling argon gas was added into the flask. The mixture was stirred at reflux temperature under an argon atmosphere for 14 h. The reaction mixture was cooled to ambient temperature, extracted with DCM, and washed with water and brine. The organic phase was dried over $MgSO_4$ and the volatiles were evaporated *in vacuo*. The residue was purified by column chromatography on silica gel with an eluent of DCM. Yield: 61%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.66 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.52 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.47 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 3.82 (t, *J* = 6.0 Hz, HO–CH_2, 2H), 3.19 (t, *J* = 6.0 Hz, S–CH_2, 2H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 137.1, 136.3, 132.6, 132.6, 129.9, 129.9, 127.7, 127.7, 127.4, 127.4, 118.8, 110.9, 60.4, 36.7 ppm.

1''-[(4-Cyanobiphenyl-4'-yl)carbonyloxy]-2''-(4-cyanobiphenyl-4'-ylthio)ethane CBCOO2SCB

OH2SCB (0.150 g, 0.672 mmol), 4'-Cyano-4-biphenylcarboxylic acid (0.172 g, 0.672 mmol), and DMAP (8.20 mg, 67.2 μmol) were dissolved with DCM (1.5 mL) in a two-necked flask under an argon atmosphere. In another two-necked flask, DCC (0.166 g, 0.806 mmol) was dissolved in DCM (1.5 mL) under an argon atmosphere, and the solution was slowly dropped into the prior mixture at 0 °C. After stirring for 24 h at ambient temperature, the reaction mixture was filtrated off, to remove the insoluble by-product, and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel with an eluent of DCM and recrystallized from a mixed solvent of DCM and hexane. Yield: 23%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.0 Hz, Ar–*H*, 2H), 7.76 (d, *J* = 8.0 Hz, Ar–*H*, 2H), 7.71 (d, *J* = 8.0 Hz, Ar–*H*, 2H), 7.68 (d, *J* = 8.0 Hz, Ar–*H*, 2H), 7.65 (d, *J* = 8.0 Hz, Ar–*H*, 2H), 7.63 (d, *J* = 8.0 Hz, Ar–*H*, 2H), 7.51–7.55 (m, Ar–*H*, 4H), 4.57 (t, *J* = 6.8 Hz, O=C–O–CH_2, 2H), 3.38 (t, *J* = 6.7 Hz, S–CH_2, 2H), 1.99 (tt, *J* = 6.4 and 6.9 Hz, O=C–O–CH_2–CH_2, 2H), 1.87 (tt, *J* = 7.2 and 7.3 Hz, S–CH_2–CH_2, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 144.6, 144.2, 143.6, 137.1, 136.4, 132.7, 132.7, 132.6, 132.6, 130.4, 130.4, 129.8, 129.8, 129.8, 127.9, 127.9, 127.8, 127.8, 127.4, 127.4, 127.2, 127.2, 118.8, 118.6, 111.9, 111.0, 63.6, 32.0 ppm. FTIR (KBr): 3052, 2949, 2224, 1714, 1605, 1486, 1396, 1273, 1180, 1111, 1093, 1006, 973, 835, 806, 770, 727, 698 cm^{-1}. HRMS (ESI, m/z): [M+Na]+ calcd. for $C_{29}H_{20}N_2NaO_2S$, 483.1138; found, 483.1132.

4'-(6-Hydroxyethylthio)-4-cyanobiphenyl (OH6SPhBr)

Yield: 84%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.17 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 3.63 (dt, *J* = 6.5 Hz, HO–CH_2, 2H), 2.89 (t, *J* = 7.5 Hz, S–CH_2, 2H), 1.64 (tt, *J* = 6.5 and 7.5 Hz, HO–CH_2–CH_2, 2H), 1.56 (tt, *J* = 7.0 and 7.5 Hz, S–CH_2–CH_2, 2H), 1.33–1.49 (m, S–$(CH_2)_2$–(CH_2)$_2$, 4H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.1, 131.8, 131.8, 130.4, 130.4, 119.4, 62.8, 33.5, 32.5, 32.5, 28.9, 28.5, 25.3 ppm.

4'-(6-Hydroxyethylthio)-4-cyanobiphenyl (OH6SCB)

Yield: 56%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.66 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.51 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.39 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 3.65 (dt, *J* = 6.0 Hz, HO–CH_2, 2H), 2.98 (t, *J* = 7.0 Hz, S–CH_2, 2H), 1.71 (tt, *J* = 6.0 and 7.5 Hz, HO–CH_2–CH_2, 2H), 1.58 (tt, *J* = 7.0 and 7.4 Hz, S–CH_2–CH_2, 2H), 1.36–1.54 (m, S–$(CH_2)_2$–(CH_2)$_2$, 4H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9, 138.4, 136.1, 132.6, 132.6, 128.6, 128.6, 127.5, 127.5, 127.3, 127.3, 118.9, 110.7, 62.8, 32.9, 32.5, 28.9, 28.6, 25.3 ppm.

1''-[(4-Cyanobiphenyl-4'-yl)carbonyloxy]-6''-(4-cyanobiphenyl-4'-ylthio)heptane

CBCOO6SCB

Yield: 42%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.76 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.71 (d, *J* = 8.5 Hz, Ar–*H*, 4H), 7.65 (d, *J* = 8.5 Hz, Ar–*H*, 4H), 7.51 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.39 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 4.35 (t, *J* = 6.8 Hz, O=C–O–CH_2, 2H), 3.00 (t, *J* = 7.2 Hz, S–CH_2, 2H), 1.81 (tt, *J* = 6.8 and 7.0 Hz, O=C–O–CH_2–CH_2, 2H), 1.74 (tt, *J* = 7.2 and 7.2 Hz, S–CH_2–CH_2, 2H), 1.46–1.61 (m, S–$(CH_2)_2$–(CH_2)$_2$, 4H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 144.9, 144.4, 143.3, 138.3, 136.2, 132.7, 132.7, 132.6, 132.6, 130.4, 130.3, 130.3, 128.7, 128.7, 127.9, 127.9, 127.5, 127.5, 127.3, 127.3, 127.2, 127.2, 118.9, 118.6, 111.8, 110.9, 65.1, 33.0, 28.9, 28.6, 28.4, 25.6 ppm. FTIR (KBr): 3061, 2930, 2856, 2225, 1709, 1606, 1487, 1394, 1281, 1183, 1124, 1093, 1002, 958, 838, 820, 770, 727, 698 cm^{-1}. HRMS (ESI, m/z): [M+Na]+ calcd. for $C_{33}H_{28}N_2NaO_2S$, 539.1764; found, 539.1745.

4'-(8-Hydroxyethylthio)-4-cyanobiphenyl (OH8SPhBr)

Yield: 89%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.17 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 3.63 (dt, *J* = 6.5 Hz, HO–CH_2, 2H), 2.88 (t, *J* = 7.2 Hz, S–CH_2, 2H), 1.70 (s, CH_2–O*H*, 1H), 1.63 (tt, *J* = 6.5 and 7.5 Hz, HO–CH_2–CH_2, 2H), 1.55 (tt, *J* = 7.2 and 7.1 Hz, S–CH_2–CH_2, 2H), 1.26–1.47 (m, S–$(CH_2)_2$–$(CH_2)_4$, 8H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.2, 131.8, 131.8, 130.3, 130.3, 119.3, 63.0, 33.6, 32.7, 29.2, 29.1, 28.9, 28.7, 25.6 ppm.

4'-(8-Hydroxyethylthio)-4-cyanobiphenyl (OH8SCB)

Yield: 78%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.67 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.51 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.39 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 3.64 (dt, *J* = 6.2 Hz, HO–CH_2, 2H), 2.97 (t, *J* = 7.5 Hz, S–CH_2, 2H), 1.69 (tt, *J* = 6.2 and 7.4 Hz, HO–CH_2–CH_2, 2H), 1.57 (tt, *J* = 7.5 and 8.1 Hz, S–CH_2–CH_2, 2H), 1.29–1.51 (m, S–$(CH_2)_2$–$(CH_2)_4$, 8H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9, 138.5, 136.0, 132.6, 132.6, 128.5, 128.5, 127.5, 127.5, 127.3, 127.3, 118.9, 110.7, 63.0, 33.0, 32.7, 29.2, 29.1, 28.9, 28.7, 25.6 ppm.

1''-[(4-Cyanobiphenyl-4'-yl)carbonyloxy]-8''-(4-cyanobiphenyl-4'-ylthio)octane CBCOO8SCB

Yield: 36%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.0 Hz, Ar–*H*, 2H), 7.76 (d, *J* = 8.0 Hz, Ar–*H*, 2H), 7.71 (d, *J* = 8.5 Hz, Ar–*H*, 4H), 7.66 (d, *J* = 8.0 Hz, Ar–*H*, 4H), 7.65 (d, *J* = 8.0 Hz, Ar–*H*, 2H), 7.51 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.38 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 4.35 (t, *J* = 6.5 Hz, O=C–O–CH_2, 2H), 2.98 (t, *J* = 7.2 Hz, S–CH_2, 2H), 1.79 (tt, *J* = 6.5 and 7.1 Hz, O=C–O–CH_2–CH_2, 2H), 1.70 (tt, *J* = 7.2 and 7.5 Hz, S–CH_2–CH_2, 2H), 1.32–1.51 (m, S–$(CH_2)_2$–$(CH_2)_4$, 8H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 144.9, 144.4, 143.3, 138.5, 136.1, 132.7, 132.7, 132.6, 132.6, 130.5, 130.3, 130.3, 128.5, 128.5, 127.9, 127.9, 127.5, 127.5, 127.3, 127.3, 127.2, 127.2, 118.9, 118.6, 111.8, 110.7, 65.3, 33.0, 29.1, 29.0, 28.9, 28.7, 28.7, 25.9 ppm. FTIR (KBr): 3041, 2929, 2852, 2224, 1715, 1605, 1486, 1396, 1281, 1182, 1127, 1098, 1004, 957, 841, 809, 771, 730, 694 cm^{-1}. HRMS (ESI, m/z): [M+Na]+ calcd. for $C_{35}H_{32}N_2NaO_2S$, 567.2077; found, 567.2073.

4'-(10-Hydroxyethylthio)-4-cyanobiphenyl (OH10SPhBr)

Yield: 85%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, J = 8.5 Hz, Ar–H, 2H), 7.17 (d, J = 8.5 Hz, Ar–H, 2H), 3.64 (dt, J = 6.5 Hz, HO–CH_2, 2H), 2.88 (t, J = 7.2 Hz, S–CH_2, 2H), 1.70 (s, CH_2–OH, 1H), 1.62 (tt, J = 6.5 and 7.4 Hz, HO–CH_2–CH_2, 2H), 1.56 (tt, J = 7.1 and 7.2 Hz, S–CH_2–CH_2, 2H), 1.21–1.45 (m, S–$(CH_2)_2$–$(CH_2)_6$, 12H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.3, 131.8, 131.8, 130.3, 130.3, 119.3, 63.0, 33.6, 32.8, 29.5, 29.4, 29.4, 29.1, 28.9, 28.7, 25.7 ppm.

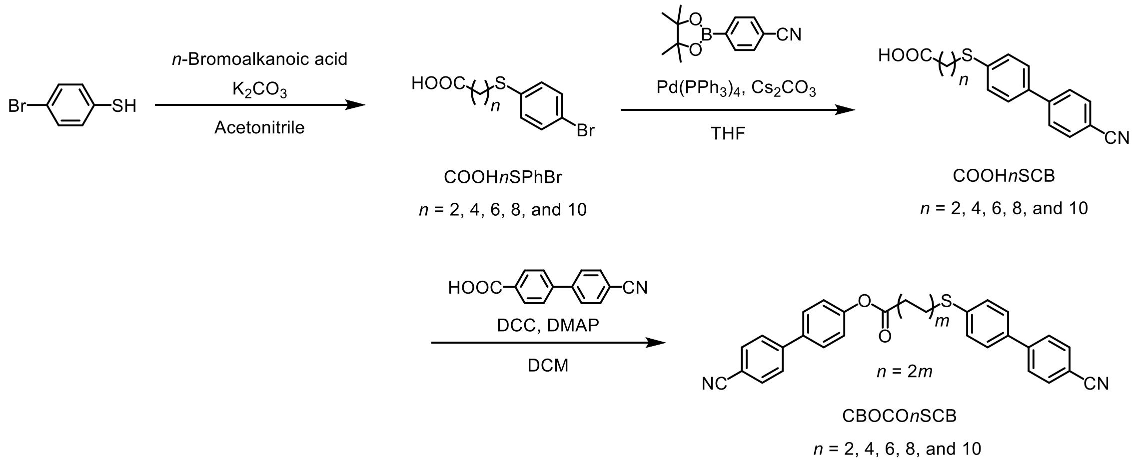
4'-(10-Hydroxyethylthio)-4-cyanobiphenyl (OH10SCB)

Yield: 84%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.8 Hz, Ar–H, 2H), 7.66 (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), 3.64 (dt, J = 6.6 Hz, HO–CH_2, 2H), 2.97 (t, J = 7.4 Hz, S–CH_2, 2H), 1.69 (tt, J = 6.6 and 7.4 Hz, HO–CH_2–CH_2, 2H), 1.56 (tt, J = 7.1 and 7.4 Hz, S–CH_2–CH_2, 2H), 1.22–1.50 (m, S–$(CH_2)_2$–$(CH_2)_6$, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 138.6, 136.0, 132.6, 132.6, 128.5, 128.5, 127.5, 127.5, 127.3, 127.3, 118.9, 110.7, 63.0, 33.0, 32.7, 29.5, 29.4, 29.3, 29.1, 29.0, 28.8, 25.7 ppm.

1''-[(4-Cyanobiphenyl-4'-yl)carbonyloxy]-10''-(4-cyanobiphenyl-4'-ylthio)decane CBCOO10SCB

Yield: 54%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.4 Hz, Ar–H, 2H), 7.76 (d, J = 8.4 Hz, Ar–H, 2H), 7.71 (d, J = 8.5 Hz, Ar–H, 4H), 7.66 (d, J = 8.4 Hz, Ar–H, 4H), 7.51 (d, J = 8.4 Hz, Ar–H, 2H), 7.38 (d, J = 8.4 Hz, Ar–H, 2H), 4.34 (t, J = 6.8 Hz, O=C–O–CH_2, 2H), 2.97 (t, J = 7.4 Hz, S–CH_2, 2H), 1.79 (tt, J = 6.8 and 7.1 Hz, O=C–O–CH_2–CH_2, 2H), 1.69 (tt, J = 7.4 and 7.4 Hz, S–CH_2–CH_2, 2H), 1.24–1.51 (m, S–$(CH_2)_2$–$(CH_2)_6$, 12H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 144.9, 144.4, 143.3, 138.6, 136.1, 132.7, 132.7, 132.6, 132.6, 130.5, 130.3, 130.3, 128.5, 128.5, 127.9, 127.9, 127.5, 127.5, 127.3, 127.3, 127.2, 127.2, 118.9, 118.6, 111.8, 110.7, 65.3, 33.0, 29.4, 29.4, 29.2, 29.1, 28.9, 28.8, 28.7, 25.7 ppm. FTIR (KBr): 3063, 2928, 2853, 2225, 1716, 1605, 1487, 1395, 1290, 1181, 1129, 1097, 957, 836, 813, 772, 726, 697 cm^{-1}. HRMS (ESI, m/z): [M+Na]+ calcd. for $C_{37}H_{36}N_2NaO_2S$, 595.2390; found, 595.2385.

S2. Characterization data of CBCOO*n*SCB



Scheme S2. Synthetic routes of CBOCO*n*SCB.

3'-(4-Bromophenylthio)propanoic acid (COOH2SPhBr)

Yield: 70%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.24 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 3.14 (t, *J* = 7.2 Hz, HOOC–CH_2, 2H), 2.67 (t, *J* = 7.2 Hz, S–CH_2, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.5, 134.1, 132.1, 132.1, 131.9, 131.9, 129.8, 34.0, 28.9 ppm.

3''-(4-Cyanobiphenyl-4'-ylthio)propanoic acid (COOH2SCB)

Yield: 49%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.66 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.53 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.45 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 3.23 (t, *J* = 7.3 Hz, HOOC–CH_2, 2H), 2.73 (t, *J* = 7.3 Hz, S–CH_2, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.3, 144.7, 137.2, 136.2, 132.7, 132.7, 130.0, 130.0, 127.8, 127.8, 118.8, 111.0, 34.0, 28.3 ppm.

(4-Cyanobiphenyl-4'-yl) 3''-(4-cyanobiphenyl-4'-ylthio)propanoate (CBOCO2SCB)

Yield: 53%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.73 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.67 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.65 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.59 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.56 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.51 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.22 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 3.37 (t, *J* = 7.2 Hz, O=C–CH_2, 2H), 2.97 (t, *J* = 7.3 Hz, S–CH_2, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.0, 150.9, 144.6, 144.6, 137.3, 137.0, 136.2, 132.7, 132.7, 132.6, 132.6, 130.3, 130.2, 130.2, 128.3, 128.3, 127.8, 127.8, 127.6, 127.6, 127.4, 127.4, 127.2, 127.2, 118.8, 118.8, 111.1, 111.0, 34.4, 28.7 ppm. FTIR (KBr): 3070, 2222, 1756, 1605, 1492, 1362, 1315, 1283, 1197, 1095, 1005, 814, 737 cm^{-1}. HRMS (ESI, m/z): [M+Na]+ calcd. for $C_{29}H_{20}N_2NaO_2S$, 483.1138; found, 483.1139.

7'-(4-Bromophenylthio)pentanoic acid (COOH6SPhBr)

Yield: 92%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.17 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 2.89 (t, *J* = 7.2 Hz, S–C*H*$_2$, 2H), 2.35 (t, *J* = 7.5 Hz, HOOC–C*H*$_2$, 2H), 1.64 (tt, *J* = 7.2 and 7.4 Hz, S–CH$_2$–C*H*$_2$ and HOOC–CH$_2$–C*H*$_2$, 4H), 1.44 (tt, *J* = 7.4 and 7.5 Hz, S–(CH$_2$)$_2$–C*H*$_2$, 2H), 1.32 (tt, *J* = 7.2 and 7.4 Hz, HOOC–(CH$_2$)$_2$–C*H*$_2$, 2H) ppm.

7''-(4-Cyanobiphenyl-4'-ylthio)pentanoic acid (COOH6SCB)

Yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.8 Hz, Ar–*H*, 2H), 7.66 (d, *J* = 8.8 Hz, Ar–*H*, 2H), 7.51 (d, *J* = 8.8 Hz, Ar–*H*, 2H), 7.39 (d, *J* = 8.8 Hz, Ar–*H*, 2H), 2.97 (t, *J* = 7.4 Hz, S–C*H*$_2$, 2H), 2.36 (t, *J* = 7.4 Hz, HOOC–C*H*$_2$, 2H), 1.70 (tt, *J* = 7.0 and 7.4 Hz, S–CH$_2$–C*H*$_2$, 2H), 1.65 (tt, *J* = 7.1 and 7.4 Hz, HOOC–CH$_2$–C*H*$_2$, 2H), 1.34-1.53 (m, HOOC–(CH$_2$)$_2$–(C*H*$_2$)$_2$, 4H) ppm.

(4-Cyanobiphenyl-4'-yl) 7''-(4-cyanobiphenyl-4'-ylthio)heptanoate (CBOCO6SCB)

Yield: 49%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.71 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.66 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.65 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.58 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.56 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.40 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.19 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 3.00 (t, *J* = 7.3 Hz, S–C*H*$_2$, 2H), 2.60 (t, *J* = 7.8 Hz, O=C–C*H*$_2$, 2H), 1.79 (tt, *J* = 7.3 and 7.5 Hz, S–CH$_2$–C*H*$_2$, 2H), 1.74 (tt, *J* = 7.8 and 7.5 Hz, O=C–CH$_2$–C*H*$_2$, 2H), 1.43–1.52 (m, S–(CH$_2$)$_2$–(C*H*$_2$)$_2$, 4H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.0, 151.1, 144.8, 144.7, 138.3, 136.8, 136.1, 132.6, 132.6, 132.6, 132.6, 128.7, 128.7, 128.3, 128.3, 127.6, 127.6, 127.5, 127.5, 127.3, 127.3, 122.3, 122.3, 118.9, 118.8, 111.0, 110.7, 34.2, 32.9, 28.7, 28.6, 28.4, 24.7 ppm. FTIR (KBr): 3053, 2925, 2862, 2225, 1746, 1605, 1487, 1460, 1358, 1307, 1278, 1196, 1168, 1139, 1095, 1004, 922, 813, 757, 728, 659 cm^{-1}. HRMS (ESI, m/z): [M+Na]+ calcd. for $C_{33}H_{28}$ N_2NaO_2S, 539.1764; found, 539.1760.

9'-(4-Bromophenylthio)nonanoic acid (COOH8SPhBr)

Yield: 99%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.17 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 2.88 (t, *J* = 7.4 Hz, S–C*H*$_2$, 2H), 2.35 (t, *J* = 7.4 Hz, HOOC–

CH_2, 2H), 1.62 (tt, *J* = 7.4 and 7.5 Hz, S–CH_2–CH_2 and HOOC–CH_2–CH_2, 4H), 1.24–1.45 (m, S–$(CH_2)_2$–$(CH_2)_4$, 8H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.6, 136.2, 131.8, 131.8, 130.5, 130.4, 119.4, 33.9, 33.6, 29.0, 28.9, 28.8, 28.6, 24.6 ppm.

9''-(4-Cyanobiphenyl-4'-ylthio)nonanoic acid (COOH8SCB)
Yield: 45%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.66 (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), 2.97 (t, *J* = 7.4 Hz, S–CH_2, 2H), 2.35 (dt, *J* = 7.4 Hz, HOOC–CH_2, 2H), 1.69 (tt, *J* = 7.4 and 7.4 Hz, S–CH_2–CH_2, 2H), 1.64 (tt, *J* = 6.9 and 7.4 Hz, HOOC–CH_2–CH_2, 2H), 1.28–1.50 (m, HOOC–$(CH_2)_2$–$(CH_2)_4$, 8H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.6, 145.0, 138.5, 136.0, 132.6, 132.6, 128.6, 128.6, 127.5, 127.5, 127.3, 127.3, 118.9, 110.8, 33.9, 33.0, 29.0, 28.9, 28.9, 28.9, 28.7, 24.6 ppm.

(4-Cyanobiphenyl-4'-yl) 9''-(4-cyanobiphenyl-4'-ylthio)nonanoate (CBOCO8SCB)
Yield: 57%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.71 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.66 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.65 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.59 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.51 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.39 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.20 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 2.98 (t, *J* = 7.4 Hz, S–CH_2, 2H), 2.59 (t, *J* = 7.6 Hz, O=C–CH_2, 2H), 1.77 (tt, *J* = 7.4 and 7.9 Hz, S–CH_2–CH_2, 2H), 1.71 (tt, *J* = 7.6 and 8.0 Hz, O=C–CH_2–CH_2, 2H), 1.32–1.51 (m, S–$(CH_2)_2$–$(CH_2)_4$, 8H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.1, 151.1, 144.9, 144.7, 138.5, 136.7, 136.1, 132.6, 132.6, 132.6, 132.6, 128.5, 128.5, 128.3, 128.3, 127.6, 127.6, 127.5, 127.5, 127.3, 127.3, 122.3, 122.3, 118.9, 118.8, 111.0, 110.7, 34.3, 33.0, 29.1, 29.0, 28.9, 28.7, 28.7, 24.8 ppm. FTIR (KBr): 3051, 2948, 2928, 2848, 2224, 1751, 1605, 1491, 1469, 1370, 1306, 1269, 1196, 1169, 1132, 1095, 1006, 921, 832, 813, 722, 645 cm^{-1}. HRMS (ESI, m/z): [M+Na]+ calcd. for $C_{35}H_{32}N_2NaO_2S$, 567.2077; found, 567.2080.

11'-(4-Bromophenylthio)undecanoic acid (COOH10SPhBr)
Yield: 99%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.17 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 2.88 (t, *J* = 7.5 Hz, S–CH_2, 2H), 2.35 (t, *J* = 7.5 Hz, HOOC–CH_2, 2H), 1.62 (tt, *J* = 7.5 and 7.5 Hz, S–CH_2–CH_2 and HOOC–CH_2–CH_2, 4H), 1.20–1.45 (m, S–$(CH_2)_2$–$(CH_2)_6$, 12H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.7, 136.3, 131.8, 131.8, 130.3, 130.3, 119.3, 33.9, 33.6, 29.4, 29.3, 29.2, 29.1, 29.0,

28.9, 28.7, 24.6 ppm.

11''-(4-Cyanobiphenyl-4'-ylthio)undecanoic acid (COOH10SCB)

Yield: 25%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.8 Hz, Ar–*H*, 2H), 7.66 (d, *J* = 8.8 Hz, Ar–*H*, 2H), 7.51 (d, *J* = 8.8 Hz, Ar–*H*, 2H), 7.39 (d, *J* = 8.8 Hz, Ar–*H*, 2H), 2.97 (t, *J* = 7.2 Hz, S–CH_2, 2H), 2.33 (dt, *J* = 6.5 Hz, HOOC–CH_2, 2H), 1.68 (tt, *J* = 7.2 and 7.4 Hz, S–CH_2–CH_2, 2H), 1.62 (tt, *J* = 6.5 and 7.0 Hz, HOOC–CH_2–CH_2, 2H), 1.18–1.48 (m, HOOC–$(CH_2)_2$–$(CH_2)_6$, 12H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.6, 144.9, 133.8, 132.6, 132.6, 128.6, 128.6, 127.4, 127.4, 127.2, 127.2, 118.8, 116.7, 110.6, 34.3, 33.0, 29.3, 29.2, 29.1, 29.0, 29.0, 29.0, 28.7, 24.7 ppm.

(4-Cyanobiphenyl-4'-yl) 11''-(4-cyanobiphenyl-4'-ylthio)undecanoate CBOCO10SCB

Yield: 47%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.71 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.66 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.66 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.59 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.51 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.39 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.20 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 2.98 (t, *J* = 7.4 Hz, S–CH_2, 2H), 2.58 (t, *J* = 7.4 Hz, O=C–CH_2, 2H), 1.77 (tt, *J* = 7.4 and 7.4 Hz, S–CH_2–CH_2, 2H), 1.70 (tt, *J* = 7.4 and 7.3 Hz, O=C–CH_2–CH_2, 2H), 1.28–1.50 (m, S–$(CH_2)_2$–$(CH_2)_6$, 12H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.0, 151.2, 144.9, 144.7, 138.6, 136.7, 136.1, 132.6, 132.6, 132.6, 132.6, 128.5, 128.5, 128.3, 128.3, 127.6, 127.6, 127.5, 127.5, 127.3, 127.3, 122.3, 122.3, 118.9, 118.8, 111.0, 110.7, 34.4, 33.0, 29.4, 29.3, 29.2, 29.1, 29.1, 29.0, 28.8, 24.9 ppm. FTIR (KBr): 3050, 2927, 2852, 2225, 1750, 1606, 1490, 1470, 1345, 1312, 1280, 1196, 1170, 1133, 1096, 1007, 923, 832, 812, 723 cm^{-1}. HRMS (ESI, m/z): [M+Na]+ calcd. For $C_{37}H_{36}N_2NaO_2S$, 595.2390; found, 595.2382.

S3. Phase-transition data on first heating

Table S1. Phase-transition data on first heating for CBCOO*n*SCB. T_m and T_{NI}, denote the melting temperature and N-Iso phase-transition temperature, respectively, and $\Delta S_m/R$ and $\Delta S_{NI}/R$ represent entropy changes scaled by the gas constant (R) at the at T_m and T_{NI}, respectively.

CBCOO*n*SCB		T_m (°C)	$\Delta S_m/R$	
n = 2	Cr	165.5	11.1	Iso
4	Cr	120.2	9.4	Iso
6	Cr	104.9	10.7	Iso
8	Cr	107.3	16.6	Iso
10	Cr	105.6	16.1	Iso

Table S2. Phase-transition data on first heating for CBCOO*n*SCB.

CBOCO*n*SCB		T_m (°C)	$\Delta S_m/R$		T_{NI} (°C)	$\Delta S_{NI}/R$	
n = 2	Cr	166.9	12.2	-	-	-	Iso
4	Cr	125.2	12.4	N	152.8	0.44	Iso
6	Cr	135.7	6.1	N	151.7	0.47	Iso
8	Cr	98.0	15.1	N	147.8	0.96	Iso
10	Cr	104.8	19.1	N	142.5	1.09	Iso

S4. POM images

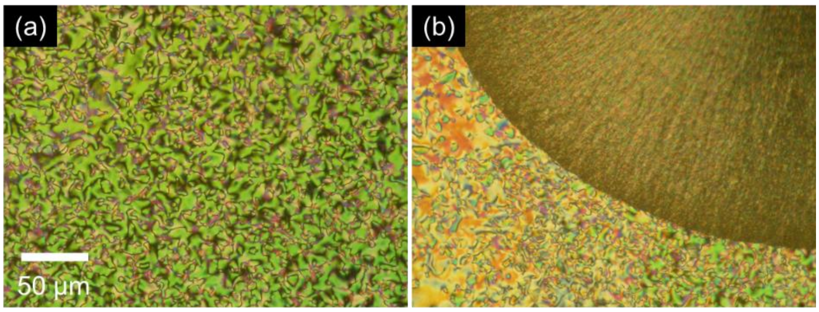


Fig. S1. POM images of CBCOO2SCB in a non-treated glass cell; (a) the N phase at 75 °C and (b) the N phase accompanied by crystallization at 75 °C.

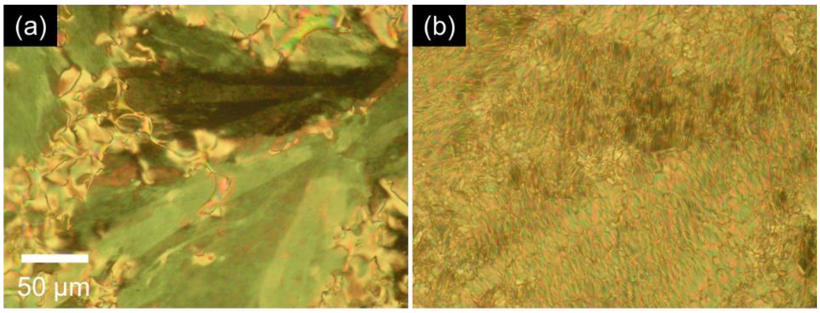


Fig. S2. POM images of CBCOO6SCB in a non-treated glass cell; (a) the N phase at 80 °C and (b) the N_{TB} phase at 58 °C.

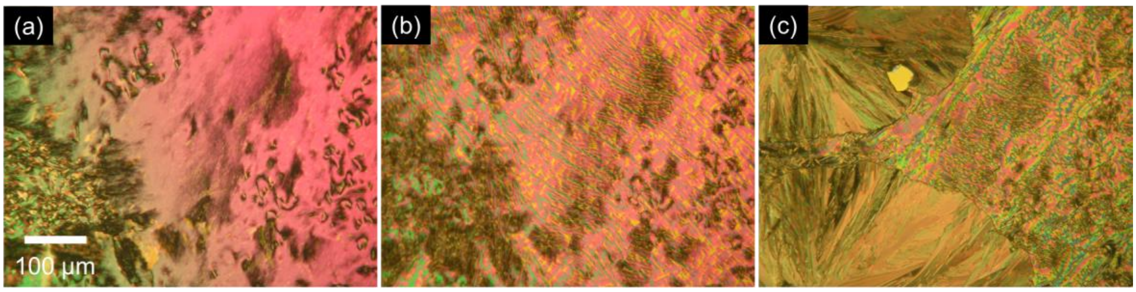


Fig. S3. POM images of CBCOO8SCB in a non-treated glass cell; (a) the N phase at 90 °C, (b) the N_{TB} phase at 83 °C, and (c) the N_{TB} phase accompanied by crystallization at 70 °C.

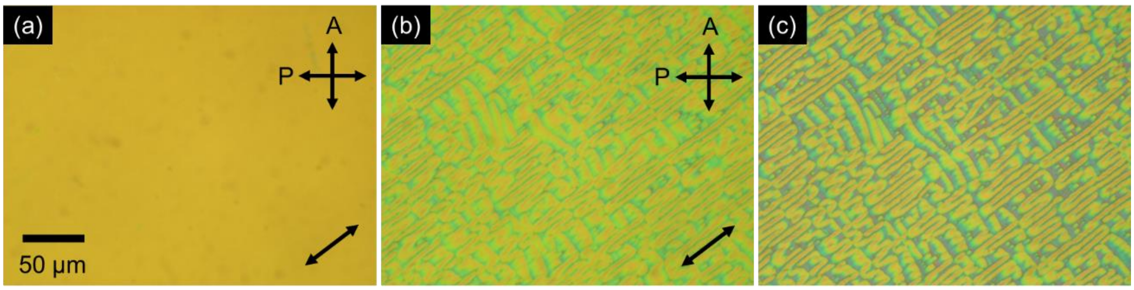


Fig. S4. POM images of CBCOO8SCB in a uniaxially rubbed polyimide-surface glass cell; (a) the N phase at 85 °C, (b) the N_{TB} phase at 82 °C, and (c) the N_{TB} phase at 77 °C. The double-headed arrows represent the rubbing direction.

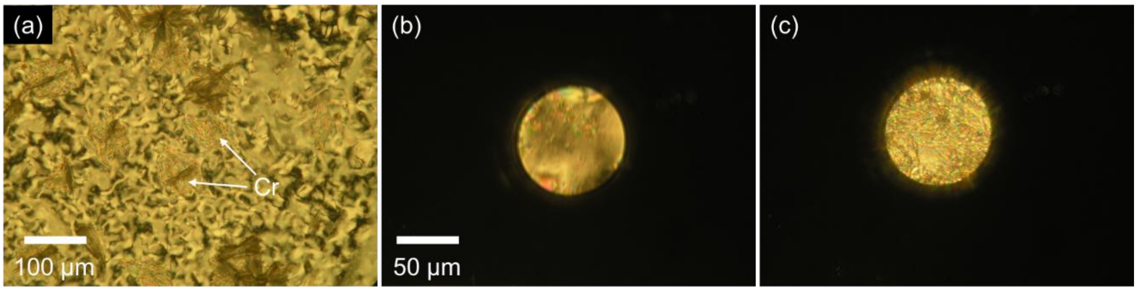


Fig. S5. POM images of CBCOO10SCB in a non-treated glass cell; (a) the N phase at 97 °C, (b) the N phase at 100 °C, and (c) the N_{TB} phase at 75 °C.

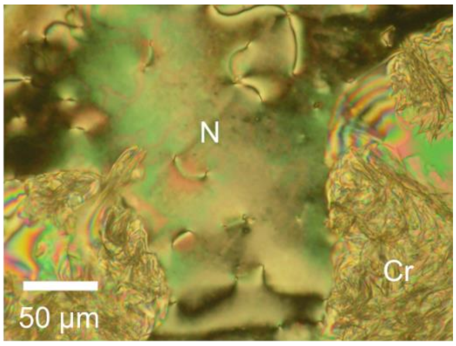


Fig. S6. POM image of CBOCO2SCB in a non-treated glass cell; the N phase accompanied by crystallization at 133 °C.

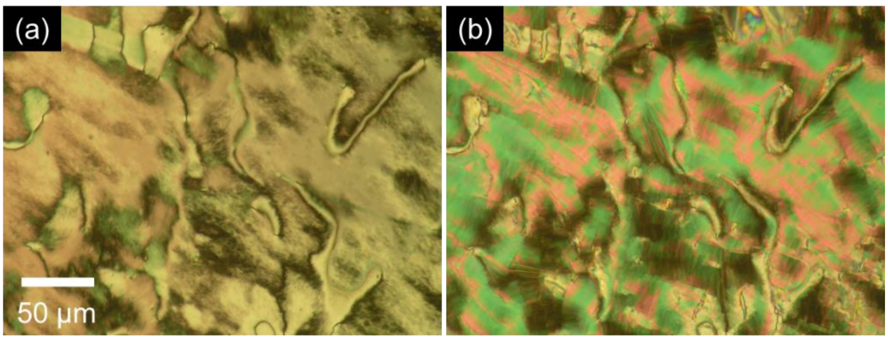


Fig. S7. POM images of CBOCO8SCB in a non-treated glass cell; (a) the N phase at 95 °C and (b) the N_{TB} phase at 87 °C.

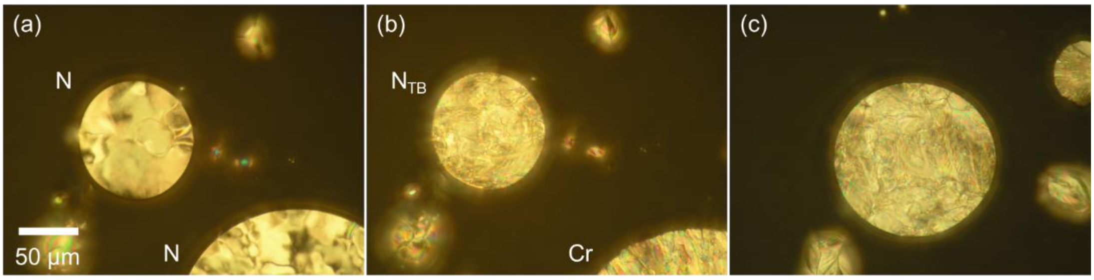


Fig. S8. POM images of CBOCO10SCB in a non-treated glass cell; (a) the N phase at 100 °C, (b) the N_{TB} phase at 70 °C, and (c) the N_{TB} phase at 69 °C.

S5. DSC curves

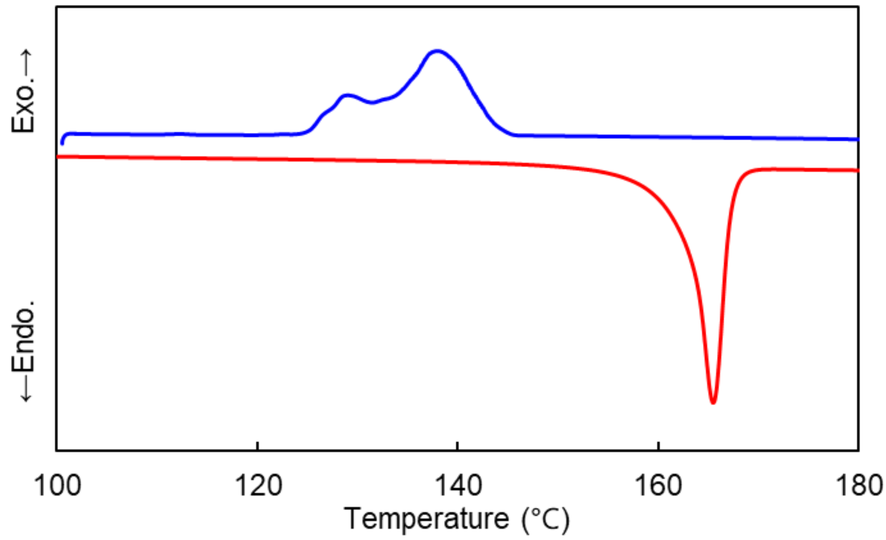


Fig. S9. DSC curves of CBCOO2SCB upon 1st heating and cooling at a rate of 10 °C min^{-1}.

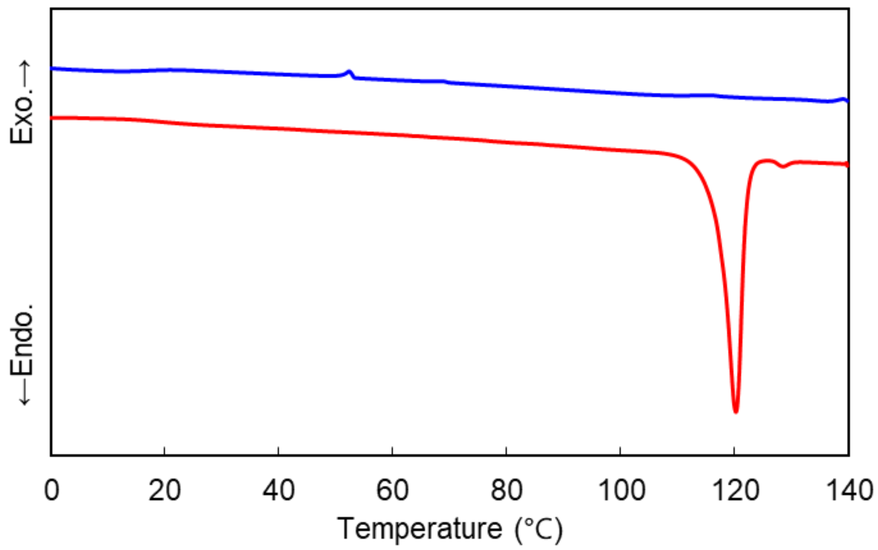


Fig. S10. DSC curves of CBCOO4SCB upon 1st heating and cooling at a rate of 10 °C min^{-1}, which was reproduced from ref. S1 with permission from Elsevier.

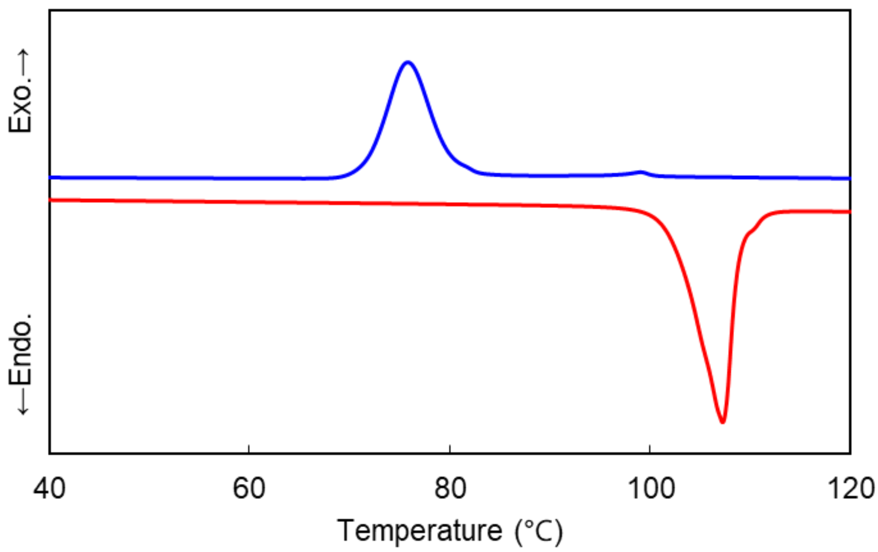


Fig. S11. DSC curves of CBCOO8SCB upon 1st heating and cooling at a rate of 10 °C min^{-1}.

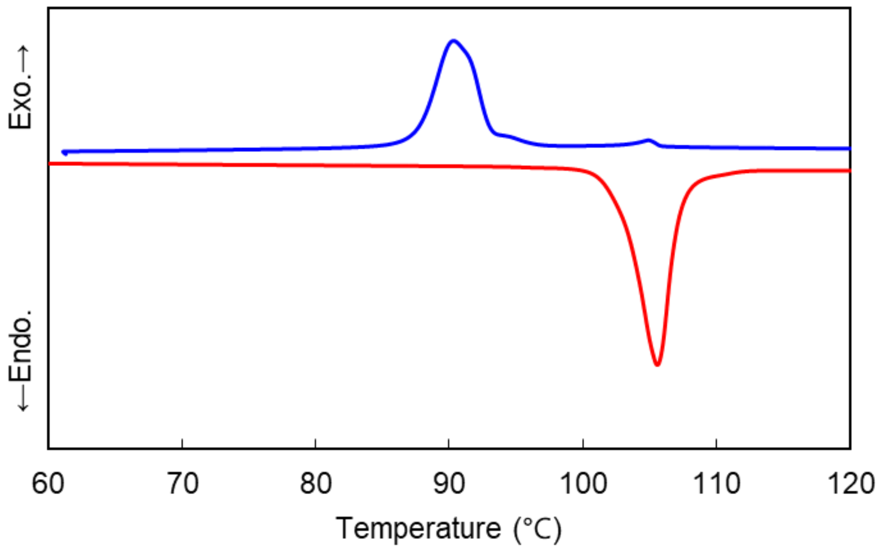


Fig. S12. DSC curves of CBCOO10SCB upon 1st heating and cooling at a rate of 10 °C min^{-1}.

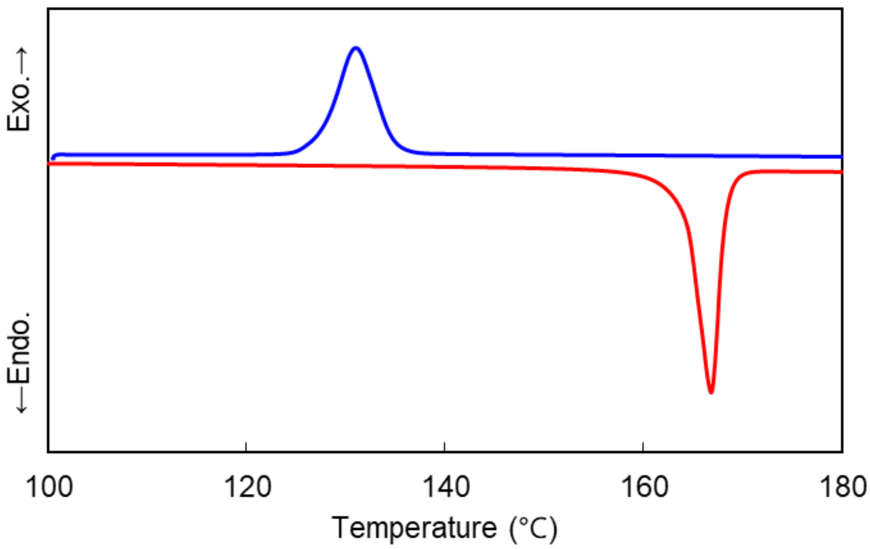


Fig. S13. DSC curves of CBOCO2SCB upon 1st heating and cooling at a rate of 10 °C min^{-1}.

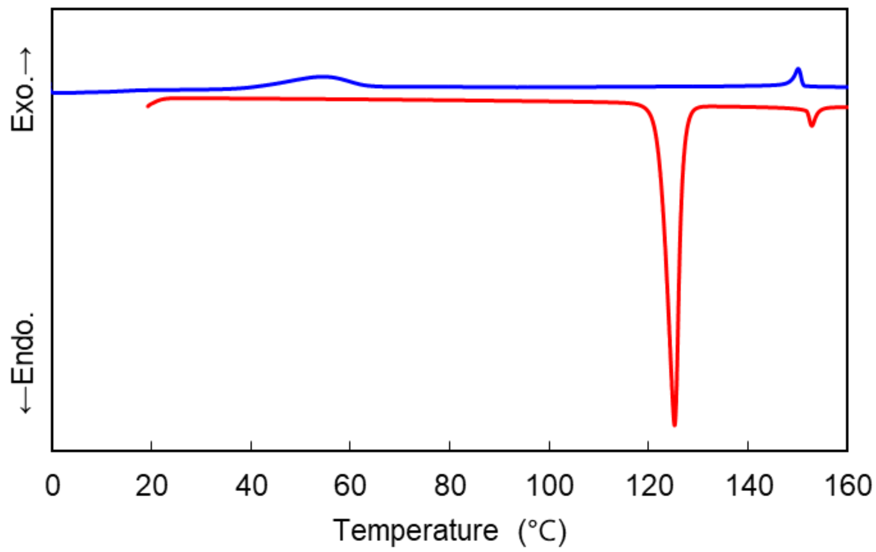


Fig. S14. DSC curves of CBOCO4SCB upon 1st heating and cooling at a rate of 10 °C min^{-1}, which was reproduced from ref. S1 with permission from Elsevier.

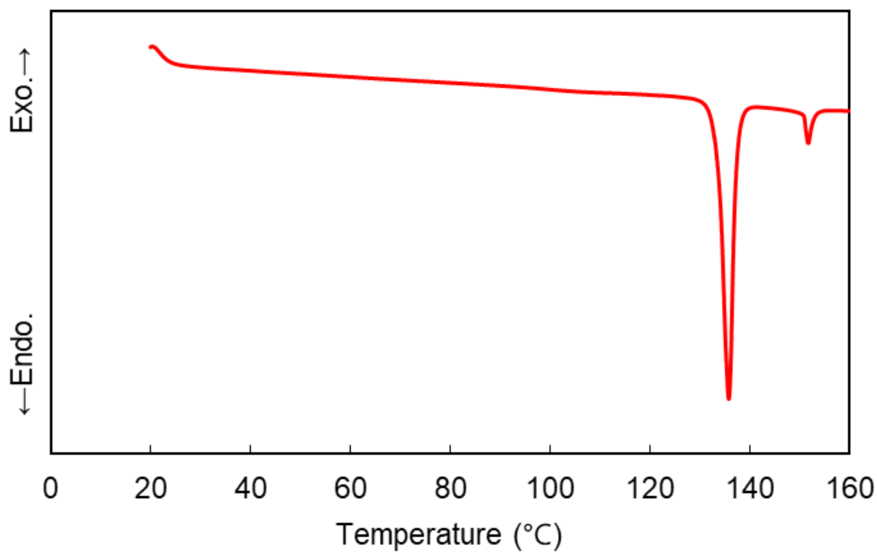


Fig. S15. DSC curves of CBOCO6SCB upon 1st heating at a rate of 10 °C min^{-1}.

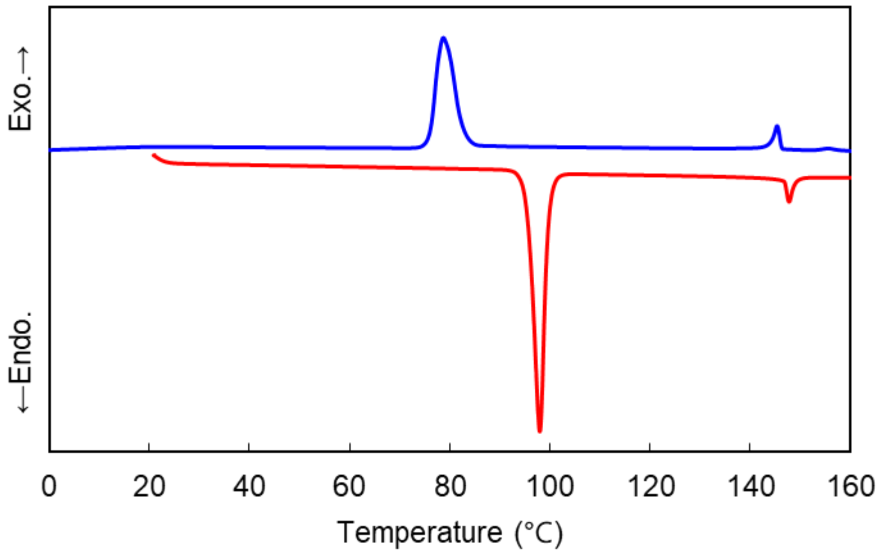


Fig. S16. DSC curves of CBOCO8SCB upon 1st heating and cooling at a rate of 10 °C min^{-1}.

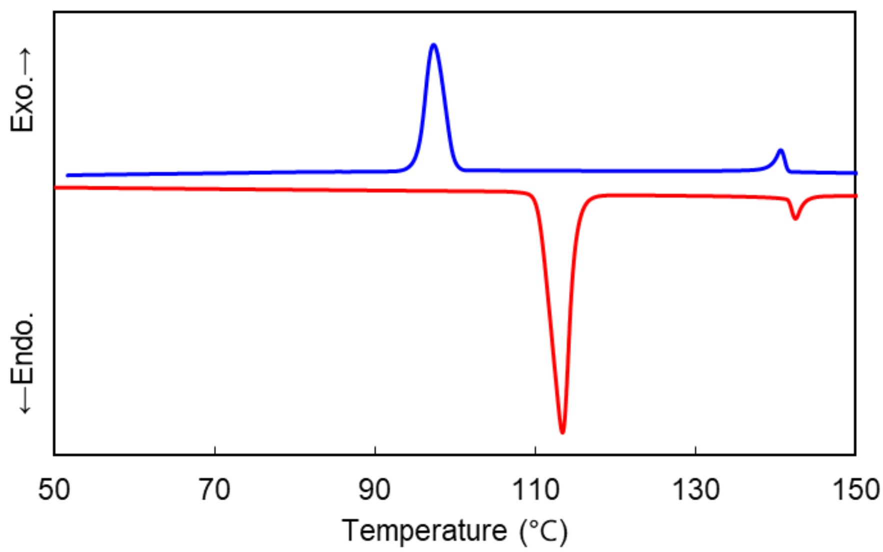


Fig. S17. DSC curves of CBOCO10SCB upon 1st heating and cooling at a rate of 10 °C min^{-1}.

S6. XRD measurements

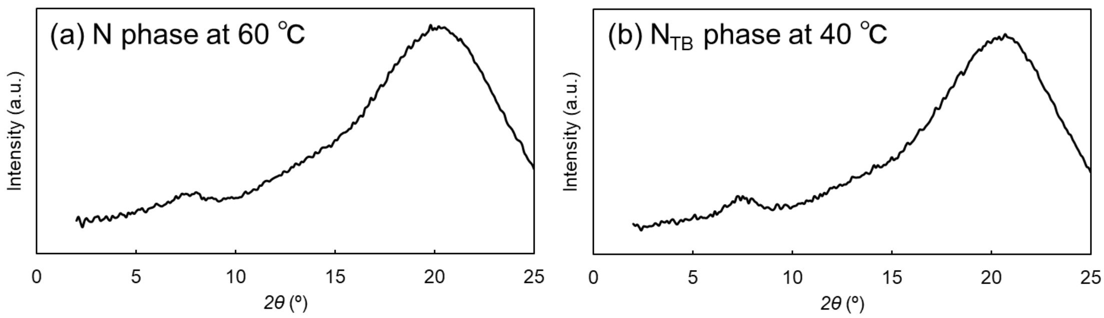


Fig. S18. 1D-XRD profiles of CBCOO4SCB; (a) the N phase at 60 °C, and (b) the N_{TB} phase at 40 °C.

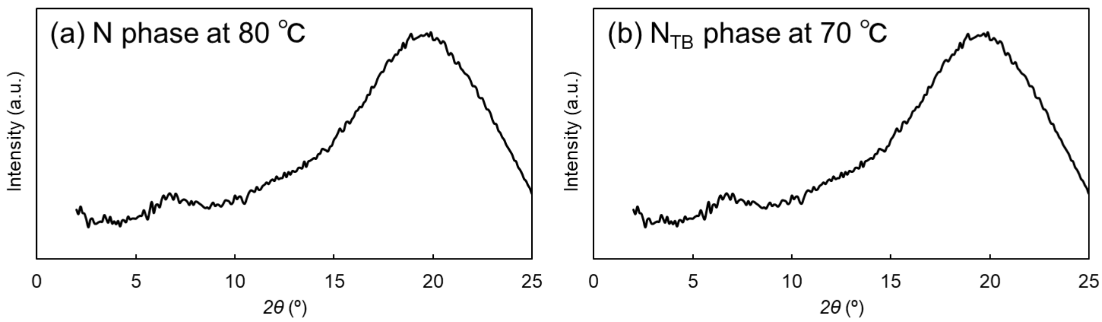


Fig. S19. 1D-XRD profiles of CBCOO6SCB; (a) the N phase at 80 °C, and (b) the N_{TB} phase at 70 °C.

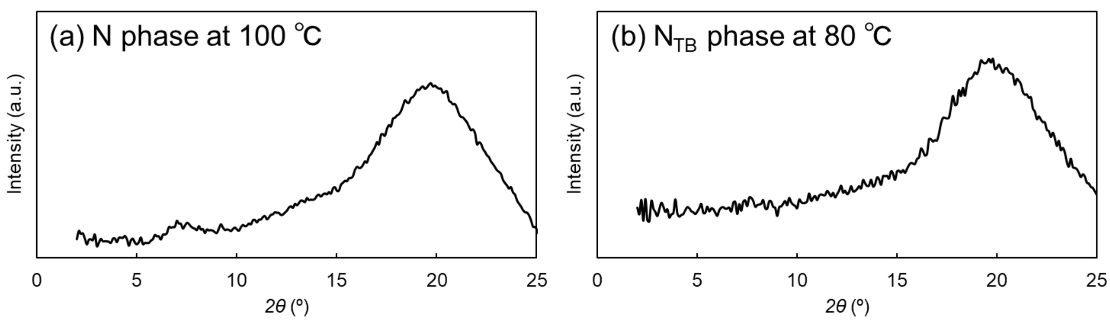


Fig. S20. 1D-XRD profiles of CBOCO4SCB; (a) the N phase at 100 °C, and (b) the N_{TB} phase at 80 °C.

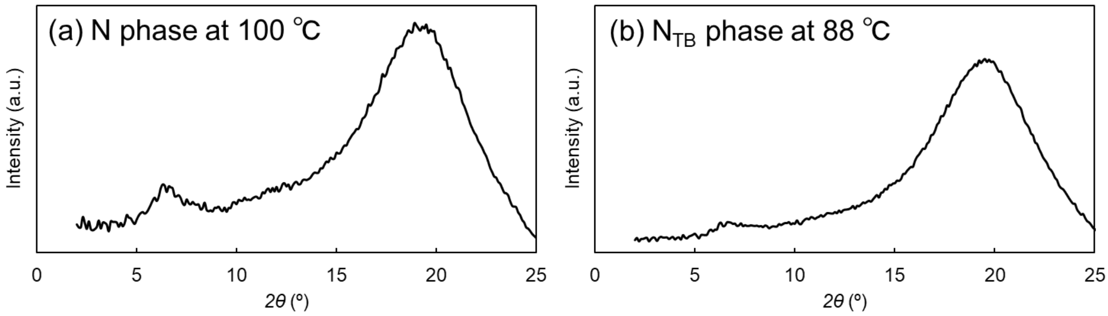


Fig. S21. 1D-XRD profiles of CBOCO6SCB; (a) the N phase at 100 °C, and (b) the N_{TB} phase at 88 °C.

S7. TReXS measurements

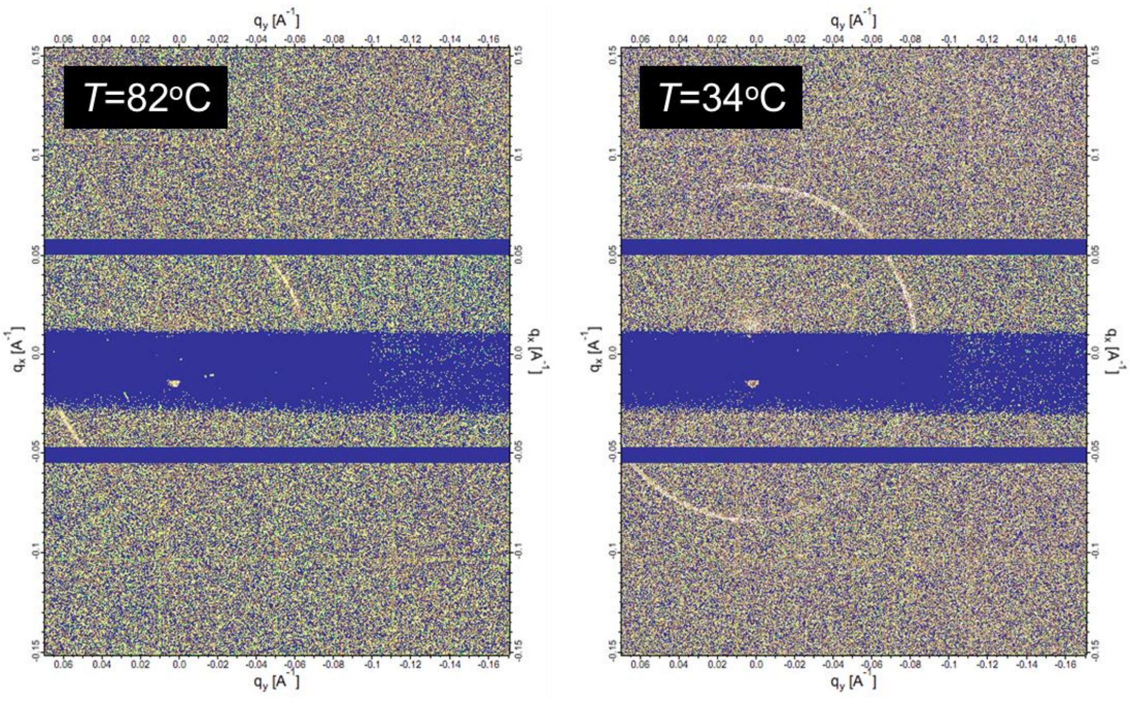


Fig. S22. 2D-TReXS data of CBCOO6SCB.

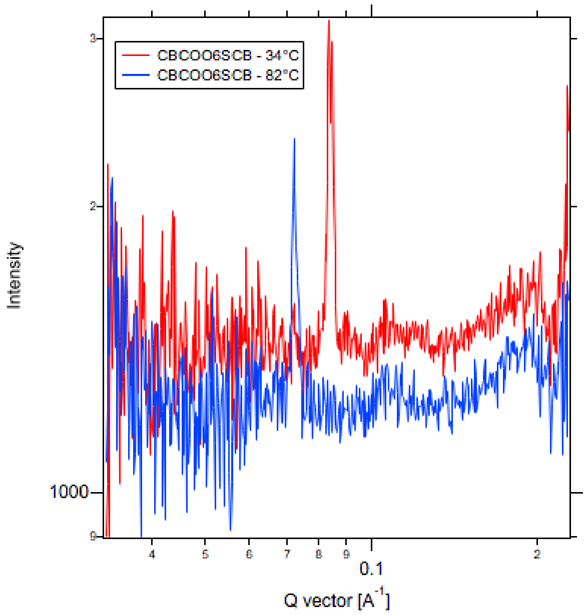


Fig. S23. 1D-TReXS profiles of CBCOO6SCB.

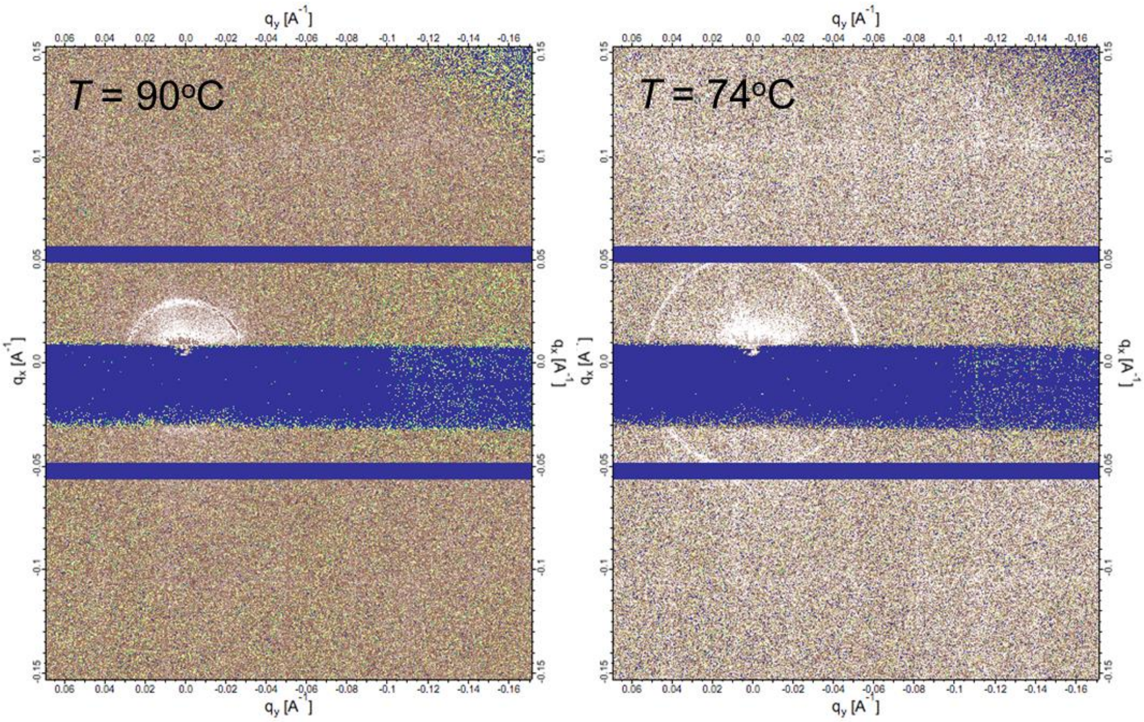


Fig. S24. 2D-TReXS data of CBOCO4SCB.

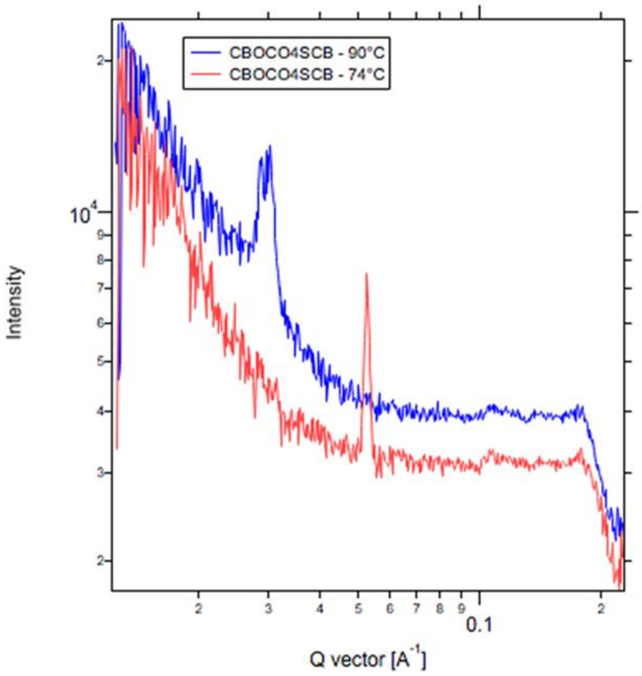


Fig. S25. 1D-TReXS profiles of CBOCO4SCB.

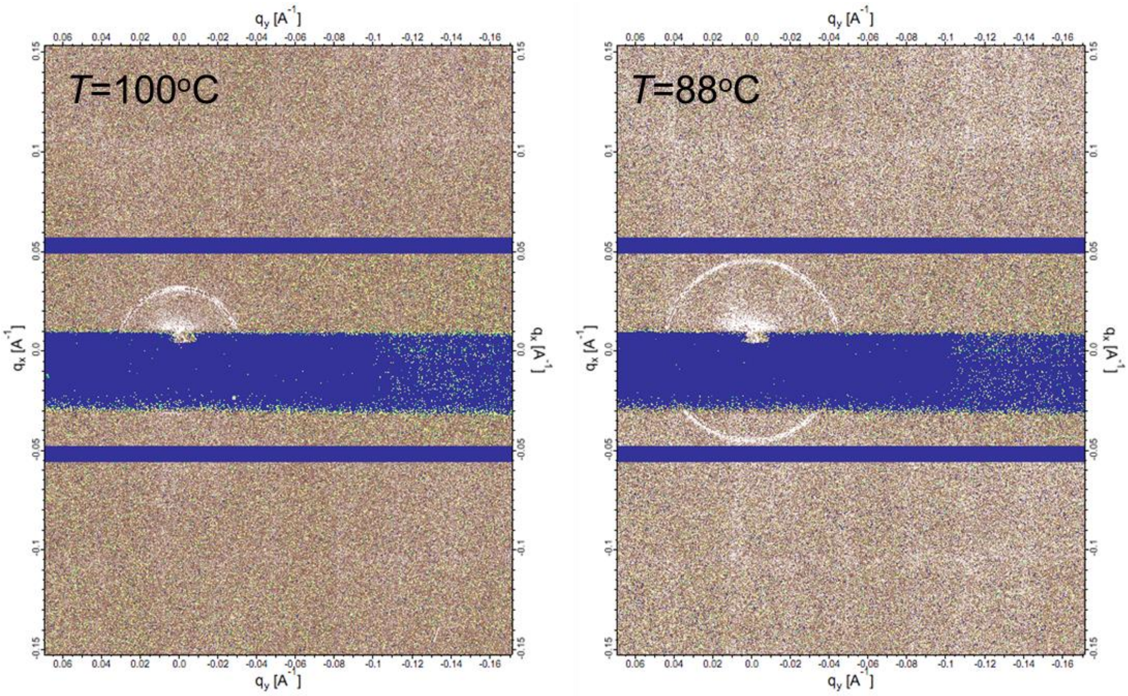


Fig. S26. 2D-TReXS data of CBOCO6SCB.

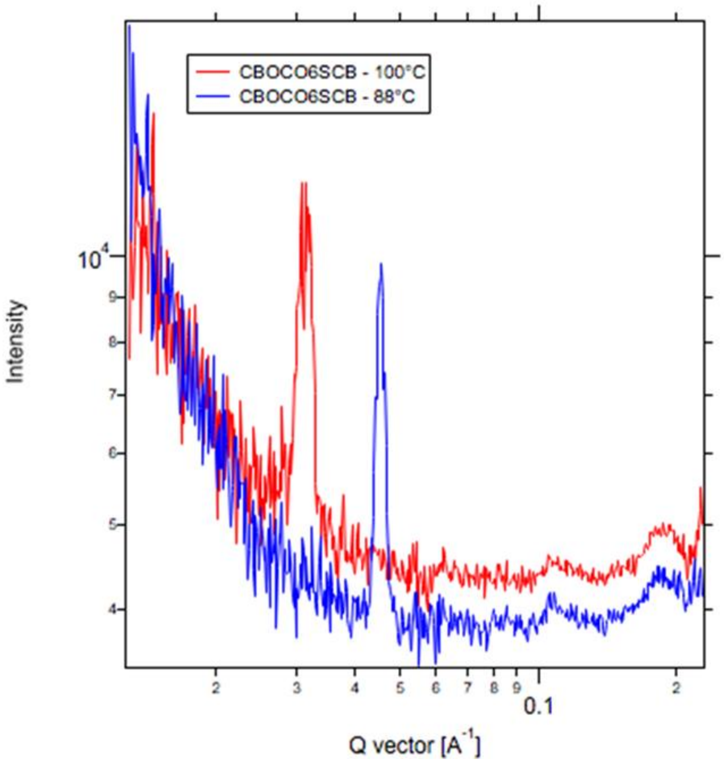


Fig. S27. 1D-TReXS profiles of CBOCO6SCB.

Reference

S1. Y. Arakawa, K. Komatsu, S. Inui and H. Tsuji, *J. Mol. Struct.*, 2020, 1199, 126913.