Electronic supplementary information

Alkylthio-based asymmetric liquid crystals: unravelling the substituent effects and intercalated cybotactic nematic and smectic phases

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1. Synthesis

General procedure for synthesis of 4-Hydroxyphenyl 4-alkylthiobenzoate

Corresponding 4-alkylthiobenzoic acid (1eq),[S1] hydroquinone (2eq), and 4-dimethylaminopyridine (DMAP) (0.1eq) were added to a double-necked flask, which was purged with an argon gas. Tetrahydrofuran (THF) (15 mL) was added to the flask *via* syringe to dissolve the solids. *N*,*N*′-Dicyclohexylcarbodiimide (DCC) (1.3 eq) dissolved in THF (15 mL) was added to the flask via a syringe, and the mixture was stirred at ambient temperature for 12 hours. After completion of the reaction, purification was carried out by column chromatography on silica gel using dichloromethane (DCM) as an eluent and recrystallization from a mixed solvent of DCM and hexane, to afford a corresponding 4-hydroxyphenyl 4-alkylthiobenzoate.

4-Hydroxyphenyl 4-methylthiobenzoate

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.31 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.07 (d, *J* = 8.8 Hz, Ar–*H*, 2H), 6.86 (d, *J* = 8.8 Hz, Ar–*H*, 2H), 4.78 (s, Ar–O*H*, 1H), 2.55 (s, CH_3, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 153.3, 146.4, 144.5, 130.4, 125.6, 125.1, 122.7, 116.0, 14.8 ppm.

4-Hydroxyphenyl 4-ethylthiobenzoate

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.34 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.07 (d, *J* = 8.8 Hz, Ar–*H*, 2H), 6.86 (d, *J* = 8.8 Hz, Ar–*H*, 2H), 4.83 (s, Ar–O*H*, 1H), 3.05 (q, *J* = 7.4 Hz, S–CH_2, 2H), 1.39 (t, *J* = 7.4 Hz, CH_3, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 153.5, 145.4, 144.2, 130.5, 126.3, 125.8, 122.5, 116.2, 26.1, 13.9 ppm.

4-Hydroxyphenyl 4-propylthiobenzoate

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.34 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.07 (d, *J* = 7.6 Hz, Ar–*H*, 2H), 6.87 (d, *J* = 7.6 Hz, Ar–*H*, 2H), 4.77 (s, Ar–O*H*, 1H), 3.00 (t, *J* = 7.2 Hz, S–CH_2, 2H) , 1.75 (tq, *J* = 7.2, 7.4 Hz, S–CH_2–CH_2, 2H), 1.07 (t, *J* = 7.4 Hz, CH_3, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 153.5, 145.6, 144.3, 130.4, 126.4, 125.8, 122.5, 116.1, 34.0, 22.2, 13.5 ppm.

4-Hydroxyphenyl 4-butylthiobenzoate

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.34 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.06 (d, *J* = 8.8 Hz, Ar–*H*, 2H), 6.85 (d, *J* = 8.8 Hz, Ar–*H*, 2H), 4.95 (s, Ar–O*H*,

1H), 3.02 (t, J = 7.4 Hz, S–CH_2, 2H), 1.71 (tt, J = 7.4, 7.4 Hz, S–CH_2–CH_2, 2H), 1.50 (tq, J = 7.4, 7.4 Hz, S–$(CH_2)_2$–CH_2, 2H), 0.96 (t, J = 7.4 Hz, CH_3, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 153.6, 145.7, 144.3, 130.5, 126.3, 125.7, 122.5, 116.2, 31.7, 30.8, 22.0, 13.6 ppm.

4-Hydroxyphenyl 4-pentylthiobenzoate

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.8 Hz, Ar–H, 2H), 7.34 (d, J = 8.8 Hz, Ar–H, 2H), 7.06 (d, J = 8.8 Hz, Ar–H, 2H), 6.86 (d, J = 8.8 Hz, Ar–H, 2H), 4.90 (s, Ar–OH, 1H), 3.01 (t, J = 7.4 Hz, S–CH_2, 2H), 1.71 (tt, J = 7.4, 7.4 Hz, S–CH_2–CH_2, 2H), 1.45 (tt, J = 7.4, 7.4 Hz, S–$(CH_2)_2$–CH_2, 2H), 1.37 (tq, J = 7.0, 7.4 Hz, S–$(CH_2)_3$–CH_2, 2H), 0.92 (t, J = 7.0 Hz, CH_3, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 153.3, 145.6, 144.5, 130.4, 126.3, 125.9, 122.6, 116.0, 32.0, 31.1, 28.5, 22.2, 13.9 ppm.

4-Hydroxyphenyl 4-hexylthiobenzoate

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.4 Hz, Ar–H, 2H), 7.36 (d, J = 8.4 Hz, Ar–H, 2H), 7.06 (d, J = 8.8 Hz, Ar–H, 2H), 6.85 (d, J = 8.8 Hz, Ar–H, 2H), 4.96 (s, Ar–OH, 1H), 3.01 (t, J = 7.4 Hz, S–CH_2, 2H), 1.72 (tt, J = 7.4, 7.6 Hz, S–CH_2–CH_2, 2H), 1.47 (tt, J = 7.0, 7.6 Hz, S–$(CH_2)_2$–CH_2, 2H), 1.27–1.38 (m, S–$(CH_2)_3$–$(CH_2)_2$, 4H), 0.90 (t, J = 6.6 Hz, CH_3, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 153.5, 145.7, 144.3, 130.4, 126.3, 125.7, 122.6, 116.1, 32.0, 31.3, 28.7, 28.6, 22.5, 14.0 ppm.

4-Hydroxyphenyl 4-heptylthiobenzoate

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.8 Hz, Ar–H, 2H), 7.34 (d, J = 8.8 Hz, Ar–H, 2H), 7.06 (d, J = 8.8 Hz, Ar–H, 2H), 6.86 (d, J = 8.8 Hz, Ar–H, 2H), 4.81 (s, Ar–OH, 1H), 3.01 (t, J = 7.4 Hz, S–CH_2, 2H), 1.72 (tt, J = 7.4, 7.4 Hz, S–CH_2–CH_2, 2H), 1.46 (tt, J = 6.8, 7.4 Hz, S–$(CH_2)_2$–CH_2, 2H), 1.24–1.38 (m, S–$(CH_2)_3$–$(CH_2)_3$, 6H), 0.89 (t, J = 6.0 Hz, CH_3, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 153.3, 145.6, 144.5, 130.4, 126.4, 125.9, 122.6, 116.0, 32.1, 31.7, 28.9, 28.81, 28.77, 22.6, 14.0 ppm.

4-Hydroxyphenyl 4-octylthiobenzoate

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.4 Hz, Ar–H, 2H), 7.34 (d, J = 8.4 Hz, Ar–H, 2H), 7.05 (d, J = 8.8 Hz, Ar–H, 2H), 6.84 (d, J = 8.8 Hz, Ar–H, 2H), 4.97 (s, Ar–OH, 1H), 3.01 (t, J = 7.4 Hz, S–CH_2, 2H), 1.72 (tt, J = 7.4, 7.4 Hz, S–CH_2–CH_2, 2H), 1.46 (tt, J = 7.0, 7.4 Hz, S–$(CH_2)_2$–CH_2, 2H), 1.23–1.38 (m, S–$(CH_2)_3$–$(CH_2)_4$, 8H), 0.90 (t, J = 6.6 Hz, CH_3, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 153.5, 145.7, 144.4, 130.4, 126.3, 125.8, 122.6, 116.1, 32.1, 31.8, 29.12, 29.10, 28.9, 28.7, 22.6, 14.1 ppm.

General procedure for synthesis of 4-[(4-alkoxybenzoyl)oxy]phenyl 4-alkylthiobenzoate (SO*n*)

SO*n* homologues were synthesized according to the similar procedure for the syntheses of 4-hydroxyphenyl 4-alkylthiobenzoates as described above, using corresponding 4-hydroxyphenyl 4-alkylthiobenzoates, 4-alkylthiobenzoic acids, and dehydrated DCM as a solvent. Purification was carried out by column chromatography on silica gel using a mixed solvent of DCM/hexane as an eluent, and recrystallization from a mixed solvent of DCM/hexane.

4-[(4-Methoxybenzoyl)oxy]phenyl 4-methylthiobenzoate (SO1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.8 Hz, Ar–*H*, 2H), 8.10 (d, *J* = 8.8 Hz, Ar–*H*, 2H), 7.32 (d, *J* = 8.8 Hz, Ar–*H*, 2H), 7.26 (s, Ar–*H*, 4H), 7.00 (d, *J* = 8.8 Hz, Ar–*H*, 2H), 3.91 (s, O–C*H*$_3$, 3H), 2.55 (s, S–C*H*$_3$, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8×2, 164.0, 148.5, 148.3, 146.7, 132.3×2, 130.5×2, 125.4×2, 125.1, 122.7×2, 122.6×2, 121.7, 113.9×2, 55.5, 14.8 ppm. HRMS (ESI, m/z): $[M+Na]^+$ calcd. for $C_{22}H_{18}NaO_5S$, 417.0773; found, 417.0774.

4-[(4-Ethoxybenzoyl)oxy]phenyl 4-ethylthiobenzoate (SO2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 9.2 Hz, Ar–*H*, 2H), 8.09 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.36 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.26 (s, Ar–*H*, 4H), 6.98 (d, *J* = 9.2 Hz, Ar–*H*, 2H), 4.14 (q, *J* = 7.0 Hz, O–C*H*$_2$, 2H), 3.06 (q, *J* = 7.4 Hz, S–C*H*$_2$, 2H), 1.47 (t, *J* = 7.0 Hz, O–CH_2–C*H*$_3$, 3H), 1.40 (t, *J* = 7.4 Hz, S–CH_2–C*H*$_3$, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8×2, 163.6, 148.8, 148.5, 145.5, 132.4×2, 130.6×2, 126.8×2, 126.2, 122.7×2, 122.6×2, 121.8, 114.5×2, 63.9, 26.4, 14.7, 14.0 ppm. HRMS (ESI, m/z): $[M+Na]^+$ calcd. for $C_{24}H_{22}NaO_5S$, 445.1080; found, 445.1059.

4-[(4-Propoxybenzoyl)oxy]phenyl 4-propylthiobenzoate (SO3)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.8 Hz, Ar–*H*, 2H), 8.07 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.34 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.25 (s, Ar–*H*, 4H), 6.97 (d, *J* = 8.8 Hz, Ar–*H*, 2H), 4.01 (t, *J* = 6.8 Hz, O–C*H*$_2$, 2H), 2.99 (t, *J* = 7.6 Hz, S–C*H*$_2$, 2H), 1.85 (tq, *J* = 6.8 and 7.2 Hz, O–CH_2–C*H*$_2$, 2H), 1.75 (tq, *J* = 7.2 and 7.6 Hz, S–CH_2–C*H*$_2$, 2H), 1.07 (t, *J* = 7.4 Hz, O–$(CH_2)_2$–C*H*$_3$, 3H), 1.06 (t, *J* = 7.4 Hz, S–$(CH_2)_2$–C*H*$_3$, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8×2, 163.6, 148.5, 148.3, 145.7, 132.3×2, 130.5×2, 126.4×2, 125.7, 122.7×2, 122.6×2, 121.4, 114.4×2, 69.8, 34.0, 22.5, 22.2, 13.5, 10.5 ppm. HRMS (ESI, m/z): $[M+Na]^+$ calcd. for $C_{26}H_{26}NaO_5S$, 473.1393; found, 473.1396.

4-[(4-Butoxybenzoyl)oxy]phenyl 4-butylthiobenzoate (SO4)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 8.08 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.35 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.26 (s, Ar–*H*, 4H), 6.98 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 4.06 (t, *J* = 6.2 Hz, O–CH_2, 2H), 3.03 (t, *J* = 7.2 Hz, S–CH_2, 2H), 1.82 (tt, *J* = 6.2 and 7.8 Hz, O–CH_2–CH_2, 2H), 1.72 (tt, *J* = 7.2 and 7.6 Hz, S–CH_2–CH_2, 2H), 1.60–1.45 (m, CH_2–CH_3, 4H), 1.00 (t, *J* = 7.2 Hz, O–$(CH_2)_3$–CH_3, 3H), 0.97 (t, *J* = 7.2 Hz, S–$(CH_2)_3$–CH_3, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8×2, 163.6, 148.6, 148.3, 145.8, 132.3×2, 130.5×2, 126.3×2, 125.7, 122.7×2, 122.6×2, 121.4, 114.4×2, 68.1, 31.7, 31.2, 30.8, 22.1, 19.2, 13.8, 13.6 ppm. HRMS (ESI, m/z): $[M+Na]^+$ calcd. for $C_{28}H_{30}NaO_5S$, 501.1706; found, 501.1697.

4-[(4-Pentyloxybenzoyl)oxy]phenyl 4-pentylthiobenzoate (SO5)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.8 Hz, Ar–*H*, 2H), 8.08 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.35 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 7.26 (s, Ar–*H*, 4H), 6.98 (d, *J* = 8.8 Hz, Ar–*H*, 2H), 4.05 (t, *J* = 6.4 Hz, O–CH_2, 2H), 3.02 (t, *J* = 7.2 Hz, S–CH_2, 2H), 1.83 (tt, *J* = 6.4 and 7.6 Hz, O–CH_2–CH_2, 2H), 1.73 (tt, *J* = 7.2 and 7.6 Hz, S–CH_2–CH_2, 2H), 1.52–1.24 (m, $(CH_2)_2$–CH_3, 8H), 0.95 (t, *J* = 7.0 Hz, O–$(CH_2)_4$–CH_3, 3H), 0.92 (t, *J* = 7.2 Hz, S–$(CH_2)_4$–CH_3, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8×2, 163.6, 148.6, 148.3, 145.8, 132.3×2, 130.5×2, 126.3×2, 125.7, 122.7×2, 122.6×2, 121.4, 114.4×2, 68.4, 32.0, 31.1, 28.8, 28.5, 28.2, 22.4, 22.3, 14.0, 13.9 ppm. HRMS (ESI, m/z): $[M+Na]^+$ calcd. for $C_{30}H_{34}NaO_5S$, 529.2019; found, 529.2024.

4-[(4-Hexyloxybenzoyl)oxy]phenyl 4-hexylthiobenzoate (SO6)

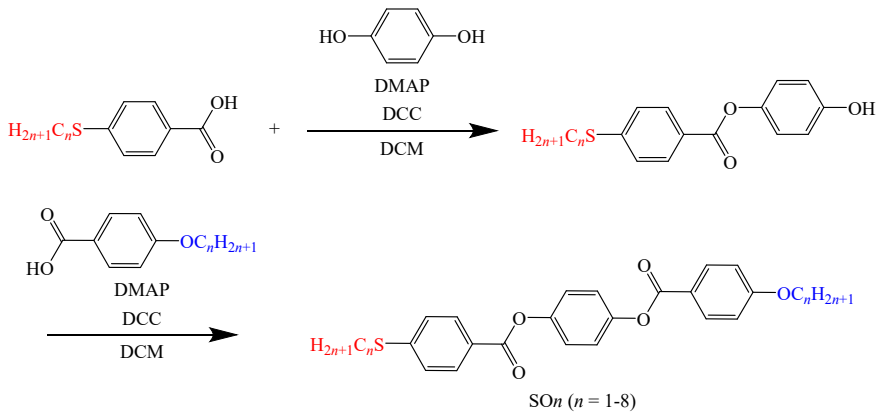
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.8 Hz, Ar–*H*, 2H), 8.08 (d, *J* = 8.6 Hz, Ar–*H*, 2H), 7.35 (d, *J* = 8.6 Hz, Ar–*H*, 2H), 7.26 (s, Ar–*H*, 4H), 6.96 (d, *J* = 8.8 Hz, Ar–*H*, 2H), 4.05 (t, *J* = 6.4 Hz, O–CH_2, 2H), 3.02 (t, *J* = 7.2 Hz, S–CH_2, 2H), 1.82 (tt, *J* = 6.4 and 6.8 Hz, O–CH_2–CH_2, 2H), 1.72 (tt, *J* = 7.2 and 7.6 Hz, S–CH_2–CH_2, 2H), 1.52–1.42 (m, CH_2–$(CH_2)_2$–CH_3, 4H), 1.40–1.28 (m, $(CH_2)_2$–CH_3, 8H), 0.92 (t, *J* = 6.8 Hz, O–$(CH_2)_5$–CH_3, 3H), 0.90 (t, *J* = 7.2 Hz, S–$(CH_2)_5$–CH_3, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8×2, 163.6, 148.6, 148.3, 145.8, 132.3×2, 130.5×2, 126.3×2, 125.6, 122.7×2, 122.6×2, 121.4, 114.4×2, 68.3, 31.9, 31.5, 31.3, 29.0, 28.64, 28.58, 25.6, 22.6, 22.5, 14.0×2 ppm. HRMS (ESI, m/z): $[M+Na]^+$ calcd. for $C_{32}H_{38}NaO_5S$, 557.2332; found, 557.2346.

4-[(4-Heptyloxybenzoyl)oxy]phenyl 4-heptylthiobenzoate (SO7)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 9.2 Hz, Ar–*H*, 2H), 8.08 (d, J = 8.4 Hz, Ar–*H*, 2H), 7.35 (d, J = 8.4 Hz, Ar–*H*, 2H), 7.26 (s, Ar–*H*, 4H), 6.96 (d, J = 9.2 Hz, Ar–*H*, 2H), 4.05 (t, J = 6.4 Hz, O–CH_2, 2H), 3.02 (t, J = 7.6 Hz, S–CH_2, 2H), 1.83 (tt, J = 6.4 and 7.2 Hz, O–CH_2–CH_2, 2H), 1.73 (tt, J = 7.2 and 7.6 Hz, S–CH_2–CH_2, 2H), 1.51–1.43 (m, CH_2–$(CH_2)_3$–CH_3, 4H), 1.41–1.24 (m, $(CH_2)_3$–CH_3, 12H), 0.91 (t, J = 6.8 Hz, O–$(CH_2)_6$–CH_3, 3H), 0.89 (t, J = 7.2 Hz, S–$(CH_2)_6$–CH_3, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 163.7, 163.6, 148.6, 148.3, 145.8, 132.3×2, 130.5×2, 126.3×2, 125.7, 122.7×2, 122.6×2, 121.4, 114.4×2, 68.4, 32.0, 31.8, 31.7, 29.1×2, 28.9, 28.8×2, 26.0, 22.6×2, 14.1×2 ppm. HRMS (ESI, m/z): $[M+Na]^+$ calcd. for $C_{34}H_{42}NaO_5S$, 585.2645; found, 585.2639.

4-[(4-Octyloxybenzoyl)oxy]phenyl 4-octylthiobenzoate (SO8)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.8 Hz, Ar–*H*, 2H), 8.08 (d, J = 8.4 Hz, Ar–*H*, 2H), 7.35 (d, J = 8.4 Hz, Ar–*H*, 2H), 7.26 (s, Ar–*H*, 4H), 6.98 (d, J = 8.8 Hz, Ar–*H*, 2H), 4.05 (t, J = 6.4 Hz, O–CH_2, 2H), 3.02 (t, J = 7.6 Hz, S–CH_2, 2H), 1.83 (tt, J = 6.4 and 8.0 Hz, O–CH_2–CH_2, 2H), 1.72 (tt, J = 7.2 and 7.6 Hz, S–CH_2–CH_2, 2H), 1.53–1.42 (m, CH_2–$(CH_2)_4$–CH_3 4H), 1.42–1.21 (m, $(CH_2)_4$–CH_3, 16H), 0.96–0.83 (m, CH_3, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8×2, 163.6, 148.5, 148.3, 145.8, 132.3×2, 130.5×2, 126.3×2, 125.6, 122.7×2, 122.6×2, 121.4, 114.4×2, 68.4, 32.0, 31.8×2, 29.3, 29.2×2, 29.13×2, 28.9, 28.8, 26.0, 22.7×2, 14.1×2 ppm. HRMS (ESI, m/z): $[M+Na]^+$ calcd. for $C_{36}H_{46}NaO_5S$, 613.2958; found, 613.2985.



Scheme S1. Synthetic route to SO*n* (*n* = 1–8).

2. POM images of SO*n*

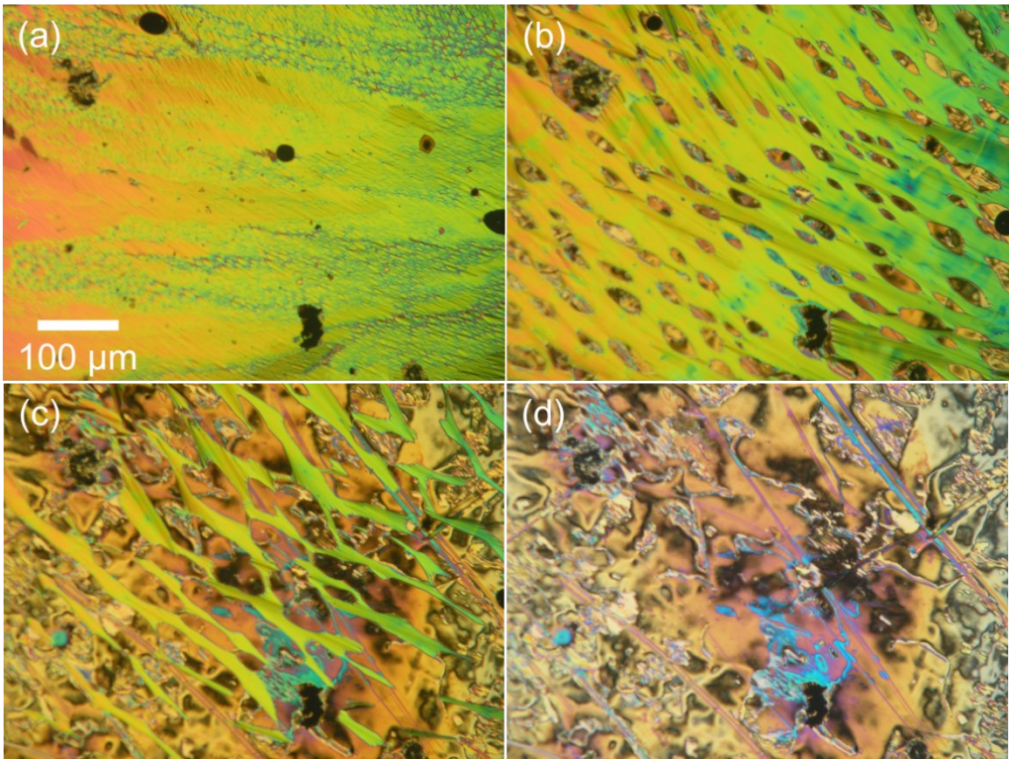


Fig. S1. POM images of SO1 upon heating in (a) smectic A (SmA) phase at 190 °C, during SmA–nematic (N) phase transition at (b) 191 and (c) 193 °C, and in (d) N phase at 195 °C.

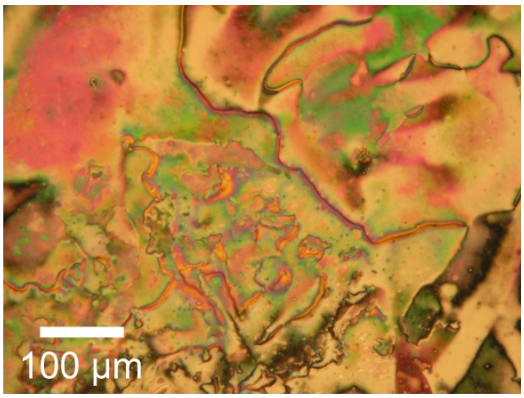


Fig. S2. POM image of SO2 in N phase at 245 °C.

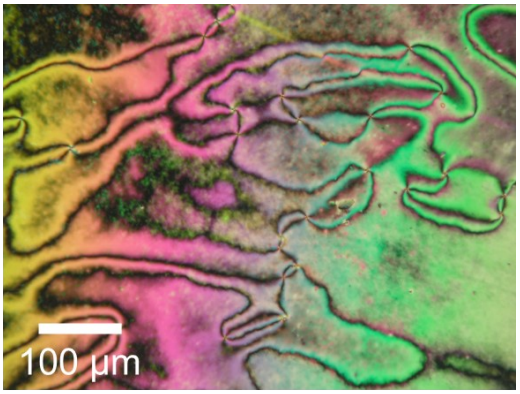


Fig. S3. POM image of SO3 in N phase at 195 °C.

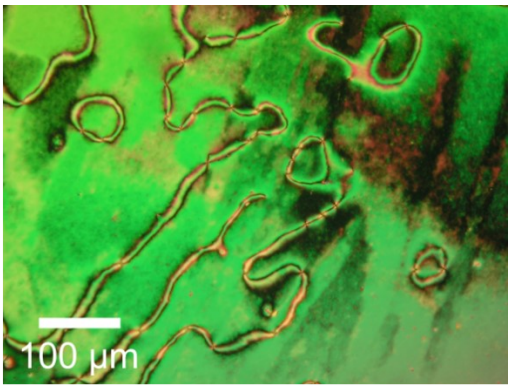


Fig. S4. POM image of SO4 in N phase at 170 °C.

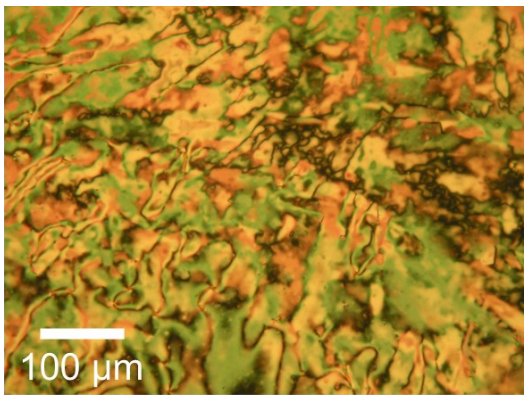


Fig. S5. POM image of SO5 in N phase at 150 °C.

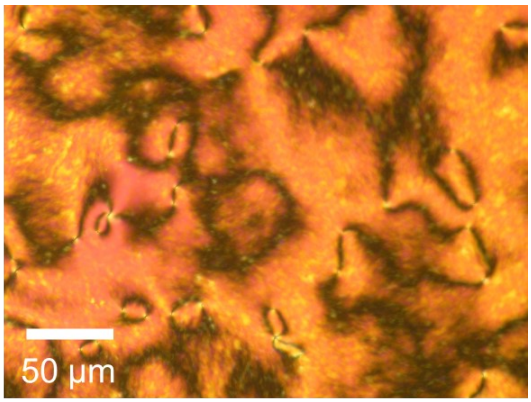


Fig. S6. POM image of SO6 in N phase at 125 °C.

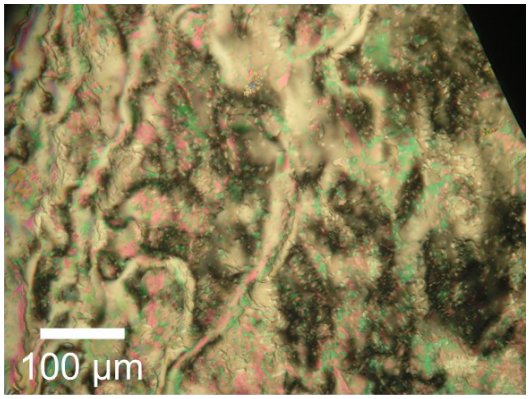


Fig. S7. POM image of SO7 in N phase at 125 °C.

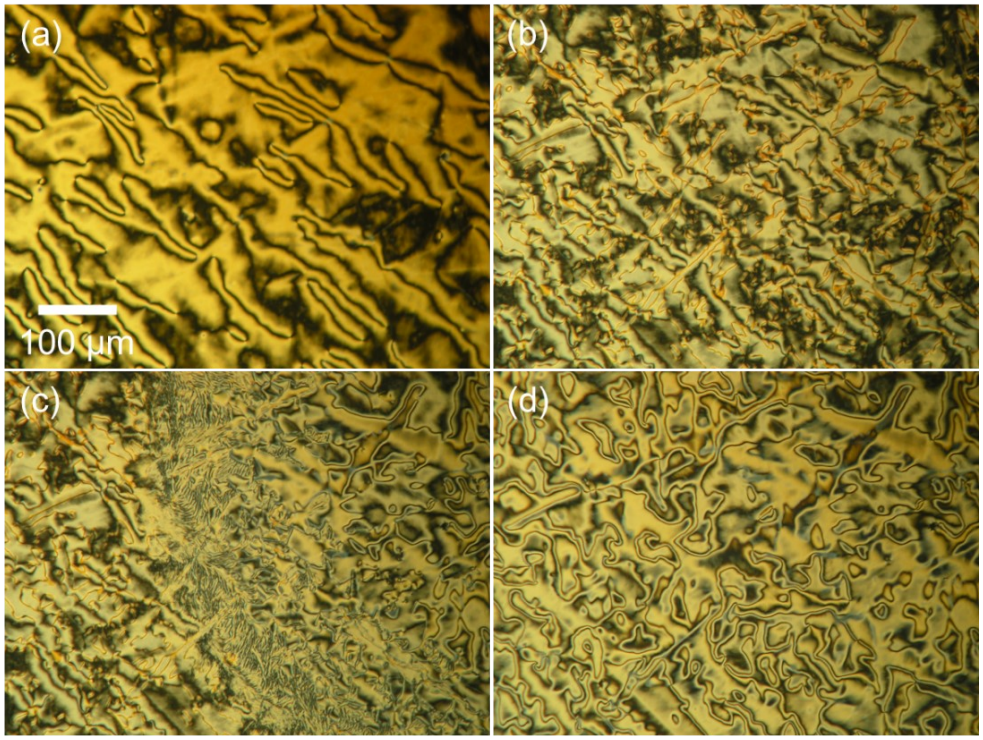


Fig. S8. POM images of SO8 (a) in the N phase at 170 ℃ and (b) 135 ℃, (c) during the N–smectic C (SmC) phase transition at 128 ℃, and (d) in the SmC phase at 125 ℃.

3. DSC

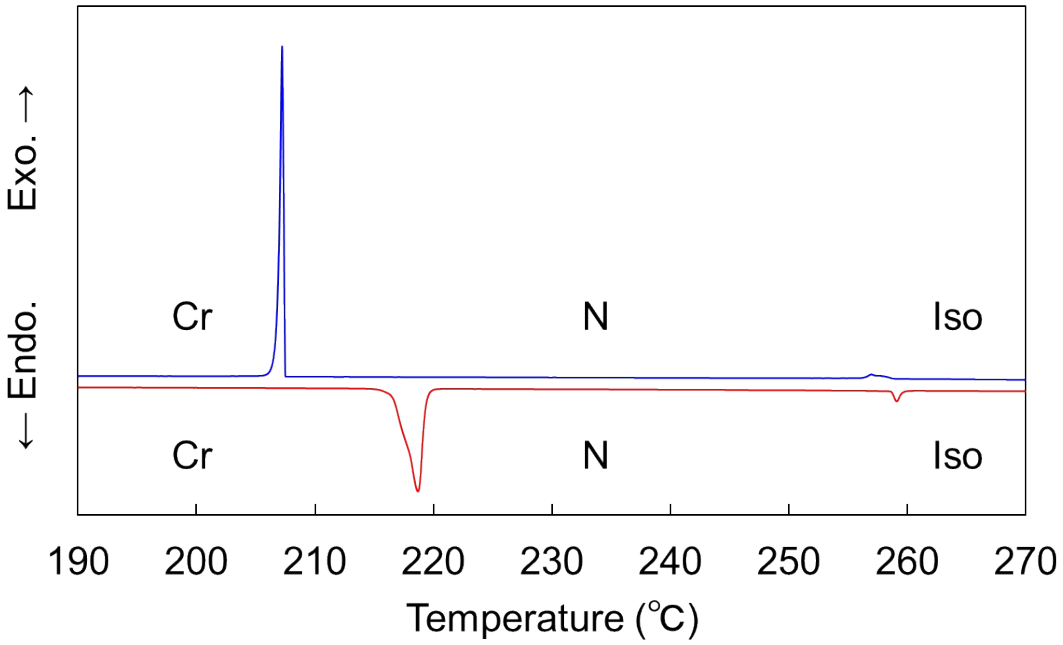


Fig. S9. DSC curves of SO2 collected at a rate of 3 ℃ min^{-1}.

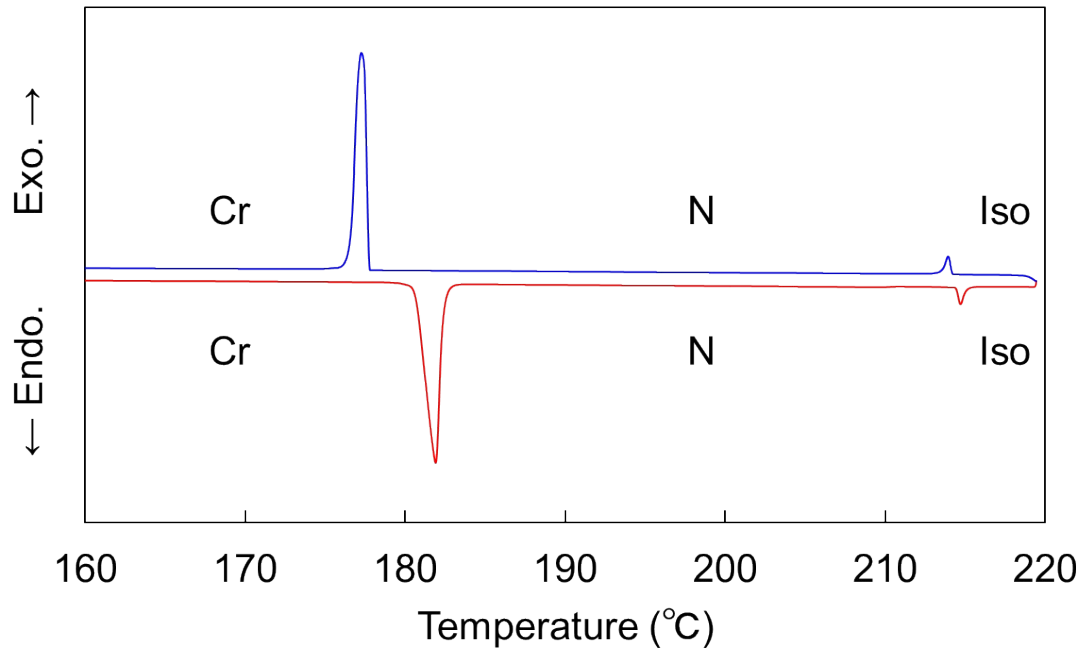


Fig. S10. DSC curves of SO3 collected at a rate of 3 °C min^{-1}.

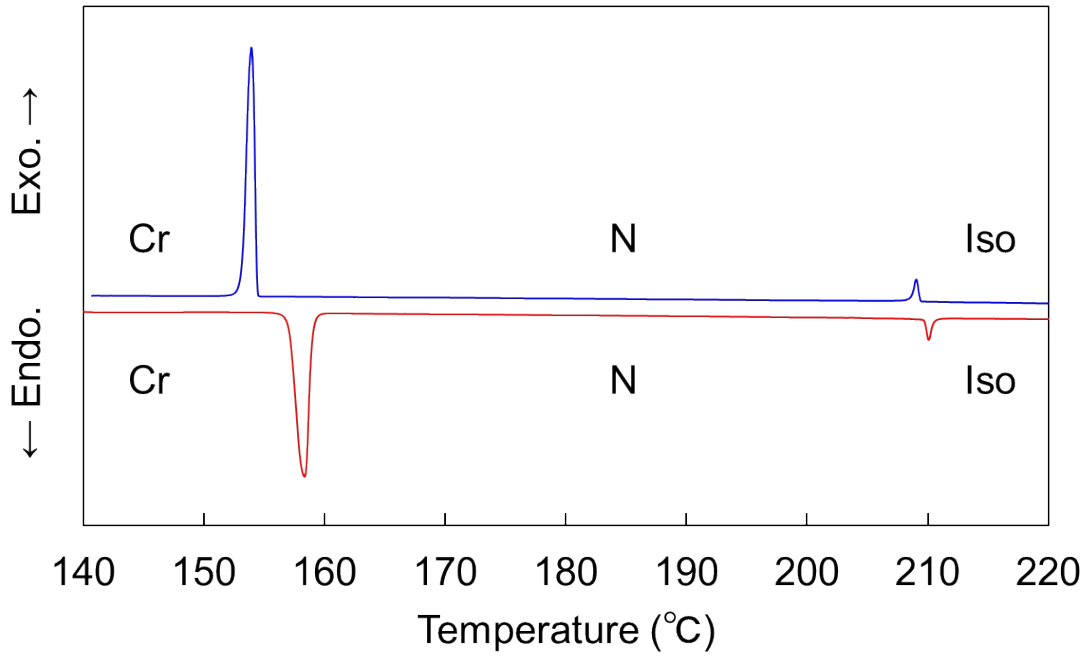


Fig. S11. DSC curves of SO4 collected at a rate of 3 °C min^{-1}.

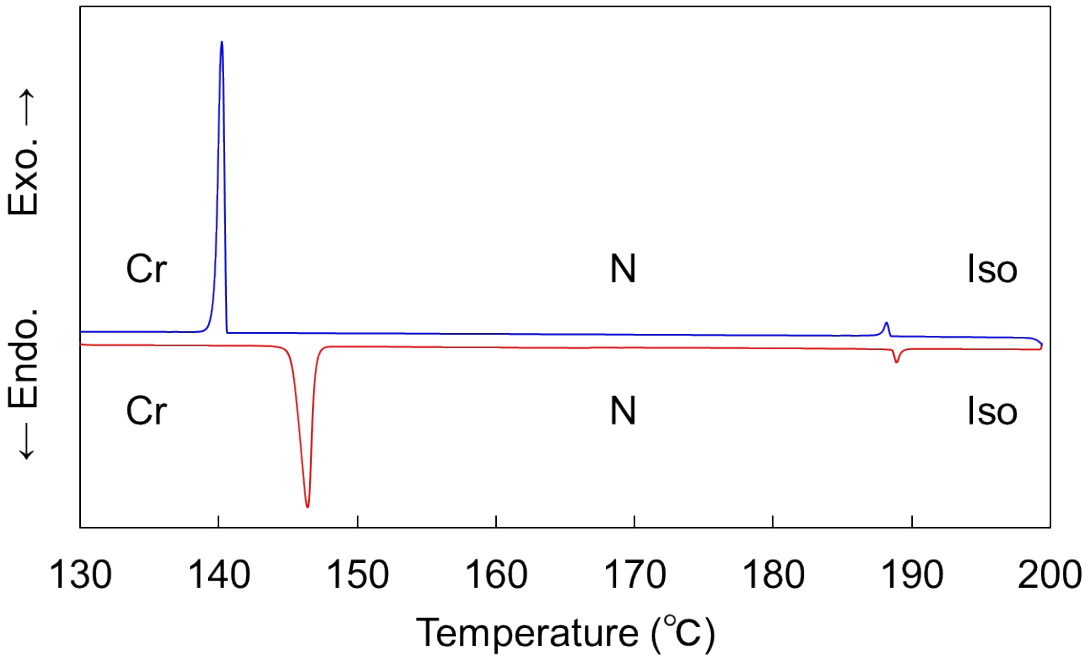


Fig. S12. DSC curves of SO5 collected at a rate of 3 °C min^{-1}.

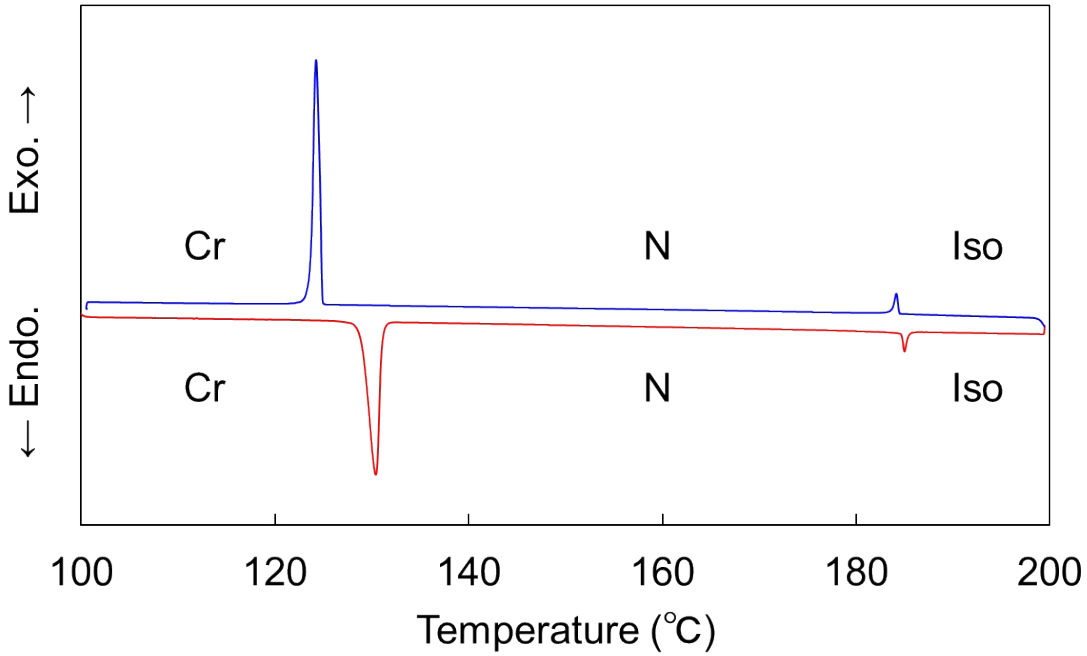


Fig. S13. DSC curves of SO6 collected at a rate of 3 °C min^{-1}.

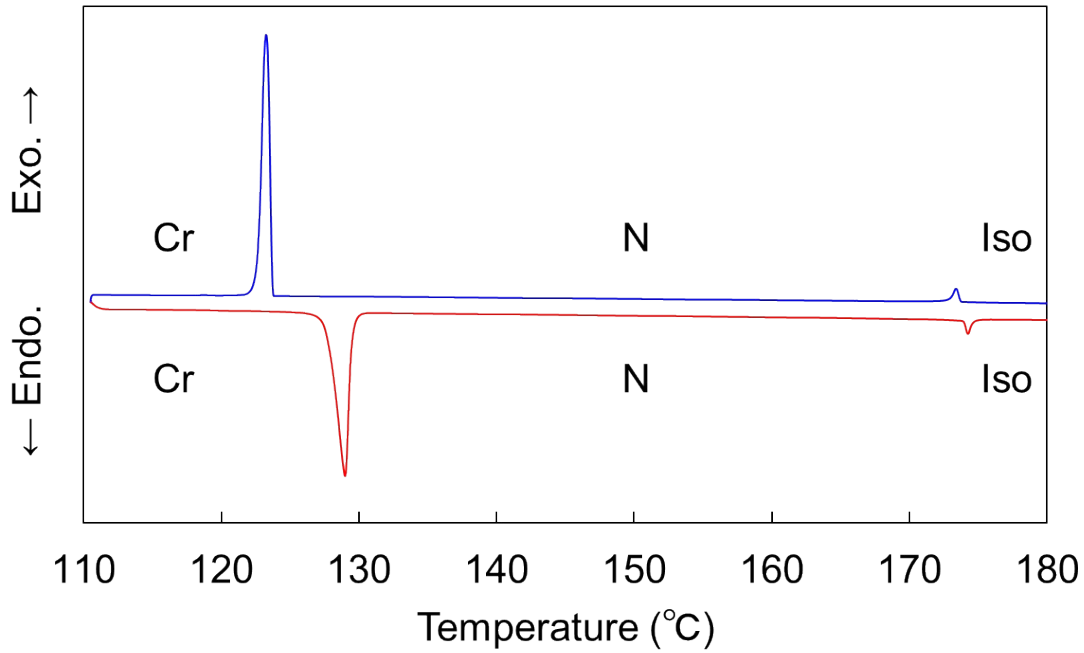


Fig. S14. DSC curves of SO7 collected at a rate of 3 °C min^{-1}.

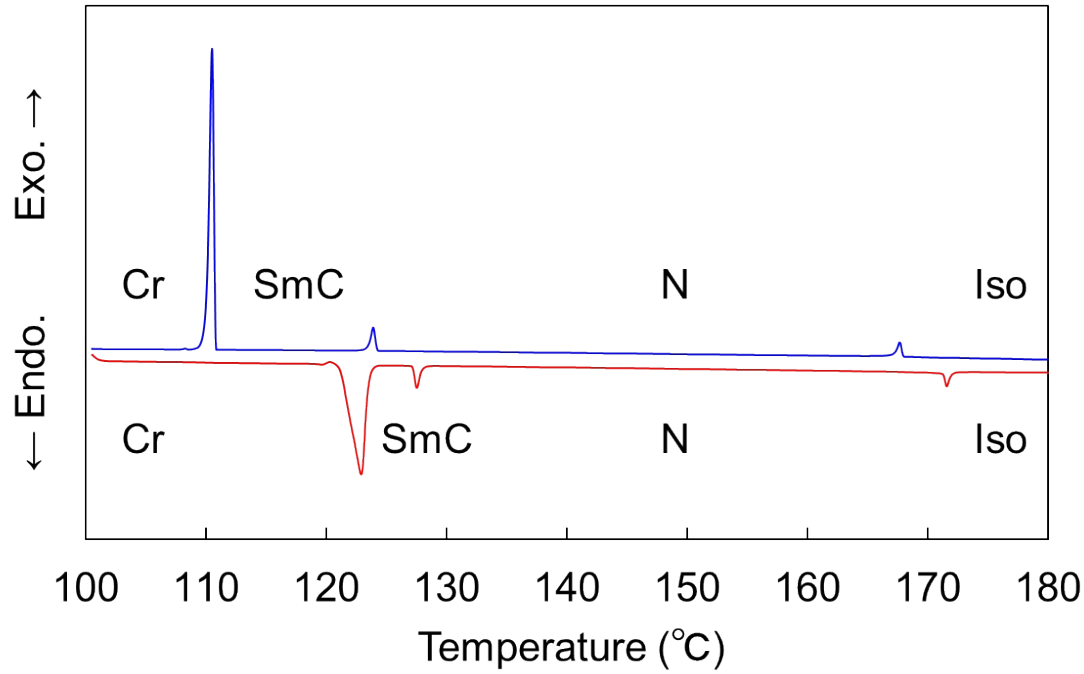


Fig. S15. DSC curves of SO8 collected at a rate of 3 °C min^{-1}.

4. TGA

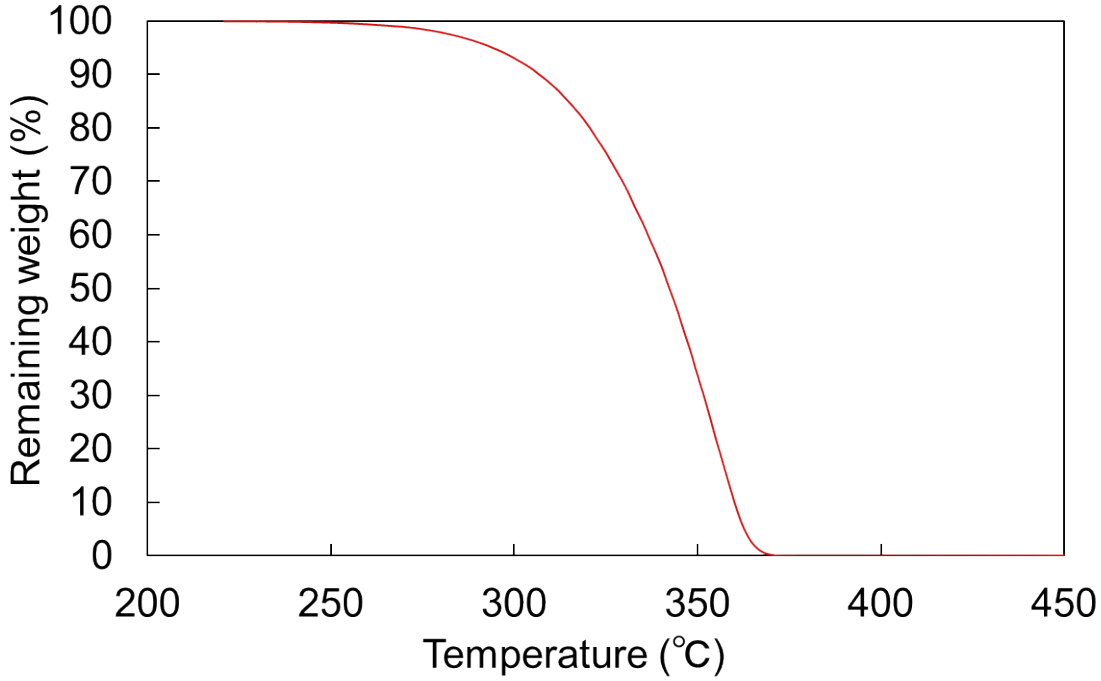


Fig. S16. TGA curve of SO1 collected at a rate of 3 °C min^{-1}.

5. XRD results of SO6

Table S1. XRD results of the N phase of SO6.

	SAX		WAX		tilt angle	S
T / °C	*2θ* / °	*d-spacing* / Å	*2θ* /°	*d-spacing* / Å	x/2 / °	
135	4.0	22.1	19.3	4.6	46	0.70
140	3.7	23.9	19.2	4.6	47	0.70
145	3.8	23.3	19.1	4.6	47	0.70
150	4.0	22.0	19.1	4.6	47	0.68
155	3.9	22.5	19.1	4.6	48	0.67
160	3.8	23.3	19.0	4.7	48	0.66
165	3.8	23.4	19.0	4.7	47	0.64
170	3.9	22.4	18.9	4.7	46	0.61
175	4.0	22.2	18.9	4.7	48	0.60
180	3.9	22.8	18.8	4.7	49	0.54
190	-	-	18.7	4.7	-	-

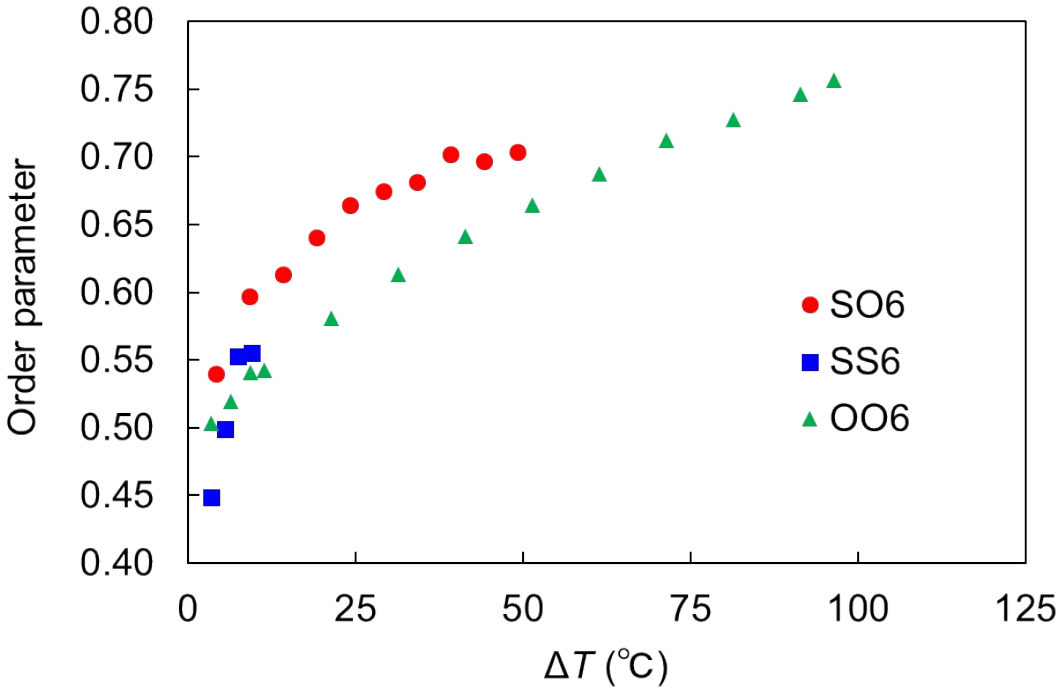


Fig. S17. Order parameters of the N phases of SO6, SS6, and OO6 as a function of the shifted temperature ($\Delta T = T_{IN}–T$).

Reference

S1. Y. Arakawa, Y. Sasaki, K. Igawa and H. Tsuji, *New J. Chem.*, 2017, **41**, 6514.