Electronic Supplementary Information

Effects of alkylthio groups on phase transitions of organic molecules and liquid crystals: A comparative study with alkyl and alkoxy groups

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Synthesis

The alkylthio-based *n*SCPB homologues (*n* = 1–8) and 1SCB were synthesized according to the Scheme S1. The syntheses of corresponding 4-alkylthiobenzoic acids were reported in our previous work.[S1]

4-Cyanophenyl 4-(methylthio)benzoate (1SCPB) (General procedure for all nSCPB)
4-Methylthiobenzoic acid (99.9 mg, 0.594 mmol), 4-hydroxycyanobenzene (89.9 mg, 0.755 mmol) and 4-dimethylaminopyridine (DMAP) (10.7 mg, 87.6 μmol) were dissolved with tetrahydrofuran (THF) in a double-necked flask purged with an argon gas. In another double-necked flask purged with an argon gas, *N*,*N*′-dicyclohexylcarbodiimide (DCC) (0.181 g, 0.877 mmol) was dissolved in THF. Subsequently, the DCC-containing solution was slowly dropped into the prior mixture in the flask in an ice bath, which was stirred at ambient temperature for 24h. The reaction mixture was filtrated off, to remove the urea, and evaporated *in vacuo*. The residue was purified by column chromatography on a silica gel with an eluent of dichloromethane, and recrystallized in a mixed solvent of dichloromethane and hexane. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.74 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.36 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.32 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 2.56 (s, S–C*H*$_3$, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.7, 154.9, 148.1, 134.3, 131.1, 125.6, 125.0, 123.5, 118.9, 110.3, 15.3 ppm. HRMS (ESI, m/z): $[M+Na]^+$ calcd. for $C_{15}H_{11}NNaO_2S$, 292.0403; found, 292.0412.

4-Cyanophenyl 4-(ethylthio)benzoate (2SCPB)
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.74 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.36 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.35 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 3.06 (q, *J* = 7.3 Hz, S–C*H*$_2$, 2H), 1.40 (t, *J* = 7.3 and 7.3 Hz, S–CH_2–C*H*$_3$, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.6, 154.9, 146.9, 134.3, 131.1, 126.7, 125.3, 123.5, 118.9, 110.3, 26.5, 14.4 ppm. HRMS (ESI, m/z): $[M+Na]^+$ calcd. for $C_{16}H_{13}NNaO_2S$, 306.0559; found, 306.0559.

4-Cyanophenyl 4-(propylthio)benzoate (3SCPB)
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.74 (d, *J* = 9.0 Hz, Ar–*H*, 2H), 7.36 (d, *J* = 8.0 Hz, Ar–*H*, 2H), 7.35 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 3.01 (t, *J* = 7.5 Hz, S–C*H*$_2$, 2H), 1.73–1.80 (tq, *J* = 7.5 Hz, S–CH_2–C*H*$_2$, 2H), 1.08 (t, *J* = 7.3 Hz, S–$(CH_2)_2$–C*H*$_3$, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.6, 154.9, 147.2, 134.3, 131.1, 126.8, 125.2, 123.5, 118.9, 110.3, 34.4, 22.7, 14.1 ppm. HRMS (ESI, m/z): $[M+Na]^+$ calcd. for $C_{17}H_{15}NNaO_2S$, 320.0716; found, 320.0705.

4-Cyanophenyl 4-(butylthio)benzoate (4SCPB)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 9.0 Hz, Ar–*H*, 2H), 7.74 (d, *J* = 9.0 Hz, Ar–*H*, 2H), 7.36 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.35 (d, *J* = 9.0 Hz, Ar–*H*, 2H), 3.03 (t, *J* = 7.3 Hz, S–CH_2, 2H), 1.72 (tt, *J* = 7.3 and 7.5 Hz, S–CH_2–CH_2, 2H), 1.47–1.54 (tq, *J* = 7.5 Hz, S–$(CH_2)_2$–CH_2, 2H), 0.97 (t, *J* = 7.3 Hz, S–$(CH_2)_3$–CH_3, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.6, 154.9, 147.3, 134.3, 131.1, 126.7, 125.2, 123.5, 118.9, 110.3, 32.1, 31.3, 22.6, 14.2 ppm. HRMS (ESI, m/z): $[M+Na]^+$ calcd. for $C_{18}H_{17}NNaO_2S$, 334.0872; found, 334.0887.

4-Cyanophenyl 4-(pentylthio)benzoate (5SCPB)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 9.0 Hz, Ar–*H*, 2H), 7.74 (d, *J* = 9.0 Hz, Ar–*H*, 2H), 7.36 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.35 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 3.02 (t, *J* = 7.5 Hz, S–CH_2, 2H), 1.73 (tt, *J* = 7.5 and 7.5 Hz, S–CH_2–CH_2, 2H), 1.46 (tt, *J* = 7.5 and 7.5 Hz, S–$(CH_2)_2$–CH_2, 2H), 1.33–1.40 (tq, *J* = 7.5 Hz, S–$(CH_2)_3$–CH_2, 2H), 0.92 (t, *J* = 7.3 Hz, S–$(CH_2)_4$–CH_3, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.6, 154.9, 147.3, 134.3, 131.1, 126.7, 125.2, 123.5, 118.9, 110.3, 32.4, 31.6, 28.9, 22.8, 14.5 ppm. HRMS (ESI, m/z): $[M+Na]^+$ calcd. for $C_{19}H_{19}NNaO_2S$, 348.1029; found, 348.1016.

4-Cyanophenyl 4-(hexylthio)benzoate (6SCPB)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.74 (d, *J* = 9.0 Hz, Ar–*H*, 2H), 7.36 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.35 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 3.02 (t, *J* = 7.5 Hz, S–CH_2, 2H), 1.72 (tt, *J* = 7.5 and 7.6 Hz, S–CH_2–CH_2, 2H), 1.47 (tt, *J* = 7.6 and 7.3 Hz, S–$(CH_2)_2$–CH_2, 2H), 1.29–1.35 (m, 4H), 0.90 (t, *J* = 7.4 Hz, S–$(CH_2)_5$–CH_3, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.7, 154.9, 147.3, 134.3, 131.1, 126.7, 125.2, 123.5, 118.9, 110.3, 32.4, 31.9, 29.18, 29.16, 23.1, 14.6 ppm. HRMS (ESI, m/z): $[M+Na]^+$ calcd. for $C_{20}H_{21}NNaO_2S$, 362.1185; found, 362.1176.

4-Cyanophenyl 4-(heptylthio)benzoate (7SCPB)

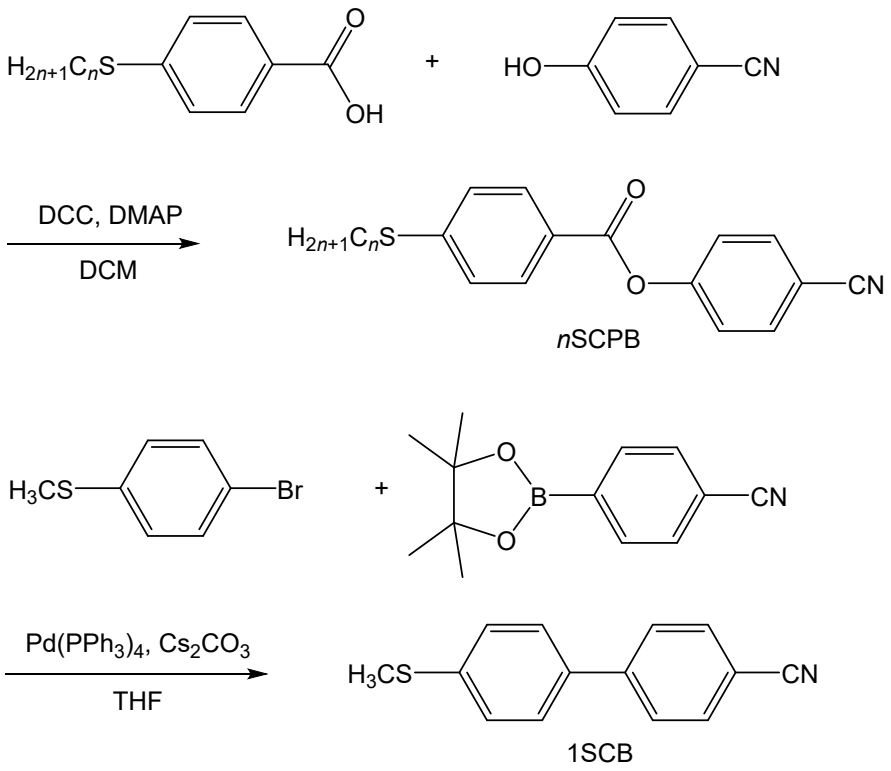
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.8 Hz, Ar–*H*, 2H), 7.74 (d, *J* = 8.8 Hz, Ar–*H*, 2H), 7.36 (d, *J* = 8.8 Hz, Ar–*H*, 2H), 7.35 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 3.02 (t, *J* = 7.4 Hz, S–CH_2, 2H), 1.73 (tt, *J* = 7.4 and 7.4 Hz, S–CH_2–CH_2, 2H), 1.47 (tt, *J* = 7.5 and 7.3 Hz, S–$(CH_2)_2$–CH_2, 2H), 1.28–1.35 (m, 8H), 0.87–0.90 (m, S–$(CH_2)_7$–CH_3, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 154.9, 147.3, 134.3, 131.1, 126.7, 125.2, 123.5, 118.9, 110.3, 32.43, 32.40, 29.71, 29.70, 29.5, 29.2, 23.2, 14.7 ppm. HRMS (ESI, m/z): $[M+Na]^+$ calcd. for $C_{21}H_{23}NNaO_2S$, 376.1342; found, 376.1349.

4-Cyanophenyl 4-(octylthio)benzoate (8SCPB)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.8 Hz, Ar–*H*, 2H), 7.74 (d, *J* = 8.8 Hz, Ar–*H*, 2H), 7.36 (d, *J* = 8.8 Hz, Ar–*H*, 2H), 7.34 (d, *J* = 8.4 Hz, Ar–*H*, 2H), 3.02 (t, *J* = 7.4 Hz, S–C*H*$_2$, 2H), 1.72 (tt, *J* = 7.4 and 7.5 Hz, S–CH_2–C*H*$_2$, 2H), 1.47 (tt, *J* = 7.5 and 7.3 Hz, S–$(CH_2)_2$–C*H*$_2$, 2H), 1.28–1.35 (m, 8H), 0.89–0.90 (m, S–$(CH_2)_7$–C*H*$_3$, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 154.9, 147.3, 134.3, 131.1, 126.7, 125.2, 123.5, 118.9, 110.3, 32.43, 32.40, 29.71, 29.70, 29.5, 29.2, 23.2, 14.7 ppm. HRMS (ESI, m/z): $[M+Na]^+$ calcd. for $C_{22}H_{25}NNaO_2S$, 390.1498; found, 390.1488.

4'-Methylthio[1,1'-biphenyl]-4-carbonitrile (1SCB)

4-Bromobenzenethiol (0.177 g, 0.871 mmol), 4-cyanophenylboronic acid pinacol ester (0.214 g, 0.934 mmol), cesium carbonate (Cs_2CO_3) (0.580 g, 1.78 mmol), and Tetrakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$] (62.4 mg, 50.4 μmol) were put in a double-necked flask and purged with an argon gas. Subsequently, THF degassed by bubbling an argon gas was added into the flask and the mixture was stirred at reflux temperature for 18h. The reaction mixture was extracted with dichloromethane, washed with water and brine, and the organic phase was dried over magnesium sulfate. After removing the volatiles in vacuo, the crude product was purified by silica-gel column chromatography with an eluent of dichloromethane/hexane = 1/2 (v/v), and recrystallized in dichloromethane.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.66 (d, *J* = 8.5 Hz, Ar–*H*, 2H), 7.52 (d, *J* = 8.0 Hz, Ar–*H*, 2H), 7.34 (d, *J* = 9.0 Hz, Ar–*H*, 2H), 2.53 (s, S–C*H*$_3$, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.5, 140.4, 136.1, 133.2, 128.0, 127.9, 127.3, 119.5, 111.3, 16.1 ppm. HRMS (ESI, m/z): $[M]^+$ calcd. for $C_{14}H_{11}NS$, 225.0612; found, 225.0610.



Scheme S1. Synthetic pathways used to obtain the alkylthio-based *n*SCPB homologues (*n* = 1–8) and 1SCB.

POM images

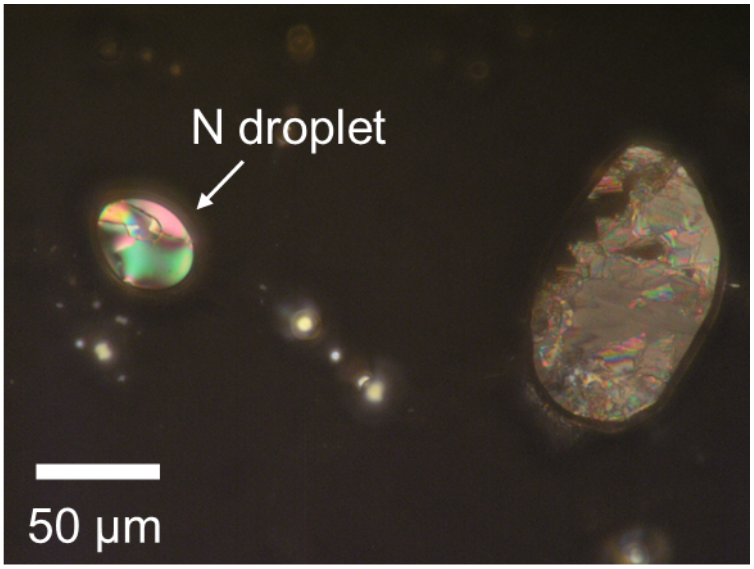


Fig. S1. POM image of the N phase of 1SCPB at 80 °C.

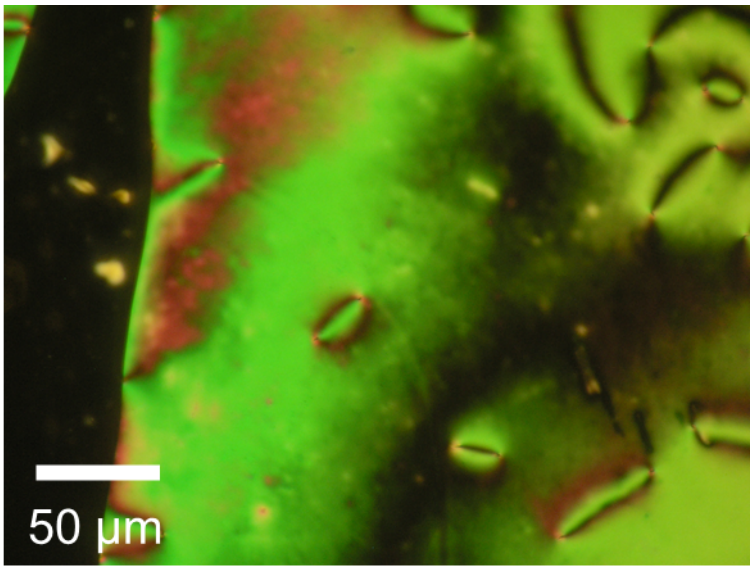


Fig. S2. POM image of the N phase of 2SCPB at 71 °C.

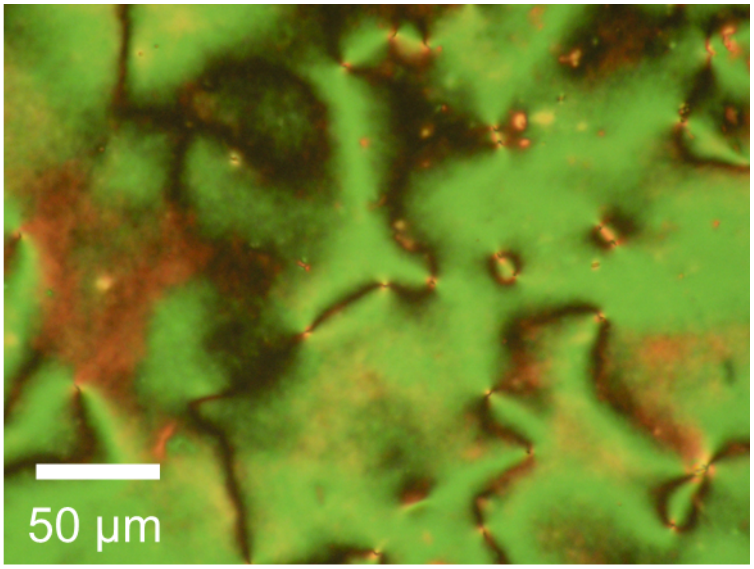


Fig. S3. POM image of the N phase of 3SCPB at 41 °C.

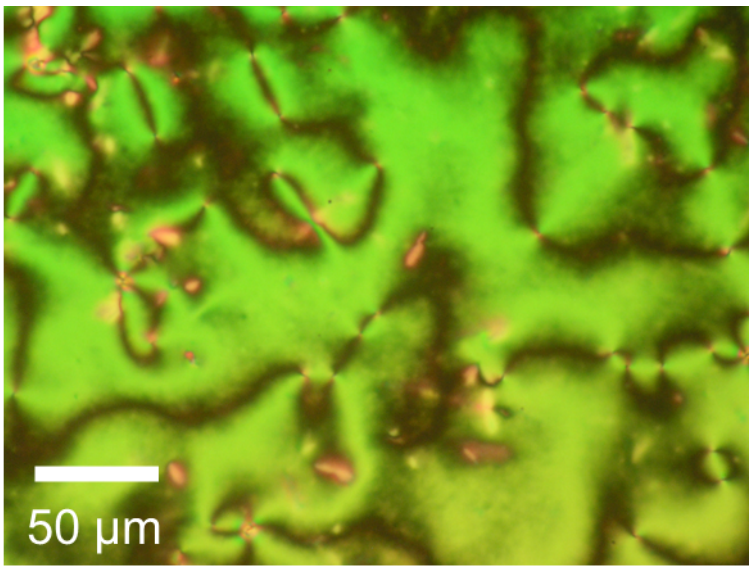


Fig. S4. POM image of the N phase of 4SCPB at 57 °C.

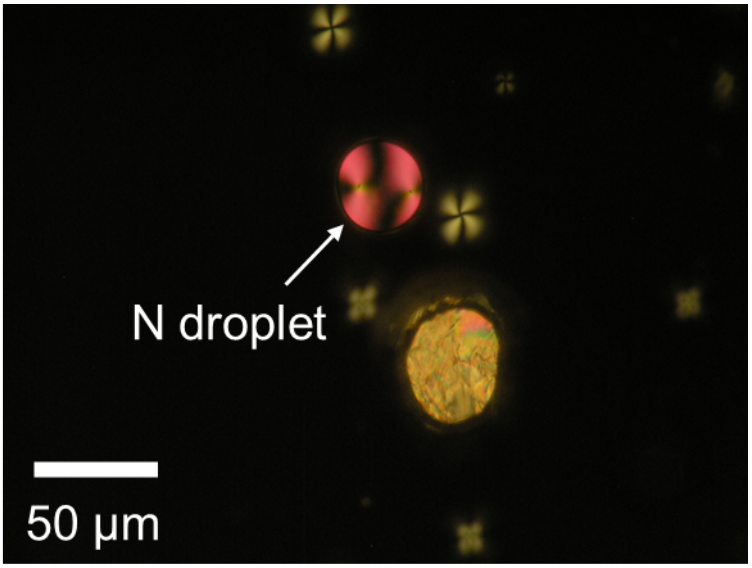


Fig. S5. POM image of the N phase of 5SCPB at 50 °C.

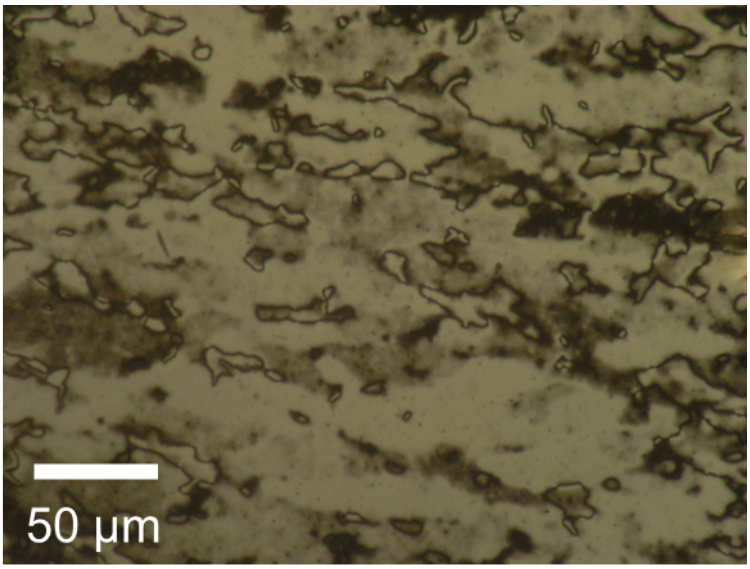


Fig. S6. POM image of the N phase of 6SCPB at 56 °C.

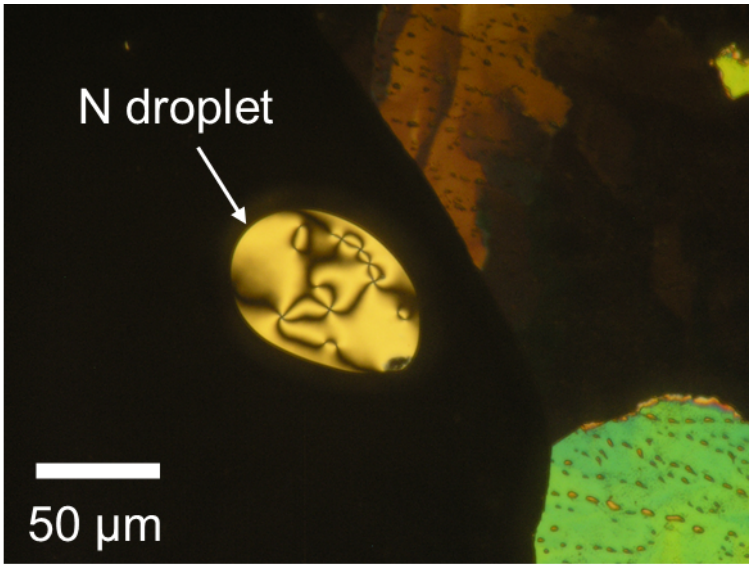


Fig. S7. POM image of the N phase of 7SCPB at 56 °C.

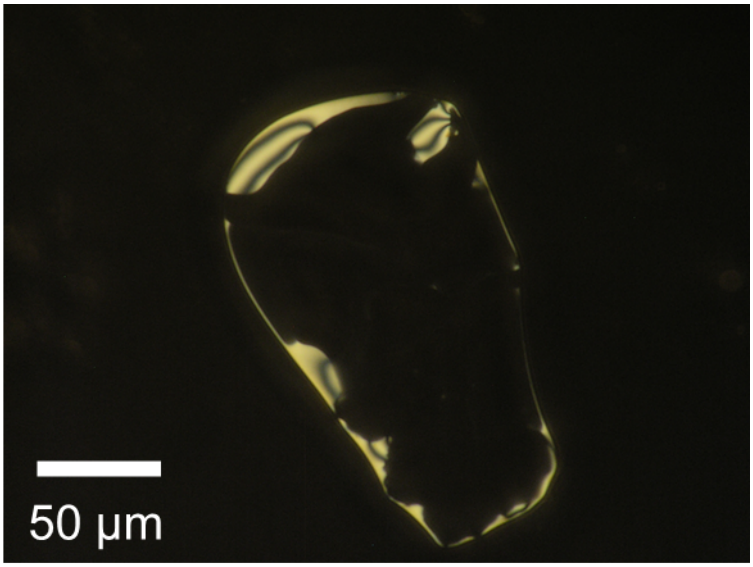


Fig. S8. POM image of the N phase of 8SCPB at 55 °C.

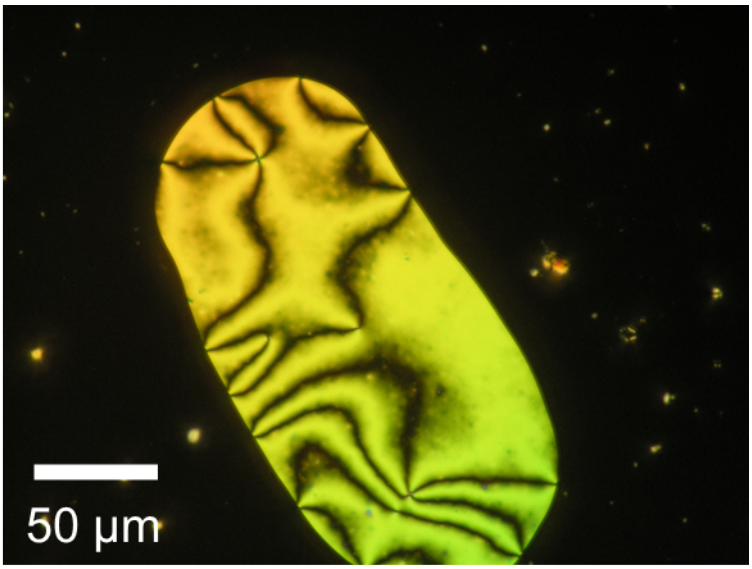


Fig. S9. POM image of the N phase of 1SCB at 73 °C.

DSC curves

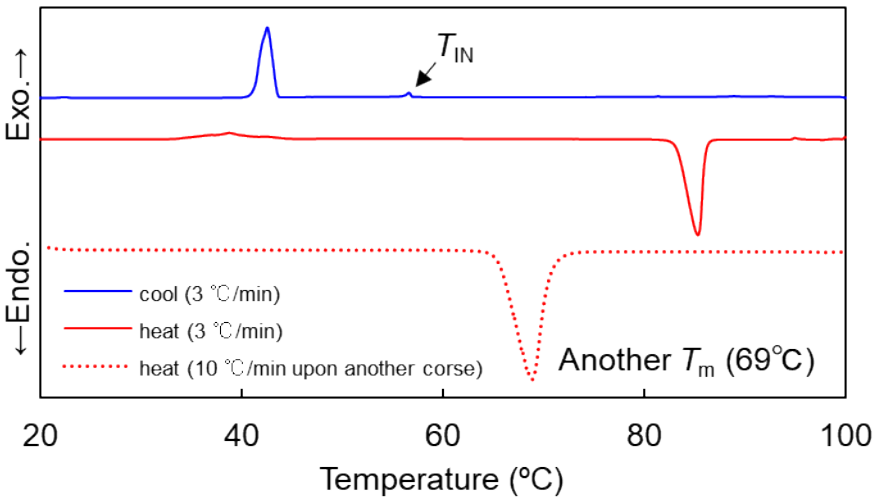


Fig. S10. DSC curves of 4SCB.

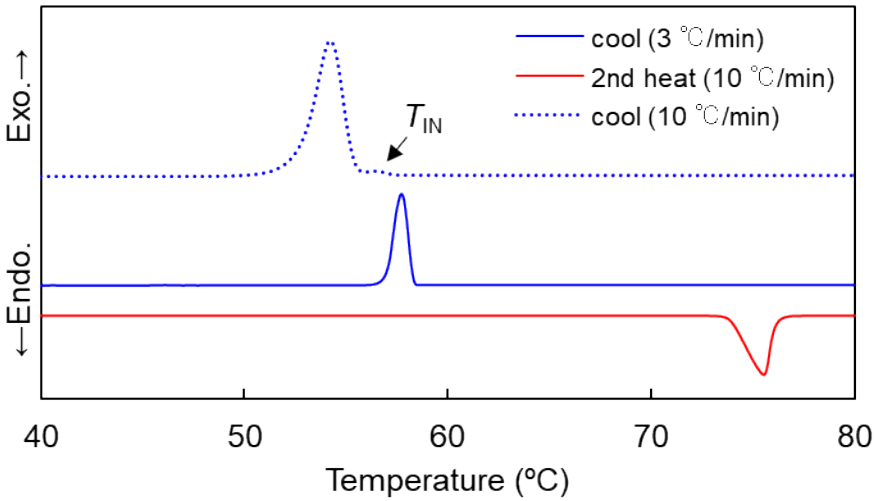
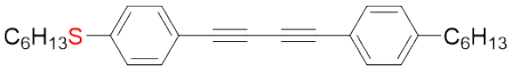


Fig. S11. DSC curves of 6SCB.

Crystallographic data



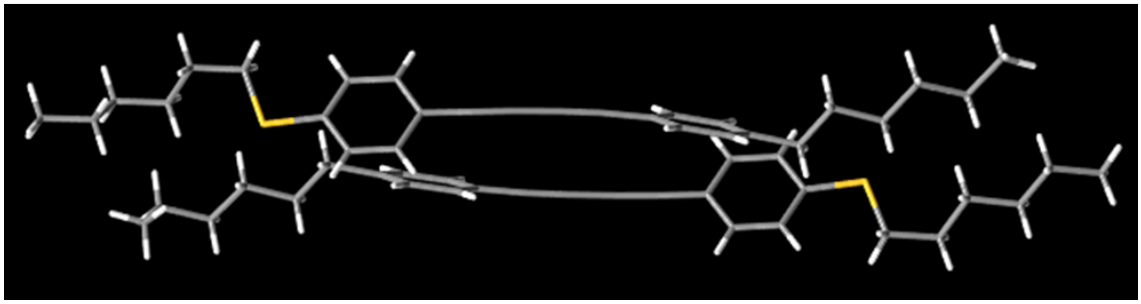


Fig. S12. The molecular structure and molecular forms in the crystal structure of previously reported 6S–DPDA–6 (CCDC No: 1882054).[S2]

Reference

S1. Y. Arakawa, Y. Sasaki, K. Igawa and H. Tsuji, *New J. Chem.*, 41, 6514.
S2. Y. Arakawa, S. Inui, K. Igawa and H. Tsuji, *Liq. Cryst.*, 2019, 46, 1621.