

Electronic Supplementary Information

4'-Alkylseleno-4-cyanobiphenyls, *n*SeCB: synthesis and substituent effects on the phase-transition and liquid crystalline behaviors

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Synthesis

The synthesis procedures of 4-hexylseleno-4'-cyanobiphenyl (6SeCB) were described below and other homologs were synthesized in a similar manner.

Synthesis of bis(4-bromophenyl)diselenide

4-Bromo-iodobenzene (6.08 g, 21.5 mmol), selenium powder (Se) (3.50 g, 44.3 mmol), copper(II) oxide (CuO) (0.373 g, 4.69 mmol), potassium hydroxide (KOH) (2.60 g, 46.3 mmol), and dimethyl sulfoxide (DMSO) (20 mL) were put in a flask which was purged with argon gas. The mixture was stirred for 18h at 100 °C. The mixture was cooled to ambient temperature and filtered to remove the insoluble portion. The filtrate was extracted with dichloromethane (DCM), the extract washed with water and brine, and dried over magnesium sulfate. The volatiles were removed under reduced pressure, and the crude product was purified by column chromatography on silica gel using hexane as an eluent) to afford the target compound (2.03 g, 40%). ¹H NMR (500 MHz, CDCl₃) δ 7.44 (d, *J* = 7.2 Hz, 4H), 7.39 (d, *J* = 7.2 Hz, 4H) ppm.

Synthesis of 1-Bromo-4-(hexylseleno)benzene (6SePhBr)

Bis(4-bromophenyl)diselenide (0.218 g, 0.464 mmol), sodium tetrahydroborate (NaBH₄) (64.1 mg, 1.69 mmol), and anhydrous EtOH (4.0 mL) were placed in a two-necked flask under argon, and the resultant mixture was stirred at 0 °C for 20 min. After a colorless solution had formed, 1-bromohexane (0.295 mL, 1.79 mmol) was added dropwise to the reaction mixture at 0 °C and the mixture was stirred at room temperature for 30min. The reaction mixture was extracted with DCM, the extract washed with water and brine, dried over MgSO₄. After filtration, the volatiles were removed under reduced pressure. The crude product was purified by column chromatograph on silica gel (eluent: DCM/hexane = 1/10, v/v) to afford the target compound (0.345 g, 94%). ¹H NMR (500 MHz, CDCl₃) δ 7.34 (d, *J* = 9.0 Hz, Ar-*H*, 2H), 7.33 (d, *J* = 8.5 Hz, Ar-*H*, 2H), 2.89 (t, *J* = 7.5 Hz, Se-CH₂, 2H), 1.68 (tt, *J* = 7.5 and 7.5 Hz, Se-CH₂-CH₂, 2H), 1.39 (tt, *J* = 7.5 and 7.4 Hz, Se-(CH₂)₂-CH₂, 2H), 1.26–1.30 (m, 4H), 0.88 (t, *J* = 7.0 Hz, Se-(CH₂)₅-CH₃, 3H) ppm.

1-Bromo-4-(methylseleno)benzene (1SePhBr)

¹H NMR (400 MHz, CDCl₃) δ 7.37 (d, *J* = 8.0 Hz, Ar-*H*, 2H), 7.26–7.28 (d, Ar-*H*, 2H), 2.34 (s, Se-CH₃, 3H) ppm.

1-Bromo-4-(ethylseleno)benzene (2SePhBr)

^1H NMR (500 MHz, CDCl_3) δ 7.38 (d, $J = 8.5$ Hz, Ar-H, 2H), 7.34 (d, $J = 8.5$ Hz, Ar-H, 2H), 2.88–2.93 (q, $J = 7.5$ Hz, Se- CH_2 , 2H), 1.42 (t, $J = 7.5$ Hz, Se- CH_2 - CH_3 , 3H) ppm.

^{13}C NMR (126 MHz, CDCl_3) δ 134.7, 132.6, 129.7, 121.5, 22.2, 16.0 ppm.

1-Bromo-4-(propylseleno)benzene (3SePhBr)

^1H NMR (500 MHz, CDCl_3) δ 7.37 (d, $J = 9.0$ Hz, Ar-H, 2H), 7.34 (d, $J = 8.5$ Hz, Ar-H, 2H), 2.88 (t, $J = 7.5$ Hz, Se- CH_2 , 2H), 1.67–1.75 (tq, $J = 7.5$ Hz, Se- CH_2 - CH_2 , 2H), 1.00 (t, $J = 7.3$ Hz, Se-(CH_2) $_2$ - CH_3 , 3H) ppm.

1-Bromo-4-(butylseleno)benzene (4SePhBr)

^1H NMR (500 MHz, CDCl_3) δ 7.36 (d, $J = 8.5$ Hz, Ar-H, 2H), 7.33 (d, $J = 8.0$ Hz, Ar-H, 2H), 2.89 (t, $J = 7.5$ Hz, Se- CH_2 , 2H), 1.67 (tt, $J = 7.5$ and 7.5 Hz, Se- CH_2 - CH_2 , 2H), 1.38–1.45 (tq, $J = 7.5$ Hz, Se-(CH_2) $_2$ - CH_2 , 2H), 0.90 (t, $J = 7.3$ Hz, Se-(CH_2) $_3$ - CH_3 , 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 134.5, 132.6, 130.2, 121.3, 32.7, 28.4, 23.5, 14.1 ppm.

1-Bromo-4-(pentylseleno)benzene (5SePhBr)

^1H NMR (500 MHz, CDCl_3) δ 7.37 (d, $J = 8.5$ Hz, Ar-H, 2H), 7.33 (d, $J = 8.5$ Hz, Ar-H, 2H), 2.89 (t, $J = 7.5$ Hz, Se- CH_2 , 2H), 1.69 (tt, $J = 7.5$ and 7.5 Hz, Se- CH_2 - CH_2 , 2H), 1.27–1.40 (m, 4H), 0.88 (t, $J = 7.3$ Hz, Se-(CH_2) $_4$ - CH_3 , 3H) ppm.

1-Bromo-4-(hexylseleno)benzene (7SePhBr)

^1H NMR (500 MHz, CDCl_3) δ 7.37 (d, $J = 8.5$ Hz, Ar-H, 2H), 7.33 (d, $J = 8.5$ Hz, Ar-H, 2H), 2.89 (t, $J = 7.5$ Hz, Se- CH_2 , 2H), 1.68 (tt, $J = 7.5$ and 7.5 Hz, Se- CH_2 - CH_2 , 2H), 1.38 (tt, $J = 7.5$ and 7.3 Hz, Se-(CH_2) $_2$ - CH_2 , 2H), 1.22–1.30 (m, 6H), 0.87 (t, $J = 7.0$ Hz, Se-(CH_2) $_6$ - CH_3 , 3H) ppm.

1-Bromo-4-(octylseleno)benzene (8SePhBr)

^1H NMR (500 MHz, CDCl_3) δ 7.36 (d, $J = 8.5$ Hz, Ar-H, 2H), 7.32 (d, $J = 8.5$ Hz, Ar-H, 2H), 2.88 (t, $J = 7.5$ Hz, Se- CH_2 , 2H), 1.67 (tt, $J = 7.5$ and 7.4 Hz, Se- CH_2 - CH_2 , 2H), 1.25–1.45 (m, 10H), 0.87 (t, $J = 6.8$ Hz, Se-(CH_2) $_7$ - CH_3 , 3H) ppm.

Synthesis of 4-Hexylseleno-4'-cyanobiphenyl (6SeCB)

6SePhBr (0.279 g, 0.871 mmol), 4-cyanophenylboronic acid pinacol ester (0.268 g, 1.17 mmol), Tetrakis(triphenylphosphine)palladium(0) [$\text{Pd}(\text{PPh}_3)_4$] (90.4 mg, 78.2 μmol), and

Cs_2CO_3 (0.788 g, 2.42 mmol) were put in a two-necked purged with argon gas. Subsequently, tetrahydrofuran (THF) (6 mL) degassed by argon bubbling was added to the flask and the mixture was stirred at the reflux temperature. for 6 h. The reaction mixture was extracted with DCM and the organic layer was washed with water and brine and dried over Magnesium sulfate (MgSO_4). After the volatiles were removed under reduced pressure, the crude product was purified by silica-gel column chromatography (eluent: DCM/hexane = 1/1, v/v) and recrystallized from methanol to afford the target compound (37.4 mg, 13%). ^1H NMR (500 MHz, CDCl_3) δ 7.72 (d, $J = 8.0$ Hz, Ar- H , 2H), 7.67 (d, $J = 8.5$ Hz, Ar- H , 2H), 7.56 (d, $J = 8.0$ Hz, Ar- H , 2H), 7.47 (d, $J = 8.5$ Hz, Ar- H , 2H), 2.97 (t, $J = 7.8$ Hz, Se- CH_2 , 2H), 1.74 (tt, $J = 7.8$ and 7.4 Hz, Se- $\text{CH}_2\text{-CH}_2$, 2H), 1.43 (tt, $J = 7.4$ and 7.4 Hz, Se-(CH_2) $_2\text{-CH}_2$, 2H), 1.25–1.33 (m, 4H), 0.88 (t, $J = 7.0$ Hz, Se-(CH_2) $_5\text{-CH}_3$, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 145.6, 137.7, 133.2, 132.9, 132.8, 128.2, 128.0, 119.5, 111.5, 31.9, 30.6, 30.1, 28.3, 23.1, 14.6 ppm. HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{19}\text{H}_{21}\text{NNaSe}$, 366.0732; found, 366.0714.

4-Methylseleno-4'-cyanobiphenyl (1SeCB)

^1H 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), 7.48 (d, $J = 8.8$ Hz, Ar- H , 2H), 2.41 (s, Se- CH_3 , 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 145.6, 137.4, 133.9, 133.2, 131.1, 128.2, 128.0, 119.5, 111.4, 7.6 ppm. HRMS (ESI, m/z): $[\text{M}]^+$ calcd. for $\text{C}_{14}\text{H}_{11}\text{NSe}$, 273.0052; found, 273.0068.

4-Ethylseleno-4'-cyanobiphenyl (2SeCB)

^1H NMR (500 MHz, CDCl_3) δ 7.72 (d, $J = 8.5$ Hz, Ar- H , 2H), 7.67 (d, $J = 9.0$ Hz, Ar- H , 2H), 7.57 (d, $J = 8.5$ Hz, Ar- H , 2H), 7.48 (d, $J = 8.0$ Hz, Ar- H , 2H), 2.97–3.01 (q, $J = 7.5$ Hz, Se- CH_2 , 2H), 1.48 (t, $J = 7.5$ Hz, Se- $\text{CH}_2\text{-CH}_3$, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 145.6, 137.9, 133.2, 133.1, 132.4, 128.2, 128.0, 119.5, 111.5, 21.7, 16.0 ppm. HRMS (ESI, m/z): $[\text{M}]^+$ calcd. for $\text{C}_{15}\text{H}_{13}\text{NSe}$, 287.0208; found, 287.0204.

4-Propylseleno-4'-cyanobiphenyl (3SeCB)

^1H 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), 7.57 (d, $J = 8.0$ Hz, Ar- H , 2H), 7.47 (d, $J = 8.5$ Hz, Ar- H , 2H), 2.96 (t, $J = 7.0$ Hz, Se- CH_2 , 2H), 1.74–1.81 (tq, $J = 7.0$ and 7.5 Hz, Se- $\text{CH}_2\text{-CH}_2$, 2H), 1.04 (t, $J = 7.5$ Hz, Se-(CH_2) $_2\text{-CH}_3$, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 145.6, 137.7, 133.2, 133.0, 132.7, 128.2, 128.0, 119.5, 111.4, 30.4, 24.0, 15.1 ppm. HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{16}\text{H}_{15}\text{NNaSe}$, 324.0262; found, 324.0260.

4-Butylseleno-4'-cyanobiphenyl (4SeCB)

^1H NMR (500 MHz, CDCl_3) δ 7.72 (d, $J = 9.0$ Hz, Ar- H , 2H), 7.67 (d, $J = 8.5$ Hz, Ar- H , 2H), 7.56 (d, $J = 8.5$ Hz, Ar- H , 2H), 7.48 (d, $J = 8.5$ Hz, Ar- H , 2H), 2.98 (t, $J = 7.5$ Hz, Se- CH_2 , 2H), 1.73 (tt, $J = 7.5$ and 7.5 Hz, Se- CH_2 - CH_2 , 2H), 1.42–1.50 (tq, $J = 7.5$ and 7.5 Hz, Se-(CH_2) $_2$ - CH_2 , 2H), 0.93 (t, $J = 7.5$ Hz, Se-(CH_2) $_3$ - CH_3 , 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 145.6, 137.7, 133.2, 132.91, 132.85, 128.2, 128.0, 119.5, 111.5, 32.3, 30.7, 30.4, 29.3, 28.4, 23.2, 14.7 ppm. HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{17}\text{H}_{17}\text{N NaSe}$, 338.0419; found, 338.0420.

4-Pentylseleno-4'-cyanobiphenyl (5SeCB)

^1H 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), 7.56 (d, $J = 8.5$ Hz, Ar- H , 2H), 7.47 (d, $J = 9.0$ Hz, Ar- H , 2H), 2.97 (t, $J = 7.8$ Hz, Se- CH_2 , 2H), 1.75 (tt, $J = 7.8$ and 7.5 Hz, Se- CH_2 - CH_2 , 2H), 1.42 (tt, $J = 7.5$ and 7.3 Hz, Se-(CH_2) $_2$ - CH_2 , 2H), 1.30–1.37 (tq, $J = 7.3$ Hz, Se-(CH_2) $_3$ - CH_2 , 2H), 0.90 (t, $J = 7.3$ Hz, Se-(CH_2) $_4$ - CH_3 , 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 145.6, 137.7, 133.2, 132.9, 132.8, 128.2, 128.0, 119.5, 111.5, 32.6, 30.3, 28.3, 22.7, 14.5 ppm. HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{18}\text{H}_{19}\text{N NaSe}$, 352.0576; found, 352.0589.

4-Heptylseleno-4'-cyanobiphenyl (7SeCB)

^1H NMR (500 MHz, CDCl_3) δ 7.72 (d, $J = 8.0$ Hz, Ar- H , 2H), 7.67 (d, $J = 8.0$ Hz, Ar- H , 2H), 7.56 (d, $J = 8.0$ Hz, Ar- H , 2H), 7.47 (d, $J = 8.0$ Hz, Ar- H , 2H), 2.97 (t, $J = 7.5$ Hz, Se- CH_2 , 2H), 1.74 (tt, $J = 7.5$ and 7.4 Hz, Se- CH_2 - CH_2 , 2H), 1.42 (tt, $J = 7.4$ and 7.4 Hz, Se-(CH_2) $_2$ - CH_2 , 2H), 1.24–1.33 (m, 6H), 0.88 (t, $J = 7.0$ Hz, Se-(CH_2) $_6$ - CH_3 , 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 145.6, 137.7, 133.2, 132.91, 132.85, 128.2, 128.0, 119.5, 111.5, 32.3, 30.7, 30.4, 29.3, 28.4, 23.2, 14.7 ppm. HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{20}\text{H}_{23}\text{N NaSe}$, 380.0889; found, 380.0889.

4-Octylseleno-4'-cyanobiphenyl (8SeCB)

^1H NMR (500 MHz, CDCl_3) δ 7.72 (d, $J = 8.5$ Hz, Ar- H , 2H), 7.67 (d, $J = 8.0$ Hz, Ar- H , 2H), 7.56 (d, $J = 8.5$ Hz, Ar- H , 2H), 7.47 (d, $J = 8.5$ Hz, Ar- H , 2H), 2.97 (t, $J = 7.5$ Hz, Se- CH_2 , 2H), 1.74 (tt, $J = 7.5$ and 7.4 Hz, Se- CH_2 - CH_2 , 2H), 1.42 (tt, $J = 7.4$ and 7.4 Hz, Se-(CH_2) $_2$ - CH_2 , 2H), 1.22–1.33 (m, 8H), 0.87 (t, $J = 6.8$ Hz, Se-(CH_2) $_7$ - CH_3 , 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 145.6, 137.7, 133.2, 132.92, 132.86, 128.2, 128.0, 119.5, 111.5, 32.4, 30.7, 30.4, 29.7, 29.6, 28.4, 23.2, 14.7 ppm. HRMS (ESI, m/z):

[M+Na]⁺ calcd. for C₂₁H₂₅NNaSe, 394.1045; found, 394.1026.

Differential scanning calorimetry

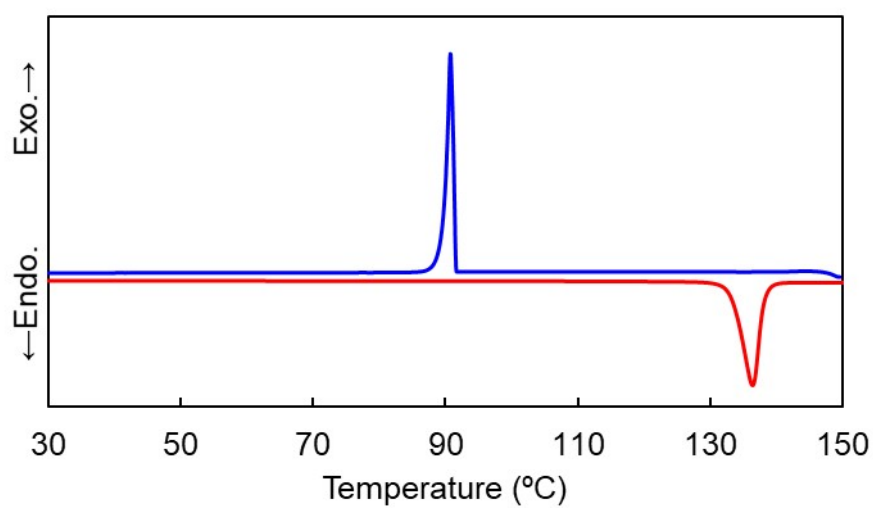


Fig. S1. DSC curves of 1SeCB.

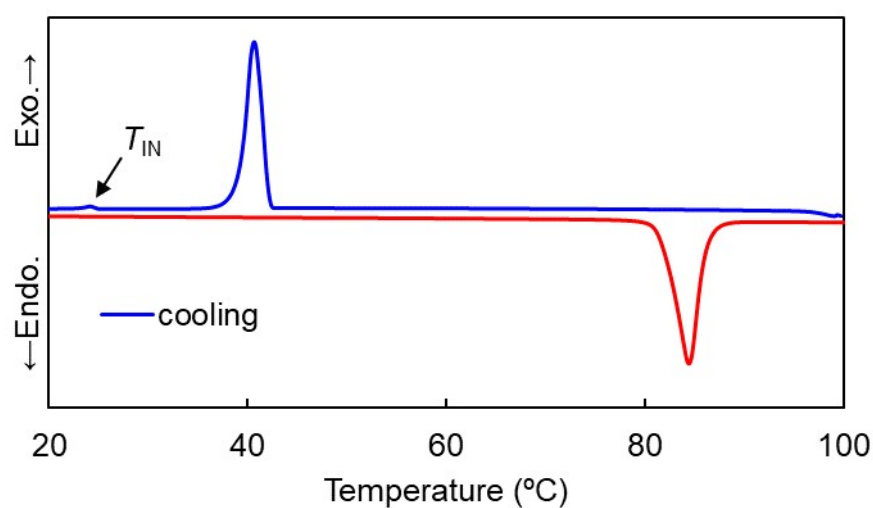


Fig. S2. DSC curves of 2SeCB.

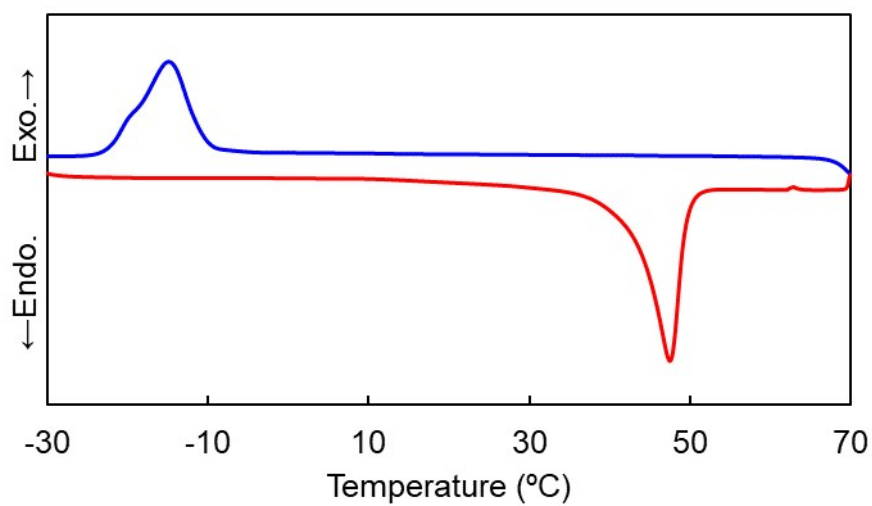


Fig. S3. DSC curves of 3SeCB.

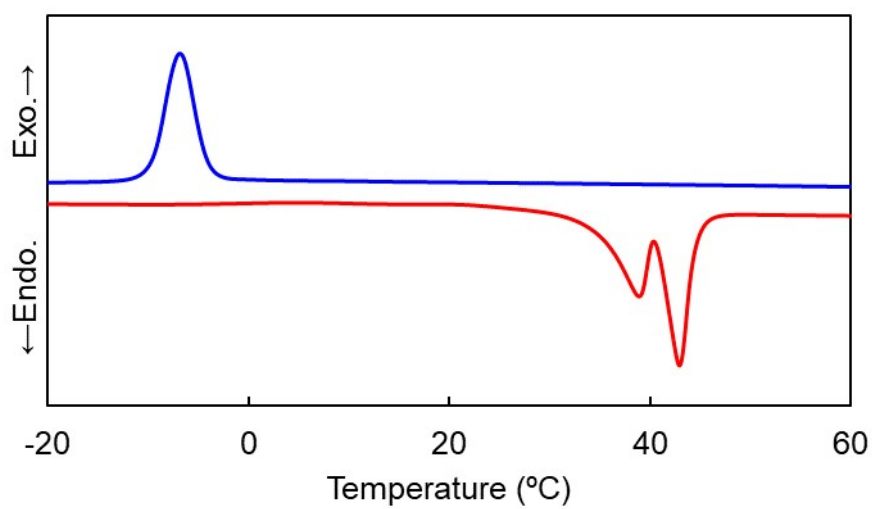


Fig. S4. DSC curves of 4SeCB.

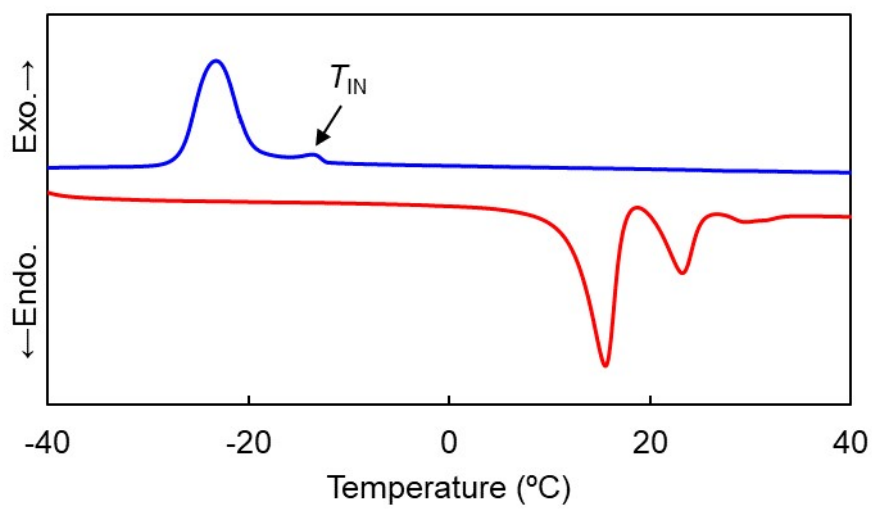


Fig. S5. DSC curves of 5SeCB.

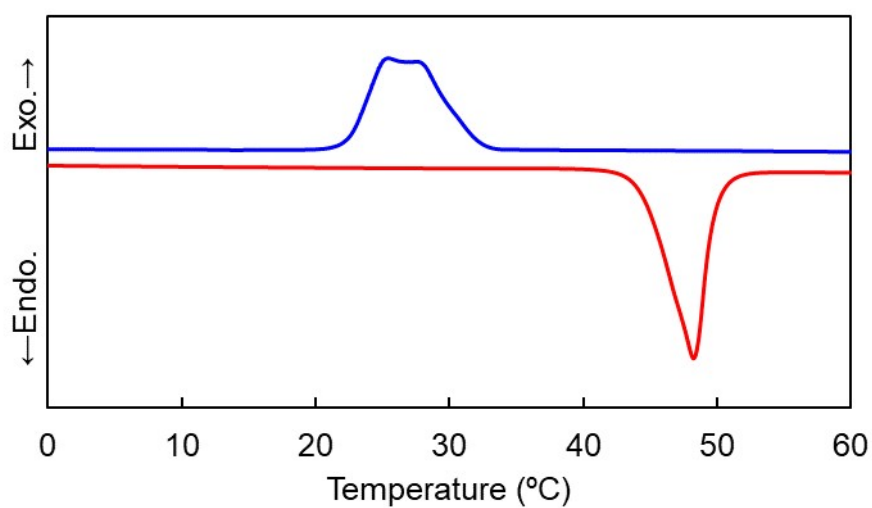


Fig. S6. DSC curves of 6SeCB.

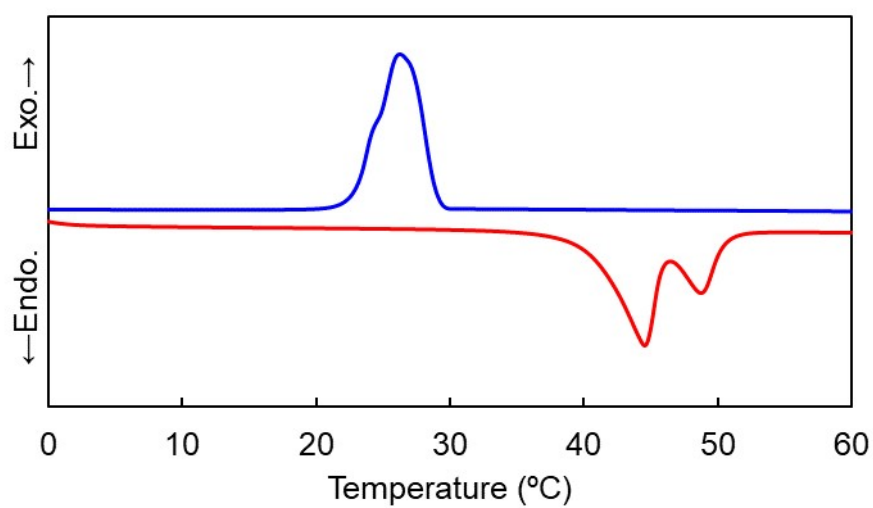


Fig. S7. DSC curves of 7SeCB.

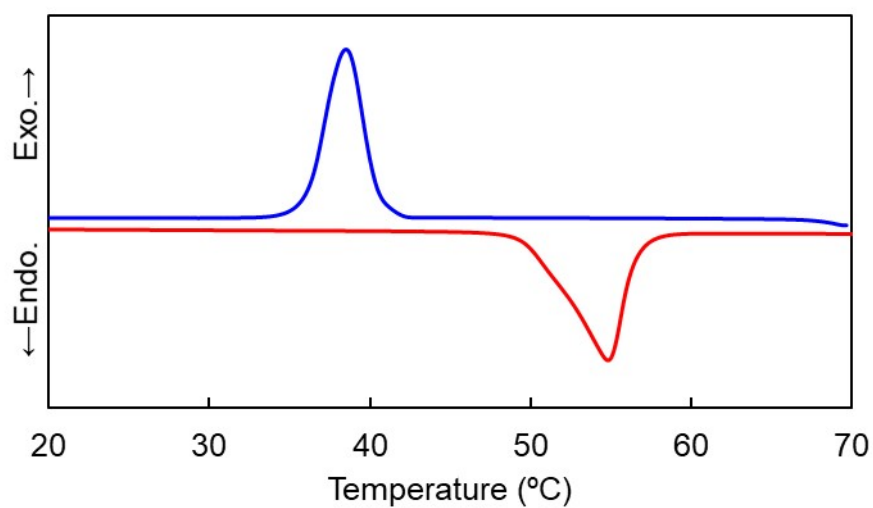


Fig. S8. DSC curves of 8SeCB.