Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

Assembly of thioether-containing rod-like liquid crystalline materials assisted by hydrogen-bonding terminal carboxyl groups

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Experimental Section

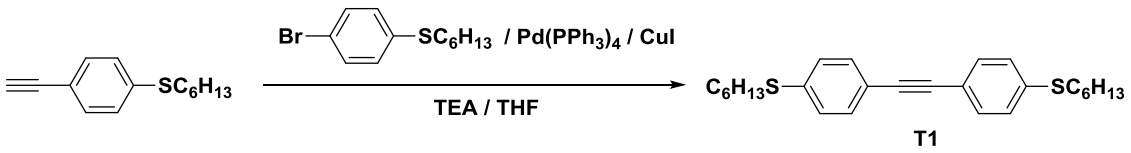
Instruments

The ^{1}H NMR and ^{13}C NMR spectra were measured in $CDCl_3$ on a JEOL LNM-EX 400 and a Bruker DPX300S spectrometer at room temperature using tetramethylsilane (TMS) as an internal standard. The FT-IR spectra were recorded on a JASCO FT-IR 460 plus spectrometer. The transition behavior was investigated by polarizing optical microscopy (POM) (Leica DM2500P microscopy with a Mettler FP90 hot stage) and differential scanning calorimetry (Perkin Elmer DSC7) with heating and cooling scans performed at 10 °Cmin^{-1}. Wide -angle X-ray scattering (WAXS) patterns were obtained using a Bruker D8 DISCOVER equipped with a Vantec-500 detector with CuKa radiation. The transmittance of light was observed by a microscope spectroscopic method using a Nikon LV100 Pol optical microscope equipped with a USB4000 (Ocean photonics) spectrometer.

Materials

1-Ethynyl-4-hexylbenzene, 4-iodophenol, trimethylsilylacetylene, 4-bromobenzoic acid, 4-bromobenzenethiol and $Pd(PPh_3)_4$ were purchased from TCI, and 6-bromohexanol, triethylamine (TEA) and PPh_3 were purchased from Wako, and CuI was purchased from Kanto chemical. Unless otherwise noted, all chemical were commercially available and use as received.

Synthesis of T1

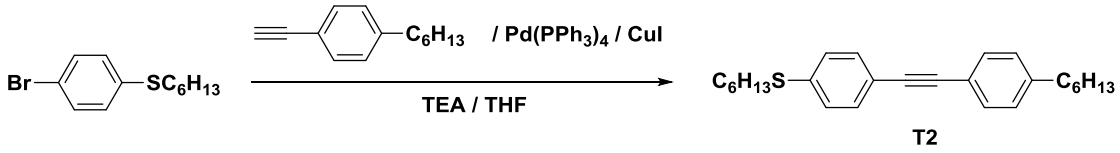


Scheme S1. Synthesis of **T1**.

T1 was synthesized according to the general procedure for Sonogashira coupling. 1-Ethynyl-4-hexylsulfanylbenzene (0.28 mmol, 60 mg), 1-bromo-4-hexylsulfanylbenzene (0.28 mmol, 75 mg), TEA (5 ml), THF (5 ml), CuI (14 µmol, 2.6 mg) and $Pd(PPh_3)_4$ (14 µmol, 16 mg) were used, and colorless solid was

obtained (Yield: 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.0 Hz, Ar-*H*, 4H), 7.25 (d, *J* = 8.0 Hz, Ar-*H*, 4H), 2.94 (t, *J* = 6.6 Hz, Ar-S-C*H*$_2$, 4H), 1.66 (tt, *J* = 7.3 and 7.6 Hz, S-CH_2-C*H*$_2$, 4H), 1.44 (tt, *J* = 7.0 and 7.6 Hz, S-CH_2-CH_2-C*H*$_2$, 2H), 1.3-1.27 (m, C*H*$_2$-C*H*$_2$-CH_3, 8H), 0.89 (t, *J* = 6.3 Hz, C*H*$_3$, 3H) ppm.

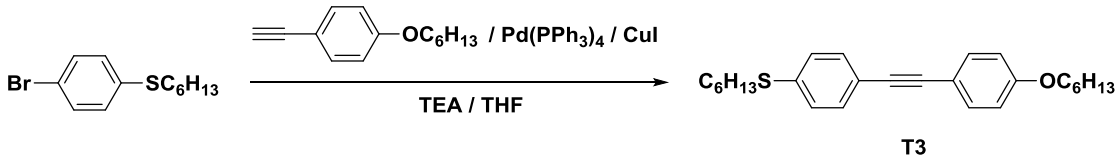
Synthesis of T2



Scheme S2. Synthesis of **T2**.

T2 was synthesized according to the general procedure for Sonogashira coupling. 1-Ethynyl-4-hexylbenzene (0.55 mmol, 0.10 g), 1-bromo-4-hexylsulfanylbenzene (0.55 mmol, 0.15 g), TEA (10 ml), THF (10 ml), CuI (27 μmol, 5.2 mg) and $Pd(PPh_3)_4$ (27 μmol, 32 mg) were used, and colorless solid was obtained (Yield: 63%). ^{1}H NMR 400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.1 Hz, Ar-*H*, 2H), 7.41 (d, *J* = 8.3 Hz, Ar-*H*, 2H), 7.25 (d, *J* = 8.3 Hz, Ar-*H*, 2H), 7.15 (d, *J* = 8.1 Hz, Ar-*H*, 2H), 2.94 (t, *J* = 7.4 Hz, Ar-O-C*H*$_2$, 2H), 2.61 (t, *J* = 6.6 Hz, Ar-S-C*H*$_2$, 2H), 1.70-1.57 (m, O-CH_2-C*H*$_2$ and S-CH_2-C*H*$_2$, 4H), 1.43 (m, O-CH_2-CH_2-C*H*$_2$, 2H), 1.36-1.24 (m, O-CH_2-CH_2-CH_2-C*H*$_2$-C*H*$_2$ and S-CH_2-CH_2-C*H*$_2$-C*H*$_2$ -C*H*$_2$, 10H), 0.92-0.84 (m, C*H3* and C*H*$_3$, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.8, 138.2, 132.2, 131.9, 128.9, 128.3, 120.79, 120.76, 36.33, 33.5, 32.1, 31.8, 31.6, 29.4, 29.3, 29.0, 23.01, 22.95, 14.5, 14.4 ppm.

Synthesis of T3

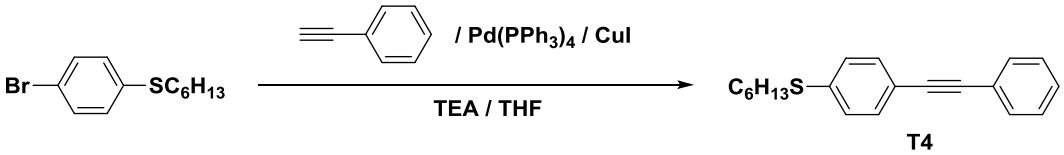


Scheme S3. Synthesis of **T3**.

T3 was synthesized according to the general procedure for Sonogashira coupling. 1-Ethynyl-4-hexyloxybenzene (0.44 mmol, 90 mg), 1-bromo-4-hexylsulfanylbenzene

(0.44 mmol, 0.12 g), TEA (5 ml), THF (5 ml), CuI (22 μmol, 4.2 mg) and $Pd(PPh_3)_4$ (22 μmol, 25 mg) were used, and colorless solid was obtained (Yield: 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.6 Hz, Ar-*H*, 4H), 7.40 (d, *J* = 8.6 Hz, Ar-*H*, 4H), 7.24 (d, *J* = 8.6 Hz, Ar-*H*, 4H), 6.86 (d, *J* = 8.6 Hz, Ar-*H*, 4H), 3.96 (t, *J* = 6.6 Hz, Ar-O-C*H*$_2$, 2H), 2.93 (t, *J* = 7.3 Hz Ar-S-C*H*$_2$, 2H), 1.78 (tt, *J* = 6.6 and 7.4 Hz, O-CH_2-C*H*$_2$, 2H), 1.66 (tt, *J* = 7.3 and 7.6 Hz, S-CH_2-C*H*$_2$, 2H), 1.51-1.20 (m, C*H*$_2$-C*H*$_2$-C*H*$_2$-CH_3, 12H), 0.97-0.82 (m, C*H*$_3$, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 130.5 134.01, 133.98, 132.74, 132.72, 128.9, 121.5, 116.1, 115.5, 90.8, 88.8, 69.1, 34.1, 32.6, 32.4, 30.2, 30.0, 29.6, 26.7, 23.64, 23.57, 15.08, 15.06 ppm.

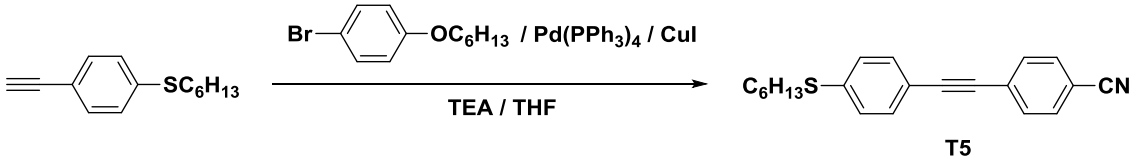
Synthesis of T4



Scheme S4. Synthesis of **T4**.

T4 was synthesized according to the general procedure for Sonogashira coupling. Ethynylbenzene (0.44 mmol, 45 mg), 1-bromo-4-hexylsulfanylbenzene (0.44 mmol, 0.12 g), TEA (5 ml), THF (5 ml), CuI (22 μmol, 4.2 mg) and $Pd(PPh_3)_4$ (22 μmol, 25 mg) were used, and colorless solid was obtained (Yield: 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.6 Hz, Ar-*H*, 2H), 7.43 (d, *J* = 8.3 Hz, Ar-*H*, 2H), 7.39-7.30 (m, Ar-H, 3H), 7.26 (d, *J* = 7.6 Hz, Ar-*H*, 2H), 2.94 (t, *J* = 7.3 Hz, Ar-S-C*H*$_2$, 2H), 1.67 (tt, *J* = 7.3 and 7.5 Hz, S-CH_2-C*H*$_2$, 2H), 1.44 (tt, *J* = 7.0 and 7.5 Hz, S-CH_2-CH_2-C*H*$_2$, 2H), 1.37-1.23 (m, C*H*$_2$-C*H*$_2$-CH_3, 4H), 0.89 (t, *J* = 6.3 Hz, C*H*$_3$, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 132.0, 131.7, 128.5, 128.4, 127.9, 123.4, 120.2, 89.7, 89.3, 33.1, 31.5, 29.1, 28.7, 22.7, 14.2 ppm.

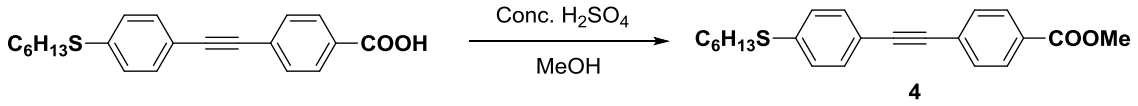
Synthesis of T5



Scheme S5. Synthesis of **T5**.

T5 was synthesized according to the general procedure for Sonogashira coupling. Ethynylbenzene (0.44 mmol, 56 mg), 1-bromo-4-hexylsulfanylbenzene (0.44 mmol, 0.12 g), TEA (5 ml), THF (5 ml), CuI (22 μmol, 4.2 mg) and $Pd(PPh_3)_4$ (22 μmol, 25 mg) were used, and colorless solid was obtained (Yield: 28%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 10.8 Hz, Ar-*H*, 4H), 7.43 (d, *J* = 8.5 Hz, Ar-*H*, 2H), 7.26 (d, *J* = 8.5 Hz, Ar-*H*, 2H), 2.96 (t, *J* = 7.3 Hz, Ar-S-C*H*$_2$, 2H), 1.68 (tt, *J* = 7.3 and 7.6 Hz, S-CH_2-C*H*$_2$, 2H), 1.45 (tt, *J* = 6.7 and 7.6 Hz, S-CH_2-CH_2-C*H*$_2$, 2H), 1.37-1.26 (m, C*H*$_2$-C*H*$_2$-CH_3, 4H), 0.89 (t, *J* = 6.5 Hz, C*H*$_3$, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 133.07, 132.99, 129.3, 128.4, 119.7, 119.6, 112.4, 94.8, 89.0, 33.7, 32.4, 29.9, 29.6, 23.5, 15.0 ppm.

Synthesis of T6

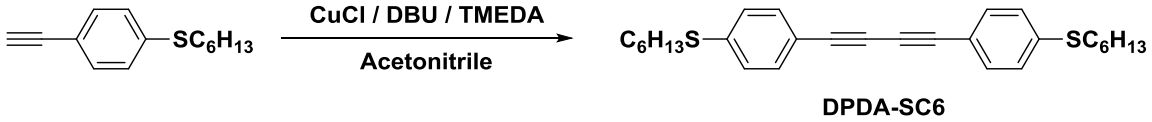


Scheme S6. Synthesis of **T6**.

Compound **3** (0.30 mmol, 0.10 g) and methanol (20 ml) were put into a flask, and then concentrated sulfuric acid was put a few drops. The mixture was stirred at reflax temperature, and after 24 h it was cooled to room temperature and the target compound was recrystalized from the solution. Colorless solid. Yield: 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.3 Hz, Ar-*H*, 4H), 7.59 (d, *J* = 8.3 Hz, Ar-*H*, 4H), 7.46 (d, *J* = 8.3 Hz, Ar-*H*, 4H), 7.28 (d, *J* = 8.3 Hz, Ar-*H*, 4H), 3.95 (s, O-CH*3*, 3H), 2.97 (t, *J* = 7.3 Hz Ar-S-C*H*$_2$, 2H), 1.70 (tt, *J* = 7.3 and 7.5 Hz, S-CH_2-C*H*$_2$, 2H), 1.46 (tt, *J* = 7.1 and 7.5 Hz, S-CH_2-CH_2-C*H*$_2$, 2H), 1.38-1.25 (m, C*H*$_2$-C*H*$_2$-CH_3, 4H), 0.91 (t, *J* = 6.8 Hz, C*H*$_3$,

3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.0, 139.4, 132.4, 131.8, 129.9, 129.8, 128.5, 127.9, 92.7, 89.3, 52.6, 33.2, 31.8, 29.3, 29.0, 22.9, 14.4 ppm.

Synthesis of DPDA-SC6

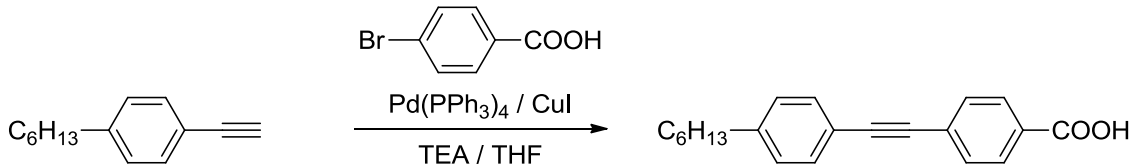


DPDA-SC6

Scheme S7. Synthesis of **DPDA-SC6**.

1-Ethynyl-hexylsulfanylbenzene (0.92 mmol, 0.20 g), TMEDA (92 μmol, 0.12 g), CuCl (46 μmol, 9.1 mg) and acetonitrile (10 ml) were put into a flask, and then TMEDA and DBU were put a few drops. The mixture was stirred at room temperature with oxygen bubbling. After 3 h, the reaction mixture was extracted with chloroform, washed with water and brine, and then the organic phase was evapolated. The crude product was purified with silica gel on a column chromatography (eluent: chloroform : hexane = 1:3). Colorless solid. Yield: 99%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.3 Hz, Ar-*H*, 4H), 7.24 (d, *J* = 8.3 Hz, Ar-*H*, 4H), 2.96 (t, *J* = 7.4 Hz, Ar-S-C*H*$_2$, 4H), 1.69 (tt, *J* = 7.3 and 7.4 Hz, S-CH_2-C*H*$_2$, 4H), 1.45 (tt, *J* = 6.6 and 7.3 Hz, S-CH_2-CH_2-C*H*$_2$, 2H), 1.37-1.26 (m, C*H*$_2$-C*H*$_2$-CH_3, 8H), 0.91 (t, *J* = 6.7 Hz, C*H*$_3$, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.2, 133.1, (133.1), 127.7 (127.7), 118.6, 82.1, 74.6, 33.0, 31.8, 29.2, 29.0, 22.9, 14.4 ppm.

Synthesis of 4-[2-(4-hexylphenyl)ethynyl]benzoic acid



1

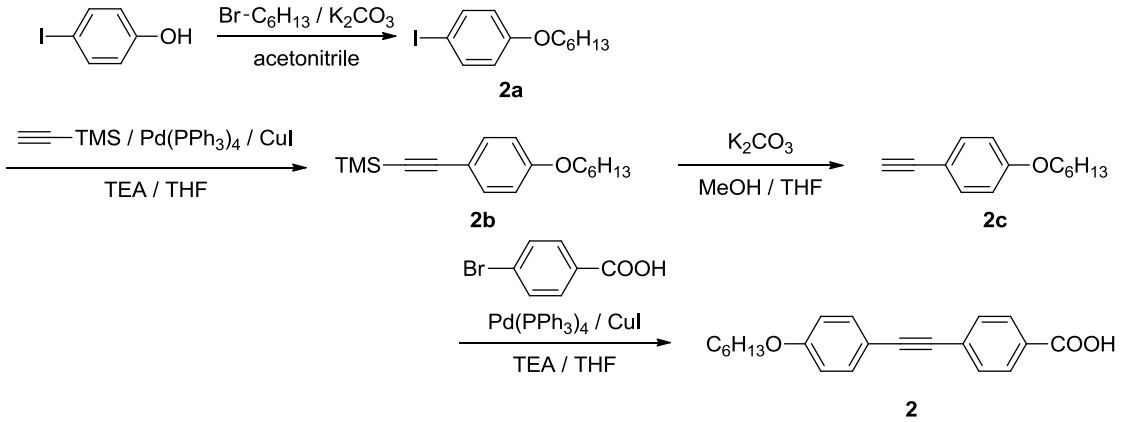
Scheme S8. Synthesis of compound **1**.

4-[2-(4-Hexylphenyl)ethynyl]benzoic acid (1, General method for Sonogashira coupling)

In a two-way flask, a mixture of 1-ethynyl-4-hexylbenzene (3.2 mmol, 0.60 g), TEA

(10 ml) and THF (10 ml) was bubbled with argon. And 4-bromobenzoic acid (3.2 mmol, 0.79 g), CuI (97 µmol, 18 mg) and $Pd(PPh_3)_4$ (97 µmol, 0.11 g) were put to another two-way flask and it was filled with argon, and then former liquid mixture was added into it. The mixture was stirred at room temperature for 12 h. To eliminate TEA, 2M HCl aq was added to the reaction mixture, and insoluble solid was filtrated. And then, the colorless solid was recrystallized with chloroform (Yield; 83%). ^{1}H NMR (300 MHz, DMSO-d6) δ 8.00 (d, *J* = 8.1 Hz, Ar-*H*, 2H), 7.68 (d, *J* = 8.1 Hz, Ar-*H*, 2H), 7.52 (d, *J* = 8.0 Hz, Ar-*H*, 2H), 7.29 (d, *J* = 8.0 Hz, Ar-*H*, 2H), 2.62 (t, *J* = 7.6 Hz, Ar-C*H*$_2$, 2H), 1.76 (tt, *J* = 6.5 and 7.6 Hz, Ar-CH_2-C*H*$_2$, 2H), 1.35-1.20 (m, C*H*$_2$-C*H*$_2$-C*H*$_2$-CH_3, 6H), 0.87 (t, *J* = 6.5 Hz, C*H*$_3$, 3H) ppm. ^{13}C NMR (75 MHz, DMSO-d6) δ 167.6, 144.8, 132.34, 132.27, 131.2, 1320.4, 129.6, 127.7, 119.8, 93.1, 88.9, 35.9, 31.9, 31.5, 29.2, 22.9, 14.8 ppm. FT-IR 3200-2500, 2956, 2925, 2853, 2213, 1681, 1601, 1424, 950 cm^{-1}. HRMS-FAB+ (m/z): [M] calcd for $C_{21}H_{22}O_2$, 306.1620; found, 306.1627. Anal. Calcd for $C_{21}H_{22}O_2$: C 82.32, H 7.24%; found C 82.43, H 7.12%.

Synthesis of 4-[2-(4-hexyloxyphenyl)ethynyl]benzoic acid (2)



Scheme S9. Synthesis of compound **2**.

1-Bromo-4-hexyloxybenzene (2a, general procedure for Wiliamson ether reaction)

A mixture of 4-iodophenol (2.4 g, 11 mmol), 1-bromohexane (1.8 g, 11 mmol), potassium carbonate (3.0 g, 22 mmol,) and acetonitrile (30 ml) was refluxed for 24 h.

The reaction mixture was extracted with ethyl acetate, washed with water and dried over $MgSO_4$. After removing the solvent under reduced pressure, colorless liquid was obtained withought further purification (Yield; >99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 9.0 Hz, Ar-*H*, 2H), 6.67 (d, *J* = 9.0 Hz, Ar-*H*, 2H), 3.91 (t, *J* = 6.6 Hz Ar-O-C*H*$_2$, 2H), 1.76 (tt, *J* = 6.6 and 7.5 Hz, O-CH_2-C*H*$_2$, 2H), 1.44 (tt, *J* = 6.9 and 7.5 Hz, O-CH_2-CH_2-C*H2*, 2H), 1.37-1.28 (m, CH_2-C*H*$_3$, 4H), 0.90 (t, *J* = 6.9 Hz, C*H*$_3$, 3H) ppm.

1-Hexyloxy-4-[2-(trimethylsilyl)ethynyl]benzene (2b)

2b was synthesized according to the general procedure for sonogashira cross coupling. **2a** (2.5 g, 8.2 mmol), trimethylsilylacetylene (1.4 mL, 9.9 mmol), $Pd(PPh_3)_4$ (0.19 g, 0.16 mmol), CuI (30 mg, 0.16 mmol), TEA (15 mL) and THF (15 mL) were used. Colorless liquid, Yield; >99%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.9 Hz, Ar-*H*, 2H), 6.80 (d, *J* = 8.9 Hz, Ar-*H*, 2H), 3.94 (t, *J* = 6.6 Hz, Ar-O-C*H*$_2$, 2H), 1.77 (tt, *J* = 6.6 and 7.5 Hz, O-CH_2-C*H*$_2$, 2H), 1.45 (tt, *J* = 7.1 and 7.5 Hz, O-CH_2-CH_2-C*H*$_2$, 2H), 1.38-1.29 (m, -C*H*$_2$-C*H*$_2$-CH_3, 4H), 0.90 (t, *J* = 7.1 Hz, C*H*$_3$, 3H), 0.24 (s, Si-C*H*$_3$, 9H) ppm.

1-Ethynyl-4-hexyloxybenzene (2c, general procedure for base-induced deprotection reaction)

A mixture of **2b** (2.3 g, 8.2 mmol), potassium carbonate (2.26 g, 16.5 mmol), THF (15 mL), and MeOH (15 mL) was stirred for 3 h, and the reaction mixture was extracted with ethyl acetate, washed with water and brine, and the combined organic layers were dried over $MgSO_4$. After the organic solvent was removed under reduced pressure, pale brown liquid was obtained without further purification (Yield; 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* =8.7 Hz, Ar-*H*, 2H), 6.83 (d, *J* = 8.7 Hz, Ar-*H*, 2H), 3.95 (t, *J* = 6.6 Hz Ar-O-C*H*$_2$, 2H), 2.99 (s, -C≡C*H*, 1H), 1.78 (tt, *J* = 6.6 and 7.4 Hz, -O-CH_2-C*H*$_2$, 2H), 1.45 (tt, *J* = 6.9 and 7.4 Hz, O-CH_2-CH_2-C*H2*, 2H), 1.38-1.28 (m, -C*H*$_2$-C*H*$_2$-CH_3, 4H), 0.90 (t, *J* = 7.0 Hz, CH_3 3H) ppm.

4-[2-(4-Hexyloxyphenyl)ethynyl]benzoic acid (2)

Compound **2** was synthesized according to the general procedure for sonogashira cross

coupling. **2c** (1.8 g, 9.0 mmol), 4-bromobenzoic acid (1.6g , 8.1 mmol), $Pd(PPh_3)_4$ (0.10 g, 87 µmol), CuI (85 mg, 0.45 mmol) and PPh_3 (0.12g , 0.45 mmol) were used. Colorless solid, Yield; 11%. ^{1}H NMR (400 MHz, DMSO-d6) δ 7.97 (d, *J* = 8.6 Hz, Ar-*H*, 2H), 7.65 (d, *J* = 8.6 Hz, Ar-*H*, 2H), 7.51 (d, *J* = 8.5 Hz, Ar-*H*, 2H), 7.34 (d, *J* = 8.5 Hz, Ar-*H*, 2H), 3.02 (t, *J* = 7.3 Hz, Ar-S-C*H*$_2$, 2H), 1.60 (tt, *J* = 7.3 and 7.4 Hz, S-CH_2-C*H*$_2$, 2H), 1.40 (tt, *J* = 7.1 and 7.4 Hz, S-CH_2-CH_2-C*H*$_2$, 2H), 1.31-1.23 (m, -C*H*$_2$-C*H*$_2$-CH_3, 4H), 0.86 (t, *J* = 7.1 Hz, C*H*$_3$, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.6, 160.2, 143.5, 134.0, 134.0, 132.1, 132.1, 130.4, 130.4, 127.8, 115.8, 115.8, 114.3, 93.2, 88.2, 68.5, 31.9, 29.4, 26.0, 22.9, 14.8 ppm. FT-IR: 3200-2500, 2942, 2210, 1686, 1599, 1423, 935 cm^{-1}. HRMS-FAB+ (m/z): [M] calcd for $C_{21}H_{22}O_3$, 322.1569; found, 322.1577. Anal. Calcd for $C_{21}H_{22}O_3$: C 78.23, H 6.88%; found C 78.25, H 6.77%.

FT-IR spectra of compound 1-3

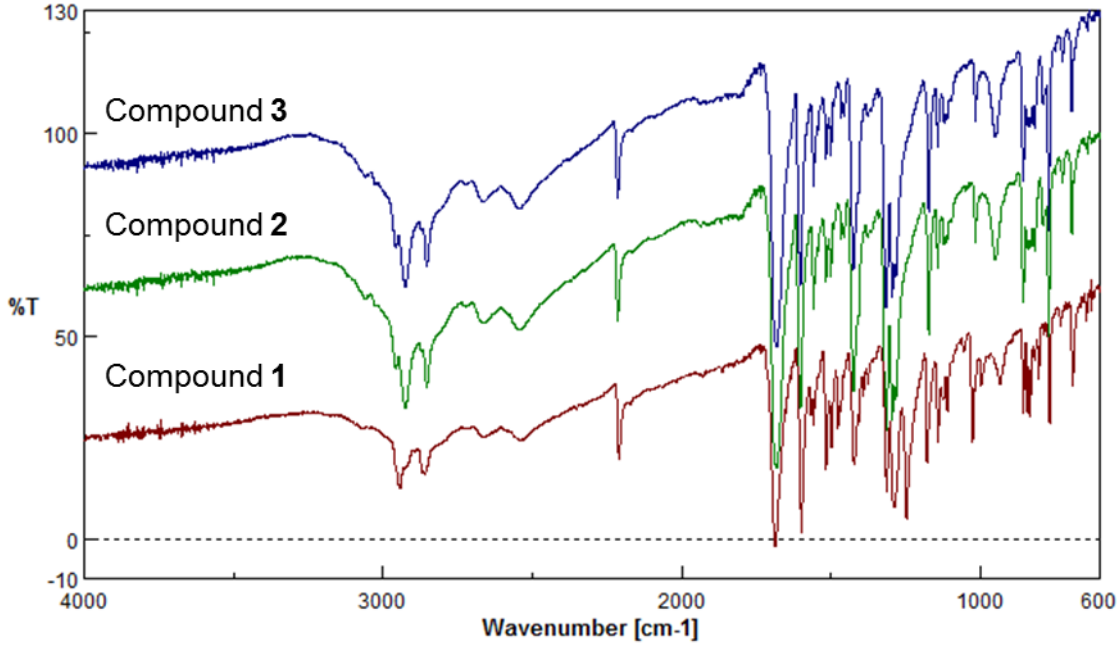


Fig. S 1. FT-IR spectra of compound **1-3**.

DSC measurements

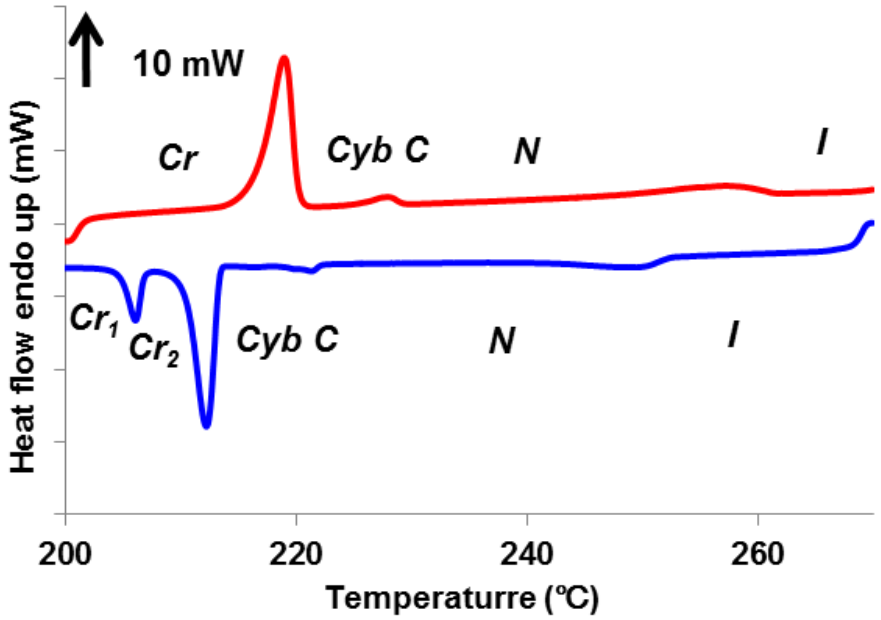


Fig. S2. DSC curve of compound **1**.

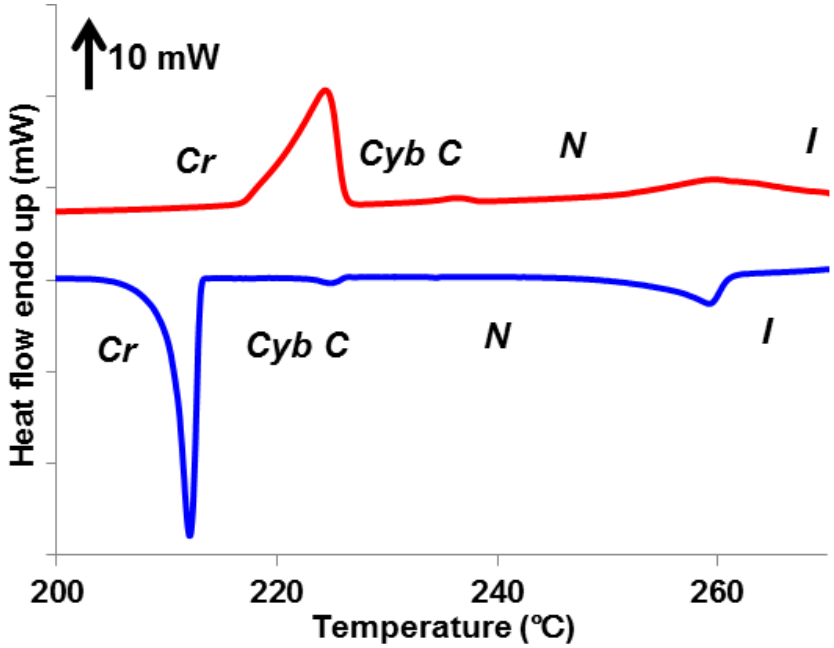
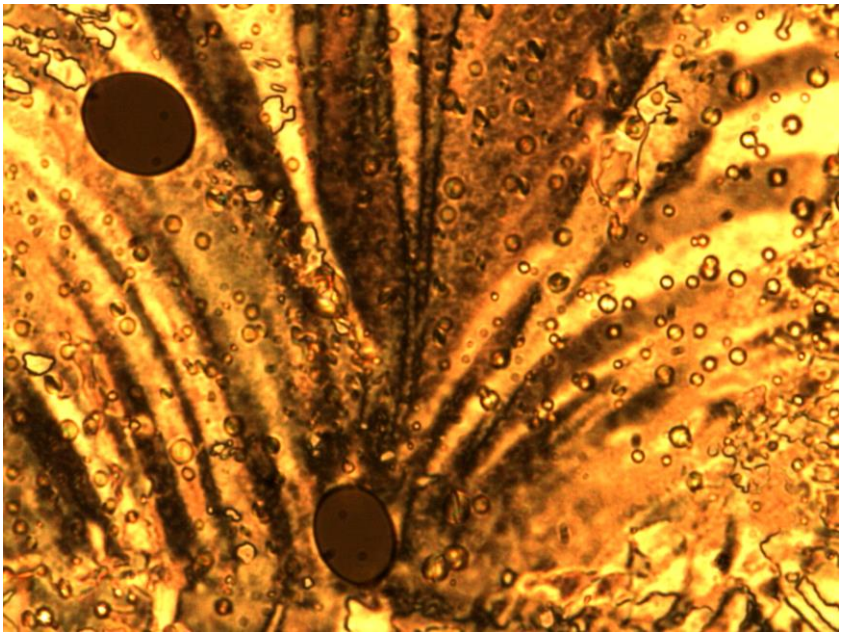
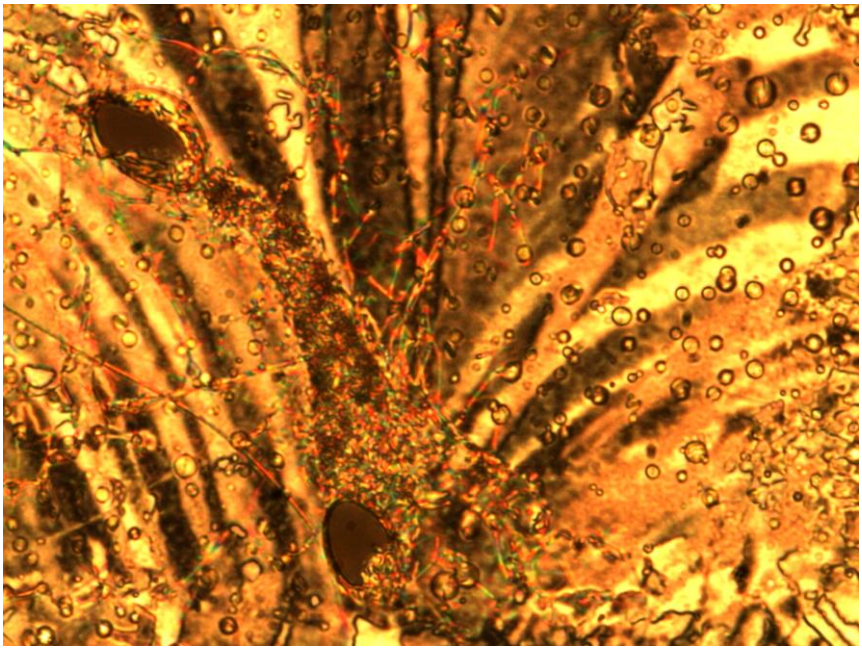


Fig. S3. DSC curve of compound **2**.

POM images



(a)



(b)

Fig. S4. POM images observed from in-plane alignment cell for of compound **1**. (a) *N* phase at 222 °C (b) *Cyb C* phase after anneling at 222 °C.

XRD measuremant from non-aligned specimens

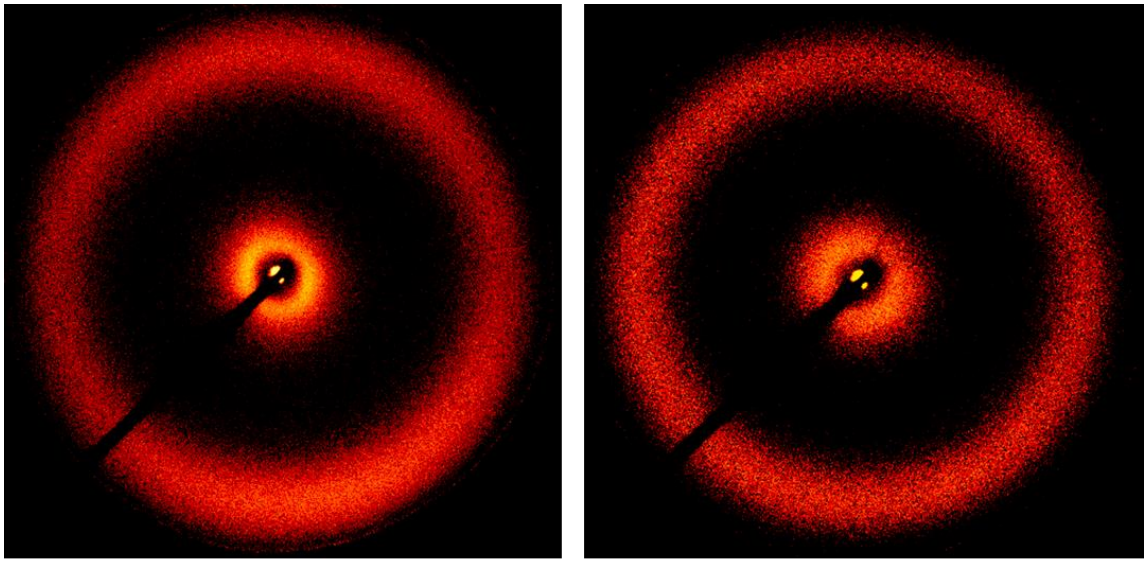


Fig. S5. 2D-XRD patterns from non-aligned specimen for compound **1**.

(a) *Cyb C* at 218 °C and (b) *N* at 228 °C

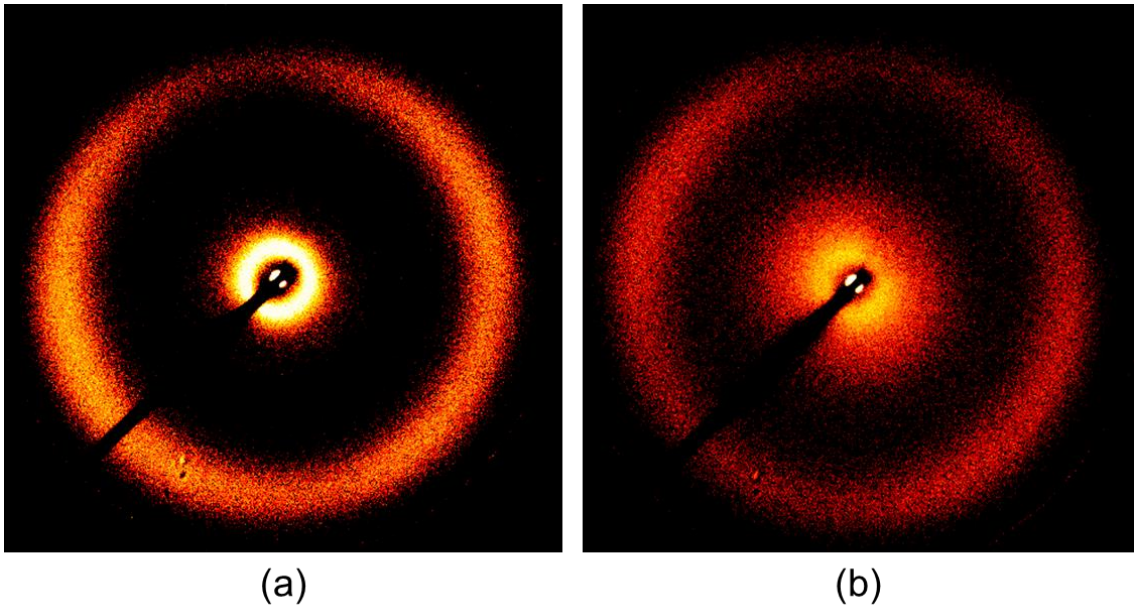


Fig. S6. 2D-XRD patterns from non-aligned specimen for compound **2**.

(a) *Cyb C* at 222 °C and (b) *N* at at 254 °C.

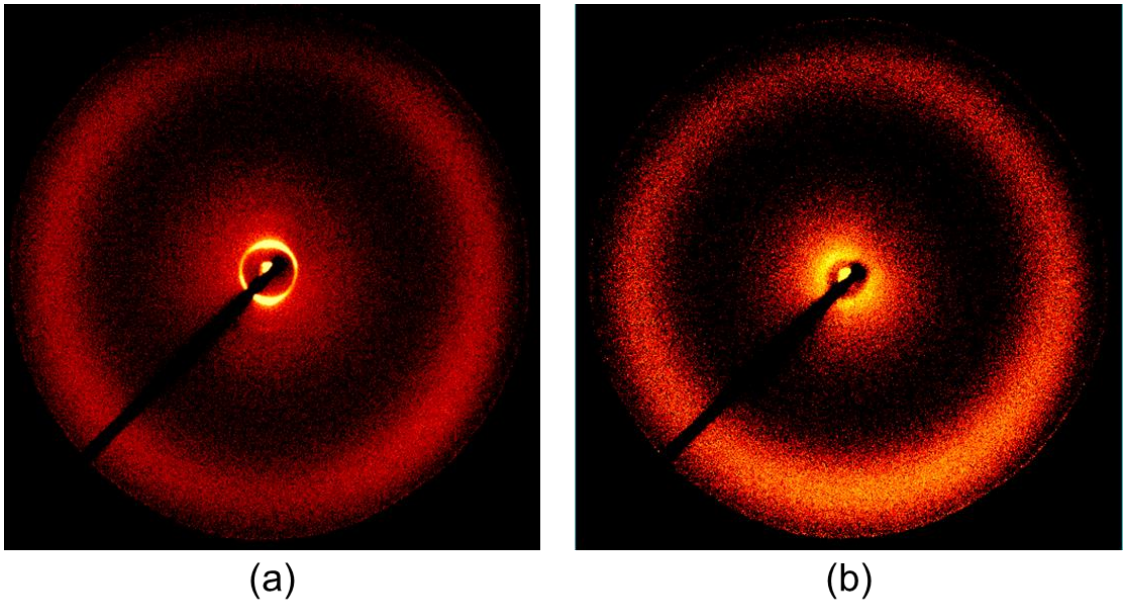


Fig. S7. 2D-XRD patterns from non-aligned specimen for compound **3**.
(a) *Sc* at 210 °C and (b) *N* at 235 °C.

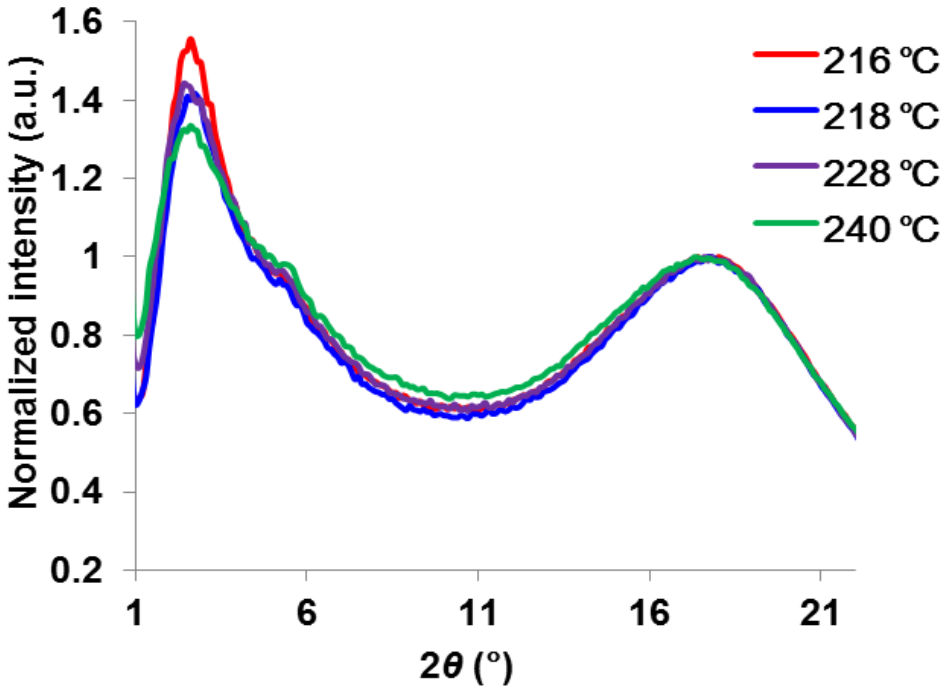


Fig. S8. Temperature dependence of 1D-XRD patterns mesured from aligned specimen for compound **1**.

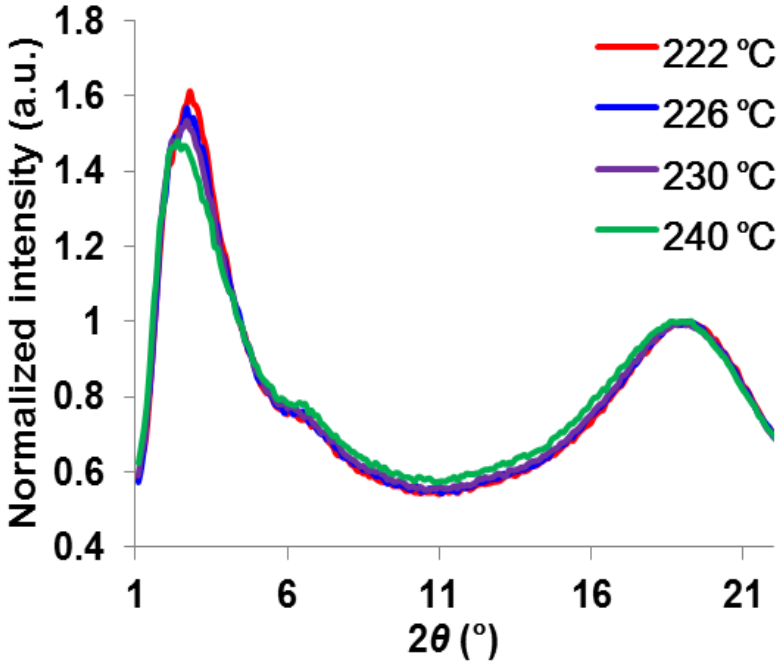


Fig. S9. Temperature dependence of 1D-XRD patterns measured from aligned specimen for compound **2**.

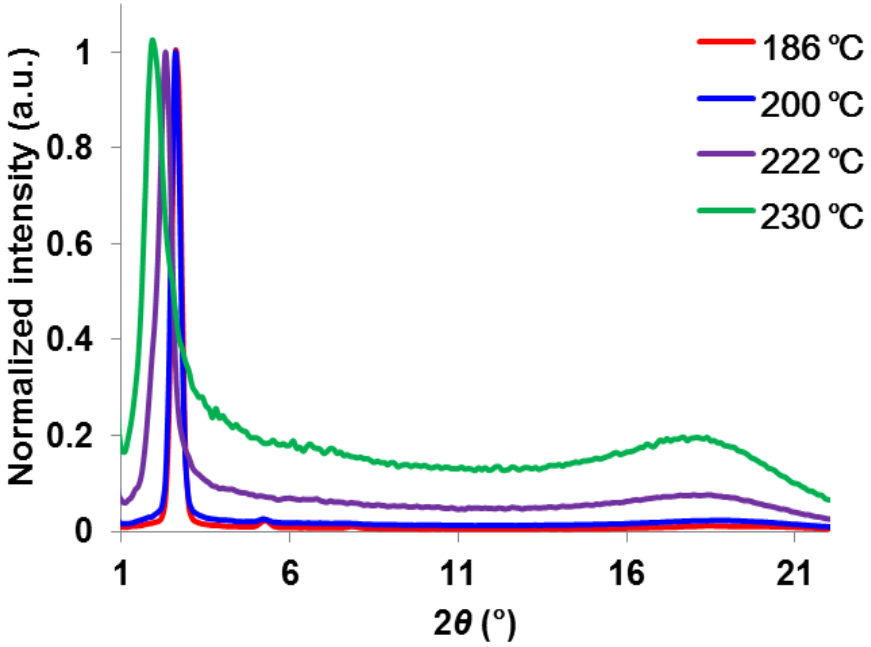


Fig. S10. Temperature dependence of 1D-XRD patterns measured from aligned specimen for compound **3**.

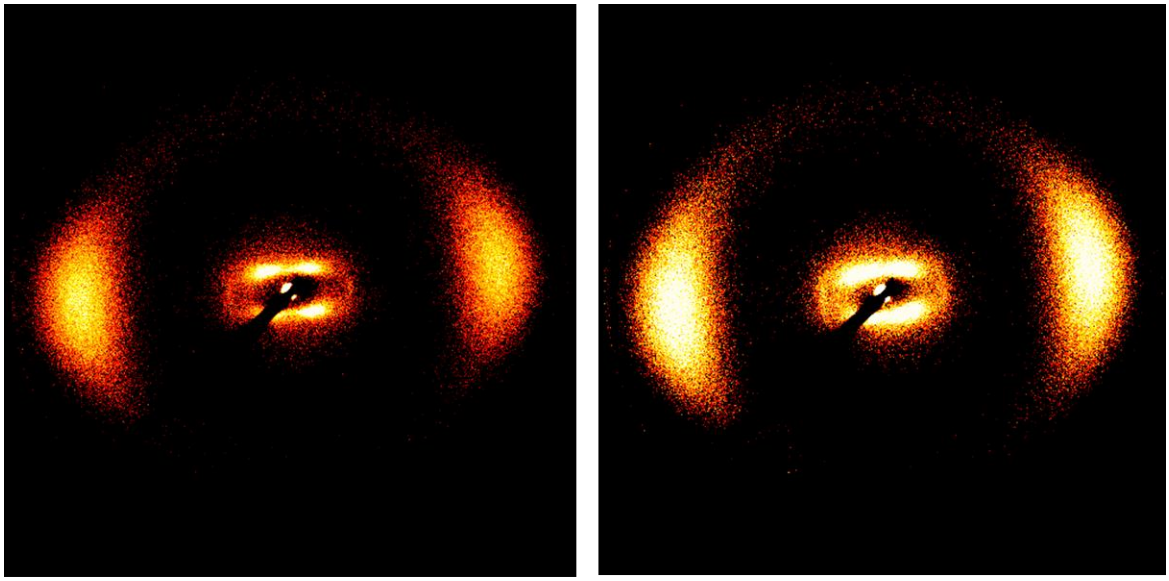


Fig. S11. 2D-XRD patterns measured from aligned specimen for compound **1**. (a) *CybC* phase at 214 °C and (b) *N* phase at 225.

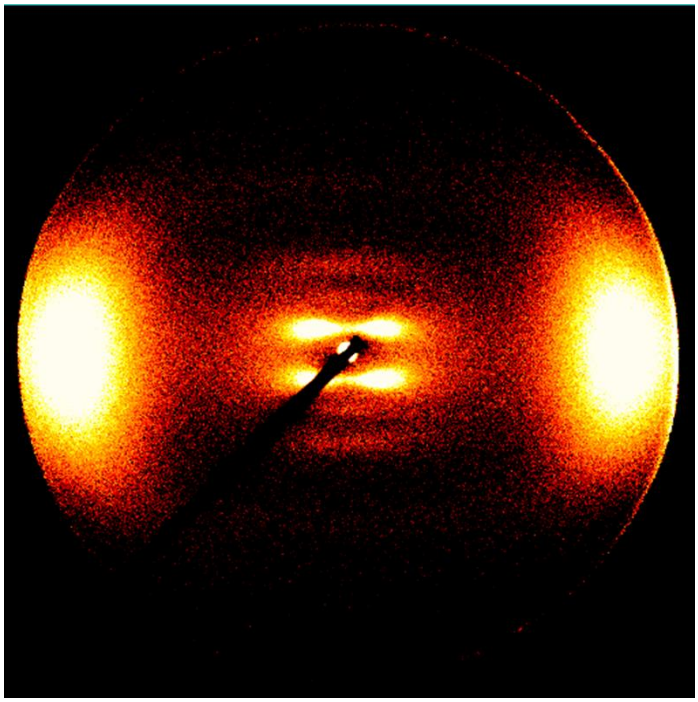


Fig. S12. 2D-XRD patterns measured form aligned specimen of *CybC* phase at 218 °C for compound **2**.

Measuement of birefringence

The measurement method of birefringence have descrived in previous reports. [1,2]

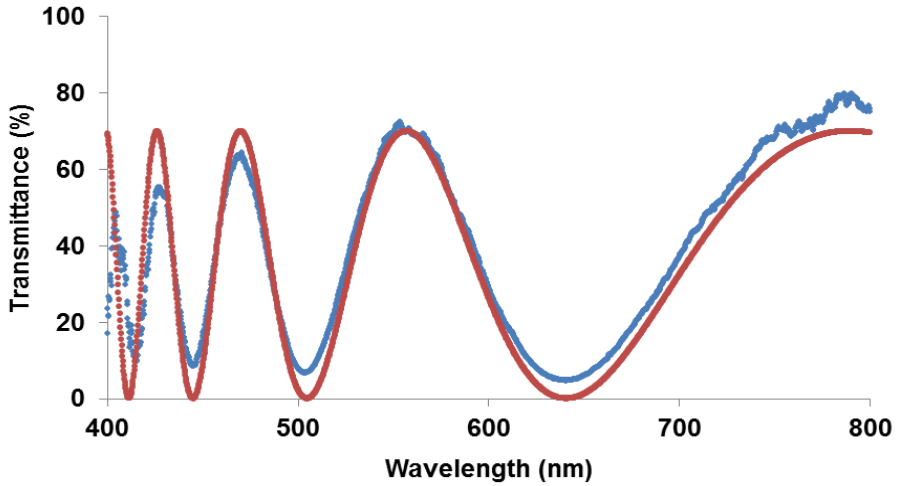


Fig. S13. Wavelength dependence of light intensity (blue line) transmitted of compound **3** under cross polarization condition. And the red curve is the fitting of equation at 225 °C for compound **3**.

(1) Y. Arakawa, S. Nakajima, R. Ishige, M. Uchimura, S. Kang, G. Konishi and J. Watanabe, *J. Mater. Chem.*, 2012,22, 8394

(2) S. Kang, S. Nakajima, Y. Arakawa, G. Konishi and J. Watanabe, *J. Mater. Chem. C*, 2013, 1, 4222.