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Supplementary Information:

Mechanochromic luminescent liquid crystals based on a bianthryl moiety

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Synthesis:

10,10'-Dibromo-9,9'-biantryl,

2-[2-(2-{2-[4-(4-*trans*-Pentylcyclohexyl)phenoxy]ethoxy}ethoxy)ethoxy]ethanol tosylate, ,

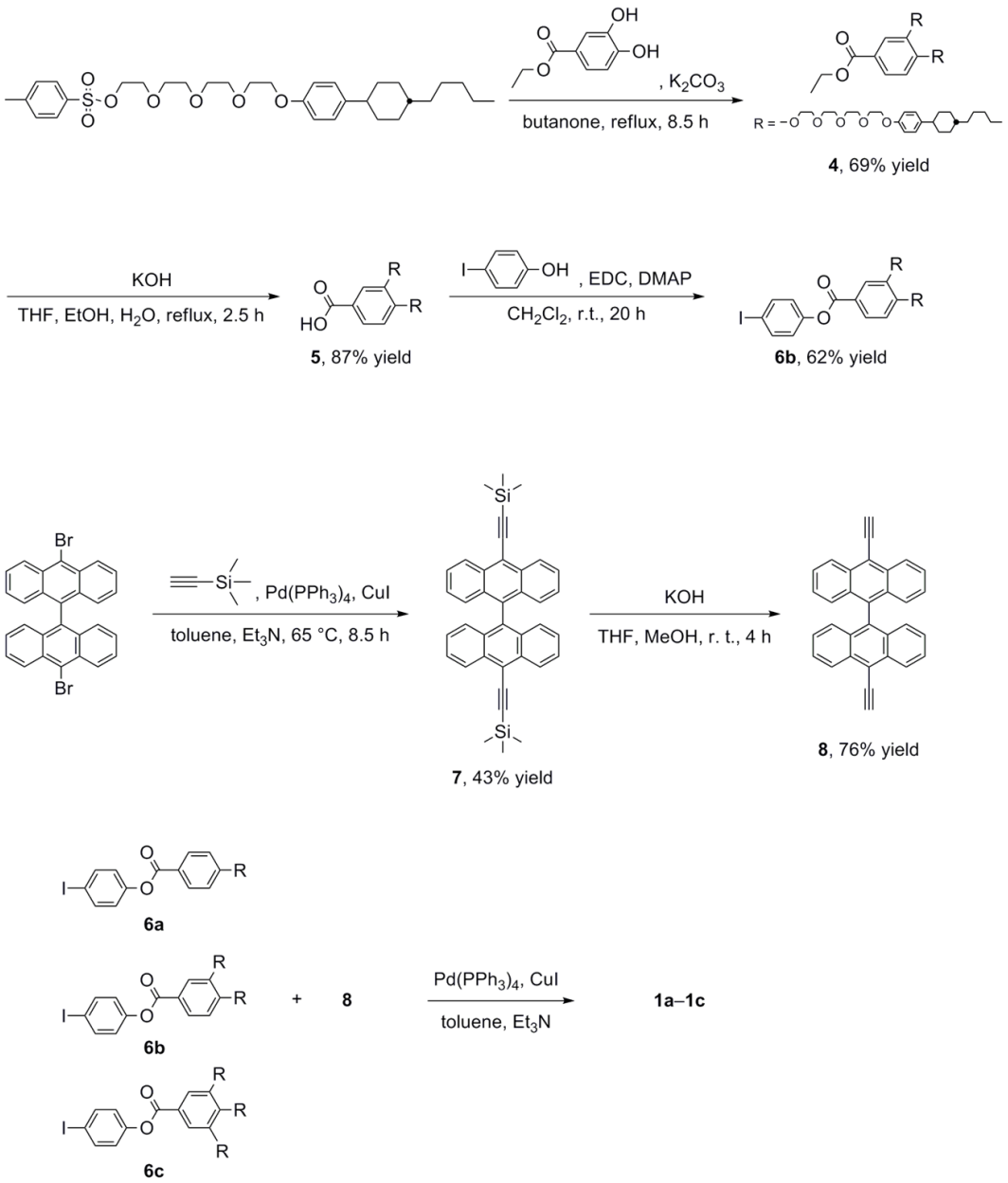
4-Iodophenyl

4-{2-[2-(2-{2-[4-(4-*trans*-pentylcyclohexyl)phenoxy]ethoxy}ethoxy)ethoxy]ethoxy}benzoate (**6a**)

and 4-Iodophenyl

3,4,5-Tris{2-[2-(2-{2-[4-(4-*trans*-pentylcyclohexyl)phenoxy]ethoxy}ethoxy)ethoxy]ethoxy}benzoat

e (**6c**) were obtained according to the reported procedures.[S1,S2]



Scheme S1. The synthesis of compounds **1a**–**c**.

Ethyl 3,4-Bis{2-[2-(2-{2-[4-(4-*trans*-pentylcyclohexyl)phenoxy]ethoxy}ethoxy)ethoxy]ethoxy}benzoate (4). A mixture of 2-[2-(2-{2-[4-(4-*trans*-pentylcyclohexyl)phenoxy]ethoxy}ethoxy)ethoxy]ethanol tosylate (2.00 g, 3.47 mmol), 3,4-dihydroxy benzoic acid ethyl ester (288 mg, 1.58 mmol), and K_2CO_3 (1.09 g, 7.88 mmol) in butanone (20 mL) was stirred for 8.5 h under reflux. After removing the solvent, the residue was poured into an ethyl acetate/water mixture. The organic layer was washed with brine and dried over anhydrous $MgSO_4$. After filtration and evaporation, the residue was purified by silica gel flush column chromatography (eluent: hexane/ethyl acetate = 1:1), and dried under vacuum to afford **4** as a white waxy solid (1.08 g, 69%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65 (dd, *J* = 2.0, 8.4 Hz, 1H), 7.57 (d, *J* = 2.0 Hz, 1H), 7.10 (d, *J* = 8.8 Hz, 4H), 6.89 (d, *J* = 8.8 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 4H), 4.34 (q, *J* = 7.6 Hz, 2H), 4.19 (t, *J* = 5.2 Hz, 4H), 4.09 (t, *J* = 4.8 Hz, 4H), 3.89–3.86 (m, 4H), 3.83 (t, *J* = 5.2 Hz, 4H), 3.75–3.66 (m, 16H), 2.43–2.35 (m, 2H), 1.86–1.83 (m, 8H), 1.43–1.19 (m, 25H), 1.06–0.98 (m, 4H), 0.89 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.27, 156.78, 152.76, 148.16, 140.28, 140.26, 127.55, 123.85, 123.26, 114.85, 114.29, 112.54, 70.87, 70.84, 70.74, 70.67, 70.61, 69.74, 69.57, 69.46, 68.74, 68.49, 67.32, 60.74, 43.66, 37.36, 37.25, 34.52, 33.57, 32.18, 26.63, 22.69, 14.37, 14.10. MS (MALDI-TOF): *m*/*z* 1029.61 $[M + K]^+$; calcd. 1029.61. Anal. calcd for $C_{59}H_{90}O_{12}$: C, 71.48; H, 9.15%; found: C, 71.70; H, 9.40%.

3,4-Bis{2-[2-(2-{2-[4-(4-*trans*-pentylcyclohexyl)phenoxy]ethoxy}ethoxy)ethoxy]ethoxy}benzoic acid (5). A mixture of **4** (1.08 g, 1.09 mmol) and KOH (183 mg, 3.27 mmol) in THF (10 mL), ethanol (20 mL) and water (1 mL) was stirred for 2.5 h under reflux. After removing the solvent, the residue was poured into a mixture of 5% hydrochloric acid/ethyl acetate. The organic phase was washed with water and brine, dried over anhydrous $MgSO_4$, filtered and evaporated to afford **5** as white waxy solid (909 mg, 87%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71 (dd, *J* = 8.8 Hz, 2.0 Hz, 1H), 7.62 (d, *J* = 1.6 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 4H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 4H), 4.22–4.18 (m, 4H), 4.09 (t, *J* = 5.2 Hz, 4H), 3.90–3.86 (m, 4H), 3.82 (t, *J* = 4.8 Hz, 4H), 3.75–3.66 (m, 16H), 2.39 (t, *J* = 12.4 Hz, 2H), 1.85–1.83 (m, 8H), 1.44–1.18 (m, 22H), 1.06–0.98 (m, 4H), 0.89 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.08, 156.78, 153.52, 148.24, 140.28, 140.25, 127.54, 124.79, 122.02, 115.24, 114.31, 112.50, 70.87, 70.84, 70.74, 70.67, 70.61, 69.75, 69.59, 69.42, 68.80, 68.50, 67.34, 43.66, 37.35, 37.26, 34.52, 33.60, 32.18, 26.62, 22.67, 14.08. MS (MALDI-TOF): *m*/*z* 985.45 $[M + Na]^+$; calcd. 985.60. Anal. calcd for $C_{57}H_{86}O_{12}$: C, 71.07; H, 9.00%; found: C, 71.13; H, 9.27%.

4-Iodophenyl 3,4-Bis{2-[2-(2-{2-[4-(4-*trans*-pentylcyclohexyl)phenoxy]ethoxy}ethoxy)ethoxy]ethoxy}benzoate (6b). A mixture of **5** (909 mg, 0.944 mmol), 4-iodophenol (228 mg, 1.04 mmol), EDC (362 mg, 1.89 mmol), and DMAP (23.1 mg, 0.189 mmol) in dry CH_2Cl_2 (20 mL) was stirred for 20 h at room temperature. The reaction mixture was washed with 5% hydrochloric acid, a saturated $NaHCO_3$ aqueous solution and brine. The organic phase was dried over anhydrous $MgSO_4$, filtered, and evaporated. The residue was purified by flush column chromatography on silica gel (eluent: hexane/ethyl acetate = 1:1) to afford **6b** as a white waxy solid (677 mg, 62%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.79 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 7.72 (d, *J* = 8.8 Hz, 2H), 7.68 (d, *J* = 1.2 Hz, 1H), 7.09 (d, *J* = 8.8 Hz, 4H), 6.98–6.94 (m, 3H), 6.82 (d, *J* = 8.4 Hz, 4H), 4.24–4.20 (m, 4H), 4.10–4.06 (m, 4H), 3.91–3.87 (m, 4H), 3.84–3.80 (m, 4H), 3.75–3.66 (m, 16H), 2.38 (t, *J* = 12.4 Hz, 2H), 1.85–1.83 (m, 8H), 1.44–1.17 (m, 22H), 1.07–0.97 (m, 4H), 0.89 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.38, 156.81, 153.72, 150.91, 148.46, 140.30, 140.28, 138.42, 127.55, 124.83, 123.97, 121.70, 115.43, 114.35, 112.70, 89.66, 70.90, 70.86, 70.75, 70.69, 70.62, 69.77, 69.75, 69.59, 69.45, 68.95, 68.62, 67.38, 43.67, 37.35, 37.28, 34.53, 33.61, 32.18, 26.62, 22.66, 14.08. MS (MALDI-TOF): *m*/*z* 1203.14 $[M + K]^+$; calcd. 1203.50. Anal. calcd for $C_{63}H_{89}IO_{12}$: C, 64.94; H, 7.70%; found: C, 64.76; H, 7.96%.

10,10'-Bis(trimethylsilylethynyl)-9,9'-biantryl (7). $Pd(PPh_3)_4$ (22.5 mg, 0.0195 mmol) and CuI (3.71 mg, 0.0195 mmol) were added to a mixture of 10,10'-dibromo-9,9'-biantryl (100 mg, 0.195 mmol), trimethylsilylacetylene (95.9 mg, 0.976 mmol), dry toluene (21 mL) and Et_3N (7 mL). After stirring for 8.5 h at 65 °C, the mixture was poured into chloroform and the organic phase was washed with 5% hydrochloric acid, a saturated $NaHCO_3$ aqueous solution and brine, then dried over anhydrous $MgSO_4$. After filtration and evaporation, the resulting residue was purified by flash column chromatography on silica gel (eluent: hexane/chloroform = 10:1) to afford **7** as an orange solid (45.8 mg, 43%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.72 (d, *J* = 8.8 Hz, 4H), 7.57–7.53 (m, 4H), 7.18–7.14 (m, 4H), 7.05 (d, *J* = 8.8 Hz, 4H), 0.48 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 134.07, 132.30, 130.75, 126.82, 126.80, 126.39, 125.94, 117.84, 106.81, 101.33, 0.00. MS (MALDI-TOF): *m*/*z* = 546.34 $[M]^+$; calcd. 546.22. Anal. calcd for $C_{38}H_{34}Si_2$: C, 83.46; H, 6.27%; found: C, 83.53; H, 5.99%.

10,10'-diethynyl-9,9'-biantryl (8). Compound **7** (136 mg, 0.248 mmol) was dispersed in a mixture of methanol/THF (4:1 v/v, 25 mL) containing an aqueous solution (1 mL) of KOH (41.7 mg, 0.744 mmol). The mixture was stirred for 4 h at room temperature. After removing the solvent, the residue was poured into a mixture of 5% hydrochloric acid/chloroform. The organic phase was washed with sat. $NaHCO_3$, followed by brine, and was dried over $MgSO_4$, filtered, and evaporated. The residue

was purified by flash column chromatography on silica gel (eluent: hexane/chloroform = 5:1) to afford **8** as a yellow powder (75.6 mg, 76 %). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.75 (d, *J* = 8.8 Hz, 4H), 7.58–7.54 (m, 4H), 7.20–7.16 (m, 4H), 7.08 (d, *J* = 8.8 Hz, 4H), 4.12 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 134.63, 132.90, 131.02, 127.17, 126.93, 126.83, 126.31, 117.18, 88.93, 80.47. MS (MALDI-TOF): *m*/*z* = 402.69 $[M]^+$; calcd. 402.14.

10,10'-Bis[*p*-(4-{2-[2-(2-{2-[4-(4-*trans*-pentylcyclohexyl)phenoxy]ethoxy}ethoxy)ethoxy]ethoxy}phenylcarbonyloxy)phenylethynyl]-9,9'-biantryl (1a). $Pd(PPh_3)_4$ (6.89 mg, 5.96×10^{-3} mmol) and CuI (1.14 mg, 5.96×10^{-3} mmol) were added to a mixture of **6a** (97.7 mg, 0.131 mmol), **8** (24 mg, 0.0596 mmol), dry toluene (5 mL) and Et_3N (1 mL). After stirring for 4 h at 60 °C, the mixture was dissolved in chloroform and the organic phase was washed with a 5% hydrochloric acid, a saturated $NaHCO_3$ aqueous solution and brine, then was dried over anhydrous $MgSO_4$. After filtration and evaporation, the resulting residues were purified by flash column chromatography on silica gel (eluent: hexane/ethyl acetate = 1:1) and GPC (eluent: chloroform) to afford **1a** as a yellow waxy solid (60.5 mg, 62%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.83 (d, *J* = 8.8 Hz, 4H), 8.19 (d, *J* = 8.8 Hz, 4H), 7.90 (d, *J* = 8.8 Hz, 4H), 7.61–7.58 (m, 4H), 7.36 (d, *J* = 8.4 Hz, 4H), 7.23–7.20 (m, 4H), 7.14 (d, *J* = 8.8 Hz, 4H), 7.11 (d, *J* = 8.4 Hz, 4H), 7.03 (d, *J* = 8.8 Hz, 4H), 6.84 (d, *J* = 8.8 Hz, 4H), 4.23 (t, *J* = 4.8 Hz, 4H), 4.11 (t, *J* = 4.8 Hz, 4H), 3.91 (t, *J* = 4.8 Hz, 4H), 3.85 (t, *J* = 5.2 Hz, 4H), 3.77–3.69 (m, 16H), 2.43–2.37 (m, 2H), 1.86–1.84 (m, 8H), 1.45–1.19 (m, 22H), 1.07–0.98 (m, 4H), 0.88 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.63, 163.33, 156.86, 151.28, 140.40, 134.29, 132.90, 132.37, 131.25, 127.61, 127.27, 127.10, 126.67, 126.32, 122.25, 121.70, 121.13, 118.28, 114.54, 114.41, 100.77, 86.53, 70.93, 70.84, 70.71, 69.84, 69.54, 67.75, 67.47, 43.73, 37.39, 37.33, 34.58, 33.65, 32.22, 26.65, 22.71, 14.10. MS (MALDI-TOF): *m*/*z* = 1634.60 $[M]^+$; calcd. 1634.82. Anal. calcd for $C_{108}H_{114}O_{14}$: C, 79.29; H, 7.02%; found: C, 79.09; H, 7.23%.

10,10'-Bis[*p*-(3,4-bis{2-[2-(2-{2-[4-(4-*trans*-pentylcyclohexyl)phenoxy]ethoxy}ethoxy)ethoxy]ethoxy}phenylcarbonyloxy)phenylethynyl]-9,9'-biantryl (1b). This compound was prepared in a similar manner to **1a**, except for the eluent of column chromatography (chloroform/ethyl acetate = 1:3), and was obtained as a yellow waxy solid (68%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.83 (d, *J* = 8.8 Hz, 4H), 7.91–7.86 (m, 6H), 7.75 (d, *J* = 1.2 Hz, 2H), 7.61–7.58 (m, 4H), 7.35 (d, *J* = 8.8 Hz, 4H), 7.24–7.20 (m, 4H), 7.15–7.08 (m, 12H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.85–6.82 (m, 8H), 4.26 (t, *J* = 5.2 Hz, 8H), 4.11–4.08 (m, 8H), 3.94–3.91 (m, 8H), 3.86–3.82 (m, 8H), 3.78–3.69 (m, 32H), 2.43–2.36 (m, 4H), 1.86–1.83 (m, 16H), 1.43–1.18 (m, 44H), 1.06–1.00 (m, 8H), 0.90–0.86 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.63, 156.82, 153.71, 151.22, 148.47, 140.35, 140.31, 134.28, 132.92, 132.35, 131.22, 127.61, 127.27, 127.09, 126.68, 126.33, 124.92, 122.26, 121.82, 121.15, 118.24, 115.35, 114.33, 112.64, 100.73, 86.53, 70.95, 70.92, 70.80, 70.74, 70.68, 69.80, 69.64, 69.48, 68.95,

68.61, 67.38, 43.71, 37.39, 37.29, 34.56, 33.63, 32.21, 26.66, 22.72, 14.13. MS (MALDI-TOF): *m*/*z* = 2497.91 $[M + Na]^+$; calcd. 2498.39. Anal. calcd for $C_{158}H_{194}O_{24}$: C, 76.61; H, 7.89%; found: C, 76.52; H, 7.98%.

10,10'-Bis[*p*-(3,4,5-tris{2-[2-(2-{2-[4-(4-*trans*-pentylcyclohexyl)phenoxy]ethoxy}ethoxy)ethoxy]ethoxy}phenylcarbonyloxy)phenylethynyl]-9,9'-biantryl (1c). This compound was prepared in a similar manner to **1a** and obtained as a yellow waxy solid (34%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.83 (d, *J* = 8.8 Hz, 4H), 7.90 (d, *J* = 8.4 Hz, 4H), 7.62–7.58 (m, 4H), 7.50 (s, 4H), 7.34 (d, *J* = 8.4 Hz, 4H), 7.24–7.20 (m, 4H), 7.14 (d, *J* = 8.8 Hz, 4H), 7.11–7.08 (m, 12H), 6.83 (d, *J* = 8.0 Hz, 12H), 4.29 (t, *J* = 5.2 Hz, 4H), 4.25 (t, *J* = 5.2 Hz, 8H), 4.10 (t, *J* = 4.8 Hz, 12H), 3.90 (t, *J* = 4.8 Hz, 8H), 3.83 (t, *J* = 4.8 Hz, 16H), 3.76–3.66 (m, 48H), 2.42–2.35 (m, 6H), 1.85–1.83 (m, 24H), 1.44–1.18 (m, 66H), 1.06–0.96 (m, 12H), 0.90–0.86 (m, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.50, 156.83, 152.52, 151.11, 143.42, 140.31, 134.31, 132.96, 132.37, 131.22, 127.60, 127.28, 127.09, 126.70, 126.34, 123.89, 122.22, 121.30, 118.21, 114.34, 109.72, 100.67, 86.62, 72.55, 70.86, 70.79, 70.73, 70.68, 70.65, 70.63, 70.59, 69.80, 69.64, 69.01, 67.37, 43.71, 37.40, 37.30, 34.56, 33.64, 32.22, 26.67, 22.72, 14.14. MS (MALDI-TOF): *m*/*z* = 3339.68 $[M + Na]^+$; calcd. 3338.96. Anal. calcd for $C_{208}H_{274}O_{34}$: C, 75.28; H, 8.32%; found: C, 75.10; H, 8.32%.

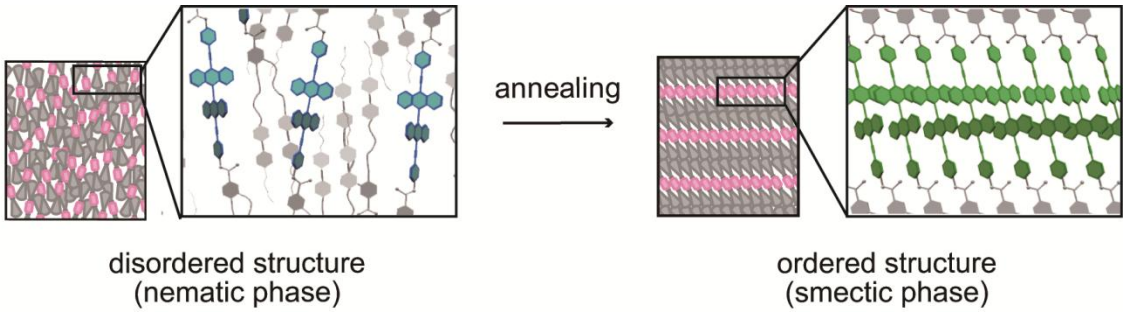


Fig. S1 Schematic illustrations of the self-assembled structures of compound **1b** before (left) and after (right) annealing at 115 °C.

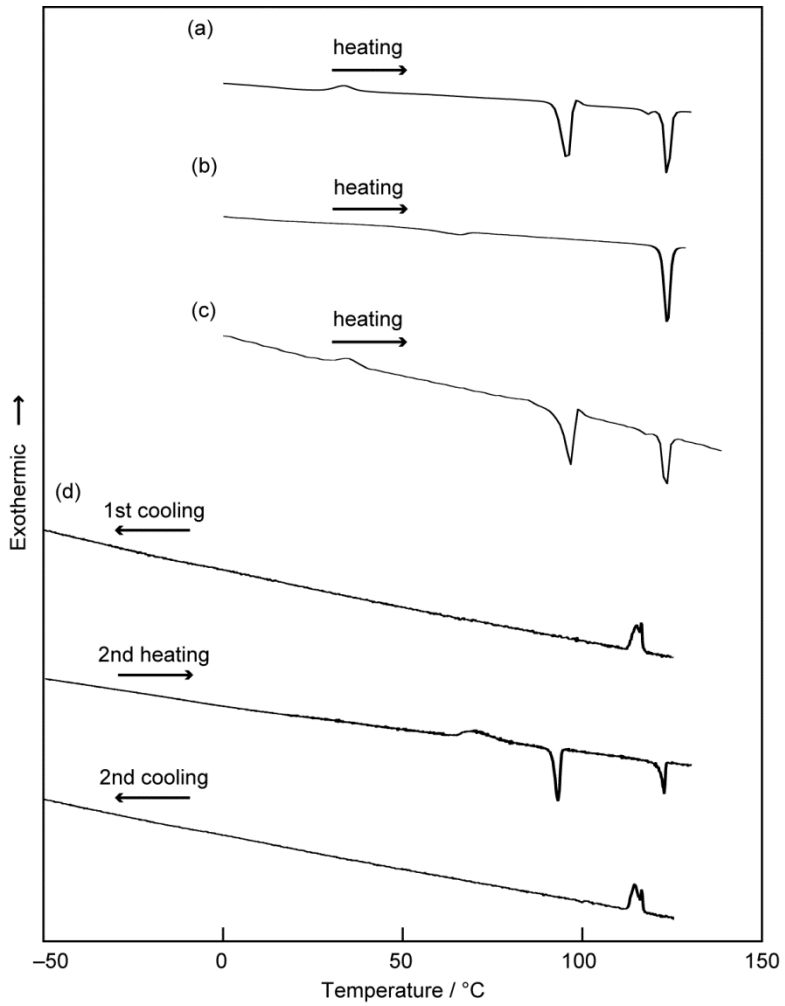


Fig. S2 DSC thermograms of compound **1b**; (a) in state A, (b) in state C and (c) in state D on heating at a scanning rate of 5 K min^{-1} and (d) at a scanning rate of 0.5 K min^{-1}.

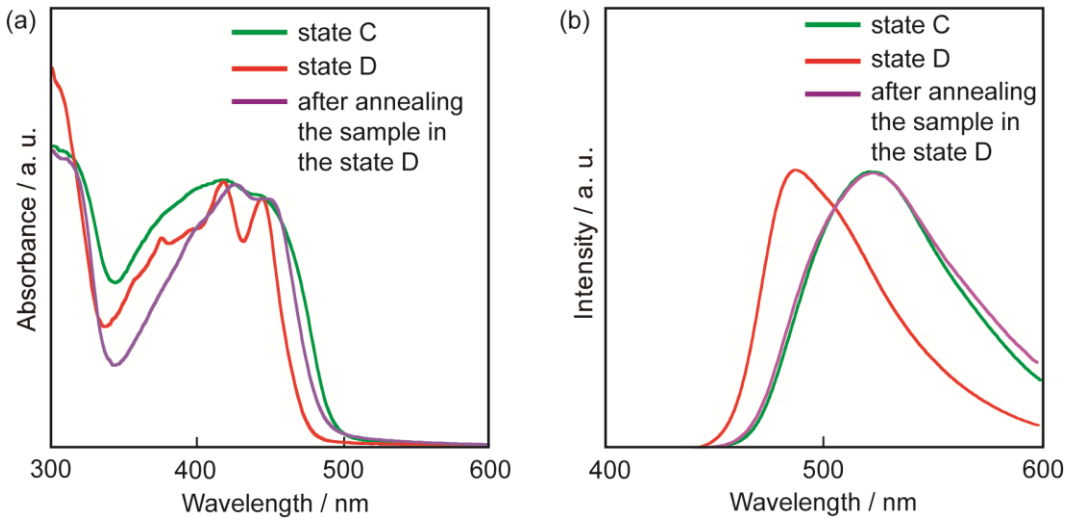


Fig. S3 (a) Absorption and (b) emission spectra of compound **1b** in state C (green), in state D (red) and after annealing the sample in state D at 115 °C (purple). All spectra were taken at room temperature. λ_{ex} = 420 nm.

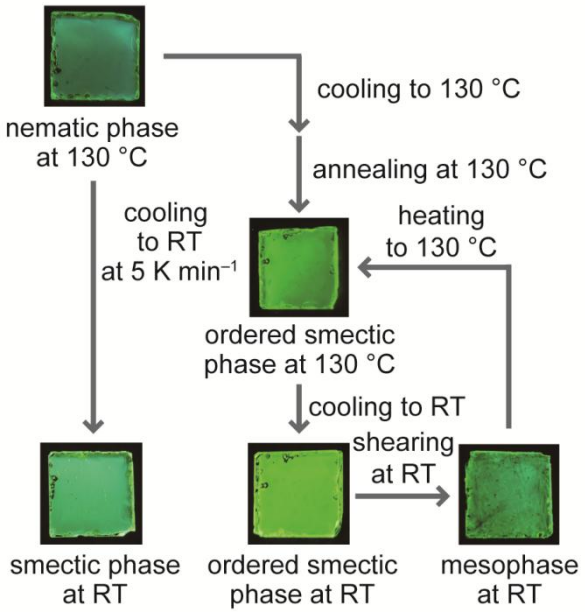


Fig. S4 Photoluminescent images of compound **1a** taken between quartz plates under UV irradiation at 365 nm.

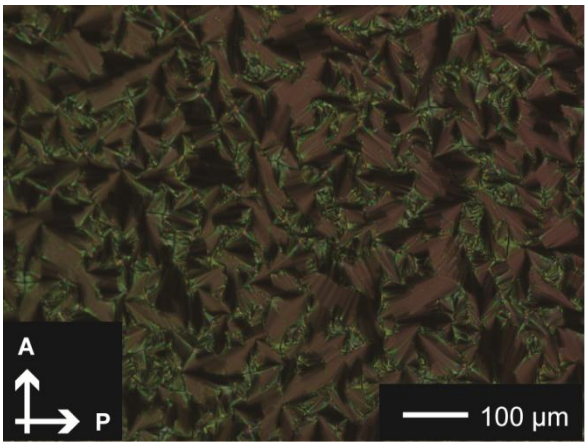


Fig. S5 Polarizing optical micrograph of compound **1b** at 109 °C.

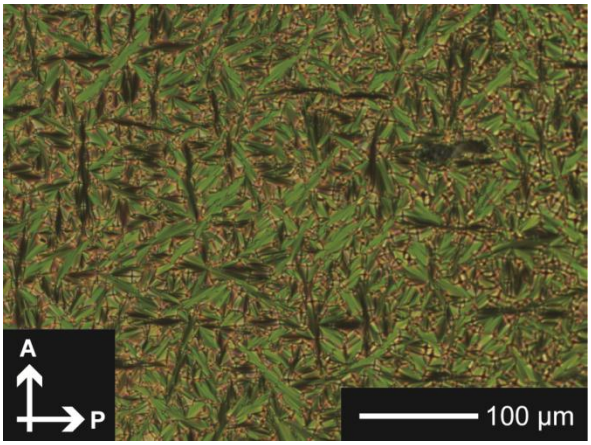


Fig. S6 Polarizing optical micrograph of compound **1c** at 77 °C.

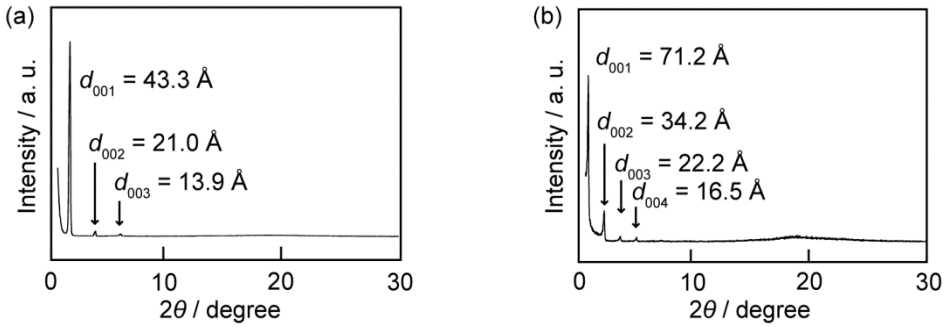


Fig. S7 XRD patterns of compound **1c**; (a) in the smectic A phase at 77 °C and (b) in the monolayer smectic phase at room temperature.

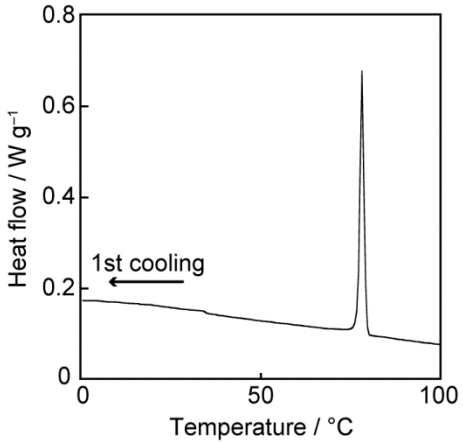


Fig. S8 DSC thermogram of compound **1c** at a scanning rate of 5 K min^{-1}.

Compound **1a** shows no peak in the DSC thermograms and the DSC thermograms of **1c** show the peaks corresponding to the smectic–isotropic phase transitions on both cooling and heating processes (Fig. S9). The thermal decomposition occurs for **1a** because high temperature is kept for a long time.

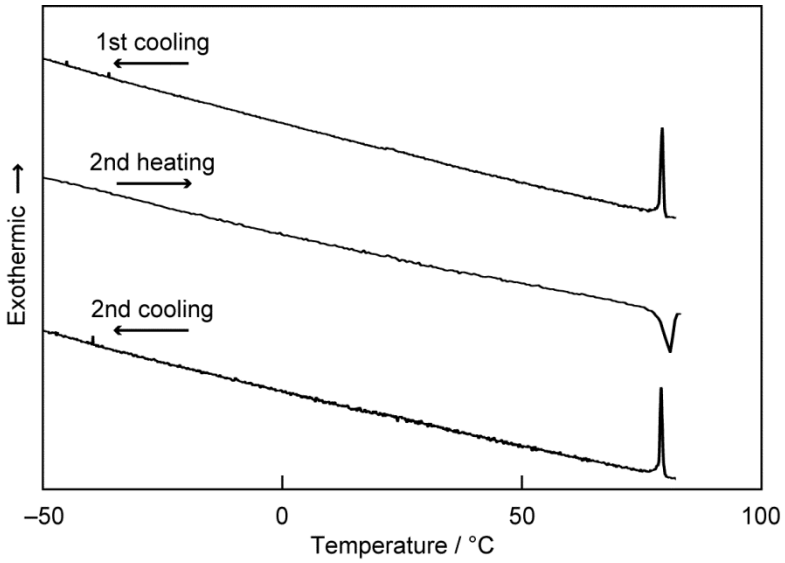


Fig. S9 DSC thermograms of compound **1c** at a scanning rate of 0.5 K min^{-1}.

Supporting references

S1 M. Baumgarten and T. Yüksel, *Phys. Chem. Chem. Phys.*, 1999, **1**, 1699.

S2 S. Yamane, Y. Sagara and T. Kato, *Chem. Commun.*, 2009, 3597.