SUPPLEMENTARY INFORMATION for

A Thermoresponsive Photoluminescent Smectic Liquid Crystal: Change of Photoluminescent Color on the Smectic–Smectic Phase Transition

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General methods and materials

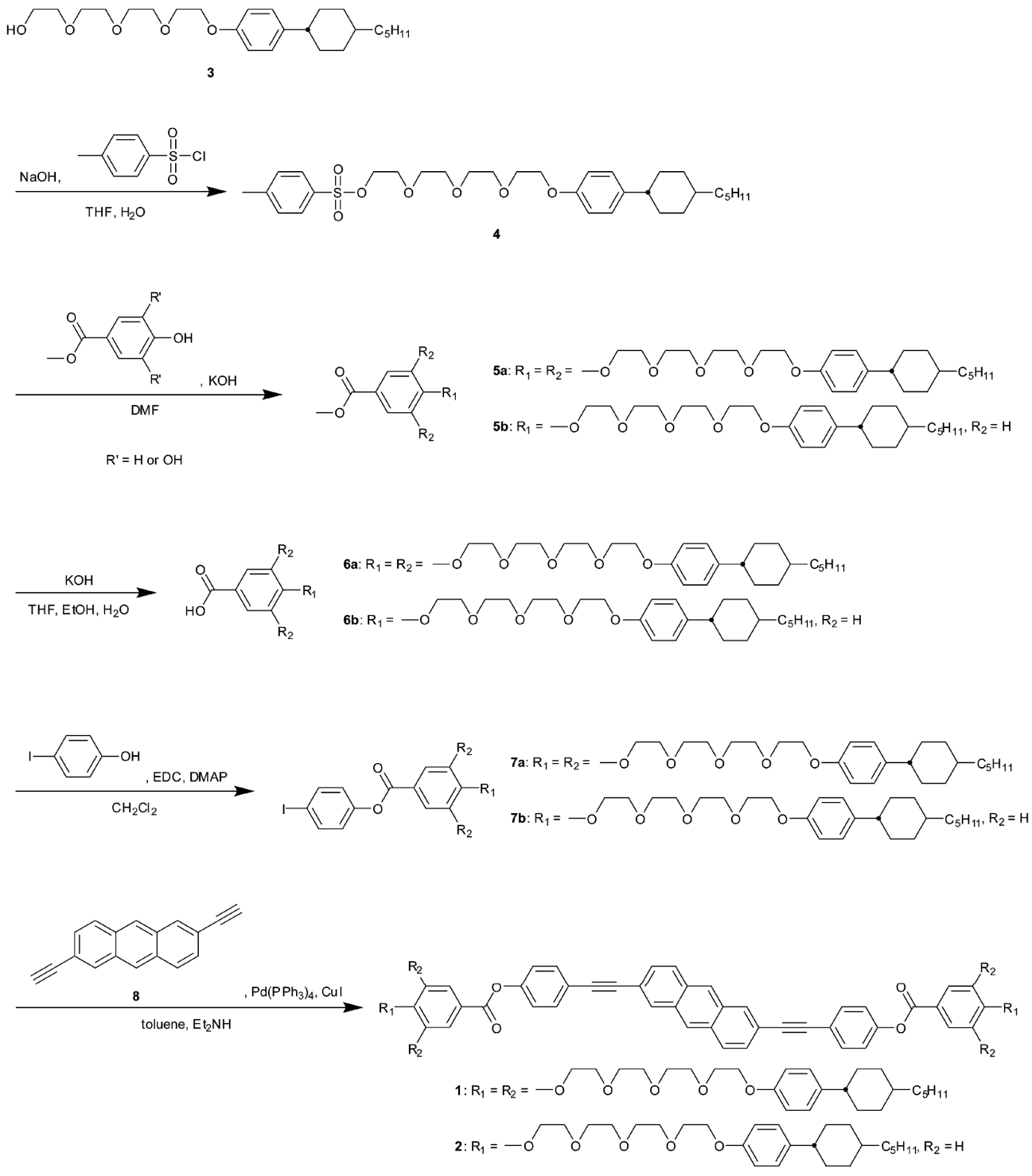
All reagents and solvents were purchased from Tokyo Kasei or Kanto Kagaku, and appropriately purified, if necessary. Unless otherwise noted, all of the reactions were carried out under argon atmosphere in dry solvents. Silica gel column chromatography was carried out with silica gel 60 from Kanto Chemicals (silica gel 60, spherical, 40-50 μm). Recycling preparative GPC was carried out with a Japan Analytical Industry LC-9201 chromatograph. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer in $CDCl_3$ solutions (400 and 100 MHz for ^{1}H NMR and ^{13}C NMR, respectively). Chemical shifts of ^{1}H and ^{13}C NMR were quoted to internal standard Me_4Si ($\delta = 0.00$) and $CDCl_3$ ($\delta = 77.00$) respectively, and expressed by chemical shifts in ppm (δ), multiplicity, coupling constant (Hz), and relative intensity. Mass spectra were recorded on a PerSeptive Biosystems Voyager-DE STR spectrometer. Elemental analyses were carried out with a Yanaco MT-6 CHN autocorder.

Polarized optical micrographs were obtained with an Olympus BX51 equipped with Mettler FP82HT hot stage. Differential scanning calorimetry (DSC) measurements were performed on a NETZCH DSC204 Phoenix calorimeter at a scanning rate of 5 °C min^{-1}. X-ray diffraction measurements were carried out on a Rigaku RINT 2500 diffractometer with a heating stage using Ni-filtered Cu Kα radiation. Absorption spectra were measured with a JASCO V-670 equipped with a Mettler FP82HT hot stage. Emission spectra were recorded on a JASCO FP-6500 spectrofluorometer equipped with a hot stage.

Synthesis of anthracene derivatives 1 and 2

2-[2-(2-{2-[4-(4-*trans*-Pentylcyclohexyl)phenoxy]ethoxy}ethoxy)ethoxy]ethanol (**3**) and 2,6-Diethynylanthracene (**8**) were obtained according to the reported procedures.[1,2] The synthetic routes used to obtain compounds **1** and **2** are shown in Scheme S1.

Scheme S1. Synthetic routes of anthracene derivatives **1** and **2**.



2-[2-(2-{2-[4-(4-*trans*-Pentylcyclohexyl)phenoxy]ethoxy}ethoxy)ethoxy]ethanol tosylate (4). To a stirred solution of **3** (6.03 g, 14.3 mmol) in dry THF (50 mL) was slowly added aqueous solution of NaOH (684 mg, 17.1 mmol in 1 mL H_2O) at 0 °C and the mixture stirred for 1 h at 0 °C. Thereafter, to the mixture was slowly added THF solution of tosyl chloride (3.26 g, 17.1 mmol in 10 mL THF) at 0 °C and the mixture was stirred for 12 h at room temperature. After removing the solvent, the resulting residue was added into 5% hydrochloric acid, and the mixture was extracted with ethyl acetate. The organic phase was washed with a saturated $NaHCO_3$ aqueous solution and brine, and dried over anhydrous $MgSO_4$. After filtration and evaporation, the crude product was purified by flush column chromatography on a silica gel (eluent: hexane/ethyl acetate = 3:2), and dried under vacuum to afford **4** as a viscous colorless liquid (6.23 g, 85%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.89 (t, *J* = 7.2 Hz, 3H), 0.98-1.07 (m, 2H), 1.20-1.44 (m, 11H), 1.84-1.86 (m, 4H), 2.37-2.43 (m, 1H), 2.43 (s, 3H), 3.59-3.70 (m, 10H), 3.83 (t, *J* = 5.2 Hz, 2H), 4.08-4.16 (m, 4H), 6.83 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.08, 21.57, 22.66, 26.60, 32.16, 33.59, 34.52, 37.25, 37.34, 43.66, 67.33, 68.60, 69.19, 69.73, 70.50, 70.60, 70.69, 70.70, 114.30, 127.54, 127.92, 129.75, 132.94, 140.27, 144.72, 156.77. MS (MALDI-TOF): *m*/*z* 599.49 $[M + Na]^+$; calcd. 599.30. Anal. calcd. for $C_{32}H_{48}O_7S$: C, 66.64; H, 8.39%; found: C, 66.43; H, 8.56%.

Methyl 3,4,5-Tris{2-[2-(2-{2-[4-(4-*trans*-pentylcyclohexyl)phenoxy]ethoxy}ethoxy)ethoxy]ethoxy}benzoate (5a). A mixture of **4** (3.00 g, 5.20 mmol), gallic acid methyl ester (274 mg, 1.49 mmol), and K_2CO_3 (1.03 g, 7.43 mmol) in dry DMF (100 mL) was stirred for 10 h at 80 °C under an Ar atmosphere. After cooling to room temperature, the reaction mixture was added into a saturated NH_4Cl aqueous solution, and the product was extracted with ethyl acetate. The organic layer was washed twice with a saturated NH_4Cl aqueous solution and washed with brine, and dried over anhydrous $MgSO_4$. After filtration and evaporation, the residue was purified by flush column chromatography on a silica gel (eluent: ethyl acetate/chloroform = 1:1), and dried under vacuum to afford **5a** as a white waxy solid (1.56 g, 75%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.89 (t, *J* = 6.8 Hz, 9H), 0.98-1.06 (m, 6H), 1.19-1.43 (m, 33H), 1.83-1.86 (m, 12H), 2.36-2.42 (m, 3H), 3.62-3.72 (m, 24H), 3.78-3.86 (m, 12H), 3.87 (s, 3H), 4.07-4.10 (m, 6H), 4.17 (t, *J* = 5.2 Hz, 4H), 4.21 (t, *J* = 5.2 Hz, 2H), 6.81-6.83 (m, 6H), 7.09 (d, *J* = 8.8 Hz, 6H), 7.29 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.11, 22.70, 26.64, 32.20, 33.62, 34.54, 37.28, 37.38, 43.69, 52.15, 67.34, 68.77, 69.57, 69.76, 70.51, 70.56, 70.59, 70.63, 70.67, 70.75, 70.79, 72.39, 108.91, 114.32, 124.91, 127.56, 140.29, 142.48, 152.25, 156.80, 166.56. MS (MALDI-TOF): *m*/*z* 1419.79 $[M + Na]^+$; calcd.

1419.90. Anal. calcd. for $C_{83}H_{128}O_{17}$: C, 71.31; H, 9.23%; found: C, 71.11; H, 9.21%.

Methyl 4-{2-[2-(2-{2-[4-(4-*trans*-Pentylcyclohexyl)phenoxy]ethoxy}ethoxy)ethoxy]ethoxy}benzoate (5b). This compound was prepared in a similar manner to **5a**, except for an eluent of column chromatography (eluent: ethyl acetate/hexane = 2:1), and obtained viscous colorless liquid (99%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.89 (t, *J* = 7.2 Hz, 3H), 0.98-1.06 (m, 2H), 1.19-1.44 (m, 11H), 1.83-1.86 (m, 4H), 2.36-2.42 (m, 1H), 3.67-3.73 (m, 8H), 3.83-3.87 (m, 4H), 3.88 (s, 3H), 4.09 (t, *J* = 5.2 Hz, 2H), 4.16 (t, *J* = 4.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 8.8 Hz, 2H), 7.97 (d, *J* = 9.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.00, 22.57, 26.52, 32.08, 33.49, 34.42, 37.15, 37.25, 43.55, 51.66, 67.24, 67.40, 69.36, 69.64, 70.52, 70.64, 70.70, 114.02, 114.20, 122.52, 127.43, 131.38, 140.13, 156.69, 162.40, 166.60. MS (MALDI-TOF): *m*/z 579.30 $[M + Na]^+$; calcd. 579.33. Anal. calcd. for $C_{33}H_{48}O_7$: C, 71.19; H, 8.69%; found: C, 70.89; H, 8.93%.

3,4,5-Tris{2-[2-(2-{2-[4-(4-*trans*-pentylcyclohexyl)phenoxy]ethoxy}ethoxy)ethoxy]ethoxy}benzoic acid (6a). A mixture of **5a** (2.85 g, 2.04 mmol) and KOH (343 mg, 6.12 mmol) in THF (50 mL), ethanol (100 mL) and water (1 mL) was stirred for 6 h under a refluxed condition. After removing the solvent, the residue was poured into a mixture of 5% hydrochloric acid/chloroform. The organic phase was washed with a saturated $NaHCO_3$ aqueous solution and brine, and dried over anhydrous $MgSO_4$, filtration and evaporation to afford **6a** as white waxy solid (2.35 g, 84%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.89 (t, *J* = 7.2 Hz, 9H), 0.98-1.06 (m, 6H), 1.19-1.43 (m, 33H), 1.83-1.85 (m, 12H), 2.36-2.42 (m, 3H), 3.63-3.72 (m, 24H), 3.78-3.86 (m, 12H), 4.07-4.11 (m, 6H), 4.19 (t, *J* = 5.2 Hz, 4H), 4.23 (t, *J* = 4.8 Hz, 2H), 6.81-6.84 (m, 6H), 7.09 (d, *J* = 8.4 Hz, 6H), 7.35 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.08, 22.67, 26.62, 32.18, 33.60, 34.52, 37.27, 37.36, 43.67, 67.35, 68.83, 69.60, 69.74, 70.51, 70.55, 70.57, 70.61, 70.66, 70.74, 70.78, 72.43, 109.52, 114.33, 124.07, 127.54, 140.26, 143.16, 152.27, 156.78, 170.40. MS (MALDI-TOF): *m*/z 1405.95 $[M + Na]^+$; calcd. 1405.89. Anal. calcd. for $C_{82}H_{126}O_{17}$: C, 71.17; H, 9.18%; found: C, 70.97; H, 9.32%.

4-{2-[2-(2-{2-[4-(4-*trans*-Pentylcyclohexyl)phenoxy]ethoxy}ethoxy)ethoxy]ethoxy}benzoic acid (6b). This compound was prepared in a similar manner to **6a**, except for an eluent of column chromatography (eluent: chloroform/methanol = 20:1), and obtained white waxy solid (76%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.89 (t, *J* = 7.2 Hz, 3H), 0.97-1.06 (m, 2H), 1.18-1.44 (m, 11H), 1.83-1.86 (m, 4H), 2.36-2.42 (m, 1H), 3.68-3.74 (m, 8H),

3.84 (t, *J* = 5.2 Hz, 2H), 3.88 (t, *J* = 4.8 Hz, 2H), 4.10 (t, *J* = 4.8 Hz, 2H), 4.18 (t, *J* = 4.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 8.8 Hz, 2H), 8.03 (d, *J* = 9.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.05, 22.62, 26.57, 32.13, 33.53, 34.46, 37.20, 37.30, 43.59, 67.28, 67.49, 69.38, 69.69, 70.56, 70.67, 70.75, 114.17, 114.25, 121.79, 127.49, 132.16, 140.21, 156.71, 163.10, 171.46. MS (MALDI-TOF): *m*/*z* 565.36 $[M + Na]^+$; calcd. 565.31. Anal. calcd. for $C_{32}H_{46}O_7$: C, 70.82; H, 8.54%; found: C, 70.61; H, 8.67%.

4-Iodophenyl

3,4,5-Tris{2-[2-(2-{2-[4-(4-*trans*-pentylcyclohexyl)phenoxy]ethoxy}ethoxy)ethoxy]ethoxy}benzoate (7a). A mixture of **6a** (1.20 g, 0.867 mmol), 4-iodophenol (190 mg, 0.867 mmol), EDC (332 mg, 1.73 mmol), and DMAP (21.2 mg, 0.173 mmol) in dry CH_2Cl_2 (100 mL) was stirred for 12 h at room temperature. The reaction mixture was washed with a saturated $NaHCO_3$ aqueous solution, water and brine. The organic phase was dried over anhydrous $MgSO_4$ and filtered, evaporated. The residue was purified by flush column chromatography on a silica gel (eluent: ethyl acetate/chloroform = 1:1) to afford **7a** as a white waxy solid (984 mg, 72%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.89 (t, *J* = 7.2 Hz, 9H), 0.97-1.06 (m, 6H), 1.19-1.44 (m, 33H), 1.83-1.86 (m, 12H), 2.36-2.42 (m, 3H), 3.65-3.72 (m, 24H), 3.80-3.83 (m, 8H), 3.86 (t, *J* = 4.8 Hz, 4H), 4.08 (t, *J* = 4.8 Hz, 6H), 4.20 (t, *J* = 4.8 Hz, 4H), 4.26 (t, *J* = 5.2 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 6H), 6.96 (d, *J* = 8.8 Hz, 2H), 7.09 (d, *J* = 8.8 Hz, 6H), 7.42 (s, 2H), 7.72 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.11, 22.70, 26.64, 32.20, 33.61, 34.54, 37.28, 37.37, 43.68, 67.34, 68.95, 69.57, 69.76, 70.54, 70.57, 70.60, 70.63, 70.67, 70.74, 70.80, 72.49, 89.88, 109.64, 114.31, 123.71, 123.94, 127.56, 138.49, 140.29, 143.39, 150.78, 152.44, 156.79, 164.31. MS (MALDI-TOF): *m*/*z* 1608.07 $[M + Na]^+$; calcd. 1607.82. Anal. calcd. for $C_{88}H_{129}IO_{17}$: C, 66.65; H, 8.20%; found: C, 66.63; H, 8.40%.

4-Iodophenyl 4-{2-[2-(2-{2-[4-(4-*trans*-Pentylcyclohexyl)phenoxy]ethoxy}ethoxy)ethoxy]ethoxy}benzoate (7b). This compound was prepared in a similar manner to **7a**, except for an eluent of column chromatography (eluent: ethyl acetate/hexane = 1:2), and obtained white waxy solid (82%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.89 (t, *J* = 7.2 Hz, 3H), 0.97-1.06 (m, 2H), 1.17-1.44 (m, 11H), 1.83-1.85 (m, 4H), 2.36-2.42 (m, 1H), 3.67-3.76 (m, 8H), 3.84 (t, *J* = 5.2 Hz, 2H), 3.89 (t, *J* = 4.8 Hz, 2H), 4.10 (t, *J* = 4.8 Hz, 2H), 4.20 (t, *J* = 5.2 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 6.97-6.99 (m, 4H), 7.10 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.8 Hz, 2H), 8.11 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.10, 22.68, 26.62, 32.17, 33.58, 34.51, 37.25, 37.34, 43.66, 67.34, 67.64, 69.44, 69.75, 70.63, 70.75, 70.84, 89.67, 114.30, 114.41, 121.44, 123.99, 127.56, 132.26, 138.40, 140.31, 150.86, 156.76,

163.23, 164.44. MS (MALDI-TOF): *m*/*z* 767.41 $[M + Na]^+$; calcd. 767.24. Anal. calcd. for $C_{38}H_{49}O_7$: C, 61.29; H, 6.63%; found: C, 61.10; H, 6.76%.

2,6-Bis[*p*-(3,4,5-tris{2-[2-(2-{2-[4-(4-*trans*-pentylcyclohexyl)phenoxy]ethoxy}ethoxy)ethoxy]ethoxy}phenylcarbonyloxy)phenylethynyl]anthracene (1). To a mixture of **7a** (101 mg, 0.0637 mmol), **8** (7.20 mg, 0.0318 mmol), dry toluene (35 mL), freshly distilled Et_2NH (8 mL) was added $Pd(PPh_3)_4$ (3.67 mg, 0.00318 mmol), CuI (0.606 mg, 0.00318 mmol). After stirring for 12 h at 60 °C, toluene and Et_2NH were removed with a rotary evaporator. The residue was dissolved in chloroform and this organic phase was washed with a 5% hydrochloric acid, a saturated $NaHCO_3$ aqueous solution and brine, and dried over anhydrous $MgSO_4$. After filtration and evaporation, the resulting residues were purified by flush column chromatography on a silica gel (eluent: chloroform/methanol = 20:1) and GPC (eluent: chloroform) to afford **1** as a yellow waxy solid (14.3 mg, 14%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.87-0.90 (m, 18H), 0.96-1.06 (m, 12H), 1.20-1.43 (m, 66H), 1.82-1.84 (m, 24H), 2.35-2.41 (m, 6H), 3.64-3.74 (m, 44H), 3.81-3.83 (m, 16H), 3.88 (t, *J* = 5.2 Hz, 8H), 4.07-4.10 (m, 16H), 4.22 (t, *J* = 4.8 Hz, 8H), 4.27 (t, *J* = 4.8 Hz, 4H), 6.82 (d, *J* = 8.4 Hz, 12H), 7.08-7.11 (m, 12H), 7.23 (d, *J* = 8.8 Hz, 4H), 7.46 (s, 4H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 4H), 7.99 (d, *J* = 8.8 Hz, 2H), 8.23 (s, 2H), 8.38 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.11, 22.70, 26.64, 32.20, 33.60, 34.53, 37.27, 37.37, 43.68, 67.34, 68.97, 69.60, 69.77, 70.55, 70.61, 70.64, 70.69, 70.75, 70.82, 72.50, 89.93, 90.13, 109.68, 114.31, 120.36, 120.90, 121.97, 123.85, 126.33, 127.56, 127.99, 128.40, 131.10, 131.56, 131.85, 132.89, 140.28, 143.37, 150.88, 152.46, 156.80, 164.39. MS (MALDI-TOF): *m*/*z* 3162.51 $[M + Na]^+$; calcd. 3162.90. Anal. calcd. for $C_{194}H_{266}O_{34}$: C, 74.16; H, 8.53%; found: C, 73.97; H, 8.72%.

2,6-Bis[*p*-(4-{2-[2-(2-{2-[4-(4-*trans*-pentylcyclohexyl)phenoxy]ethoxy}ethoxy)ethoxy]ethoxy}phenylcarbonyloxy)phenylethynyl]anthracene (2). This compound was prepared in a similar manner to **1**, except for an eluent of column chromatography (eluent: chloroform/methanol = 40:1), and obtained yellow waxy solid (62%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.89 (t, *J* = 6.8 Hz, 6H), 0.98-1.06 (m, 4H), 1.19-1.44 (m, 22H), 1.83-1.86 (m, 8H), 2.36-2.42 (m, 2H), 3.69-3.76 (m, 16H), 3.85 (t, *J* = 4.8 Hz, 4H), 3.91 (t, *J* = 4.8 Hz, 4H), 4.11 (t, *J* = 5.2 Hz, 4H), 4.21 (t, *J* = 4.8 Hz, 4H), 6.84 (d, *J* = 8.8 Hz, 4H), 7.00 (d, *J* = 9.2 Hz, 4H), 7.11 (d, *J* = 8.8 Hz, 4H), 7.25 (d, *J* = 8.4 Hz, 4H), 7.55-7.57 (m, 2H), 7.65 (d, *J* = 8.4 Hz, 4H), 7.99 (d, *J* = 9.2 Hz, 2H), 8.15 (d, *J* = 8.8 Hz, 4H), 8.23 (s, 2H), 8.38 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.11, 22.70, 26.64, 32.20, 33.61, 34.54, 37.28, 37.37, 43.69,

67.38, 67.67, 69.49, 69.79, 70.66, 70.78, 70.88, 90.01, 114.34, 114.46, 120.38, 120.71, 121.63, 122.00, 126.31, 127.59, 127.99, 128.39, 131.08, 131.54, 131.81, 132.30, 132.85, 140.36, 151.01, 156.80, 163.25, 164.55. MS (MALDI-TOF): *m*/*z* 1459.91 $[M + H]^+$; calcd. 1459.77. Anal. calcd. for $C_{94}H_{106}O_{14}$: C, 77.34; H, 7.32%; found: C, 77.06; H, 7.38%.

Thermoanalysis for 1

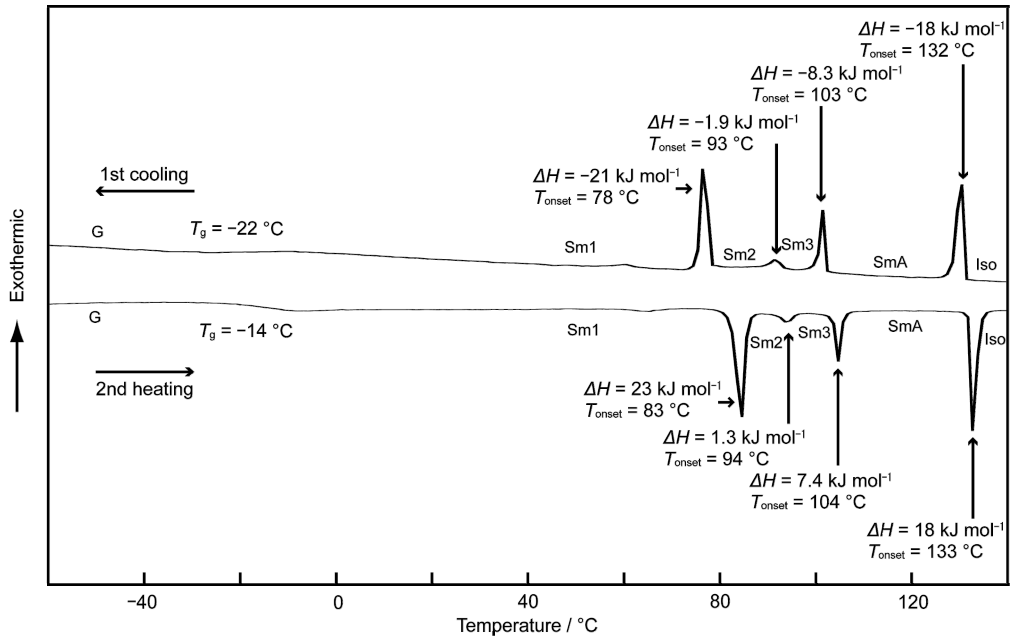


Fig. S1 DSC thermograms of **1** at a scanning rate of 5 °C min^{-1}.

POM observation for 1

In the SmA phase, focal conic textures are observed on cooling from the isotropic phase (Fig. S2a). The focal conic textures change slightly on the SmA–Sm3 and Sm3–Sm2 phase transitions on cooling (Fig. S2b and c). Homeotropic alignments were achieved for compound **1** in both the Sm2 and Sm3 phases by randomly shearing processes (Fig. S2e and f). In contrast, compound **1** in the SmA phase does not show any homeotropic alignments between glass substrates.

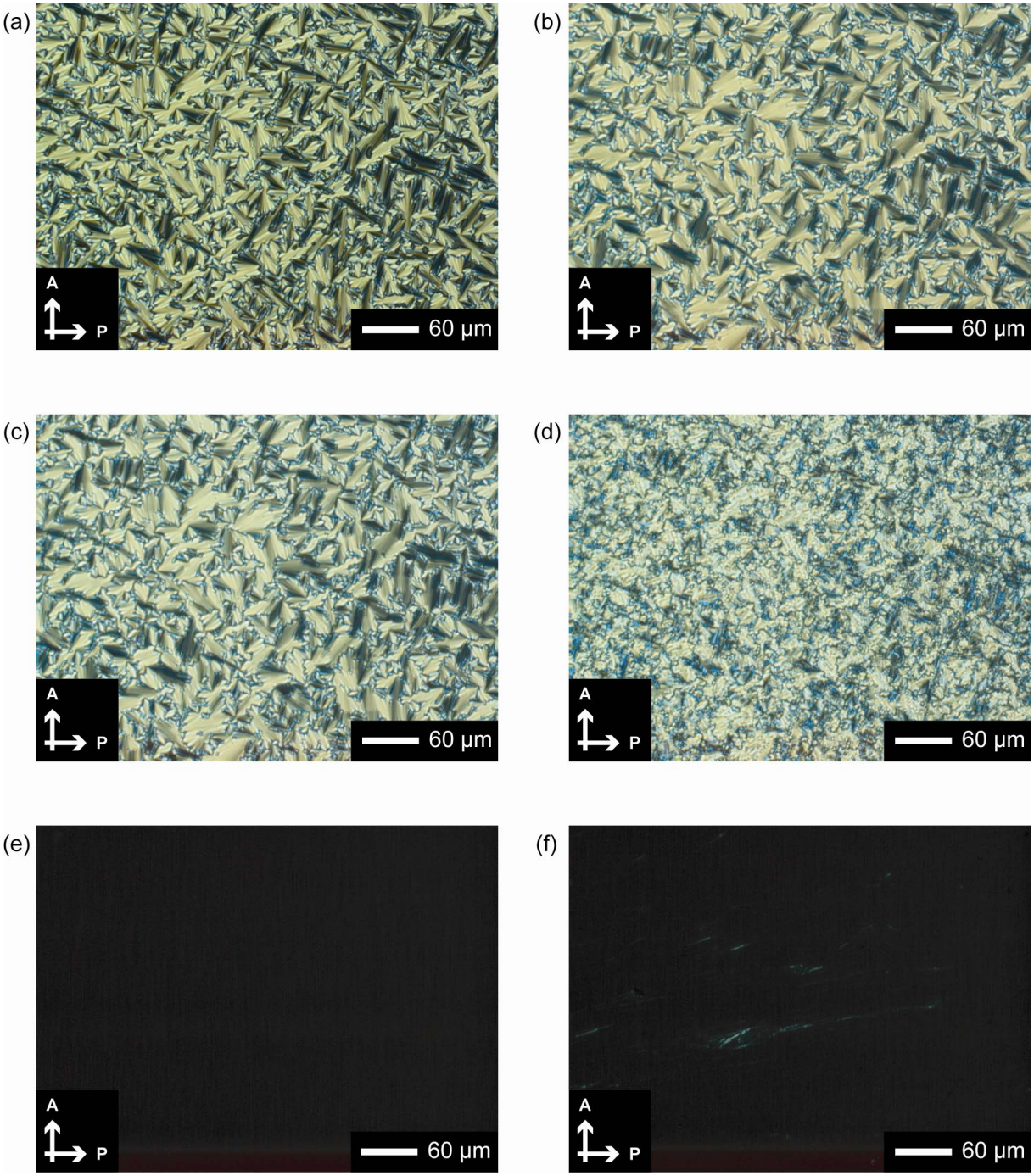


Fig. S2 Polarizing optical microscopic images of **1**; (a) in the SmA phase at 120 °C on cooling, (b) in the Sm3 phase at 98 °C on cooling, (c) in the Sm2 phase at 88 °C on cooling, (d) in the Sm1 phase at 70 °C on cooling, (e) in the Sm3 phase at 98°C after random shearing processes, and (f) in the Sm2 phase at 88 °C after randomly shearing processes. All samples are sandwiched between glass substrates. Directions of A: analyzer; P: polarizer.

X-ray diffraction pattern of 1 in the Sm1 phase

The XRD pattern of **1** in the Sm1 phase shows one diffraction at 4.3 Å in addition to some diffractions in the small angle region (Fig. S3). As for the Sm2 and Sm3 phases, no peaks observed in the small angle region (Fig. 4a, b). These results indicate that the Sm1 phase is a highly-ordered smectic phase compared to the Sm2 and Sm3 phases.

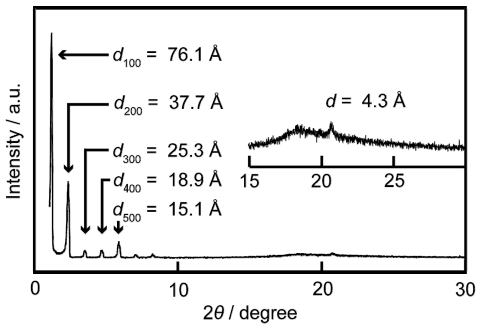


Fig. S3 X-ray diffraction pattern of **1** in the Sm1 phase at 70 °C.

Spectral analysis for 1

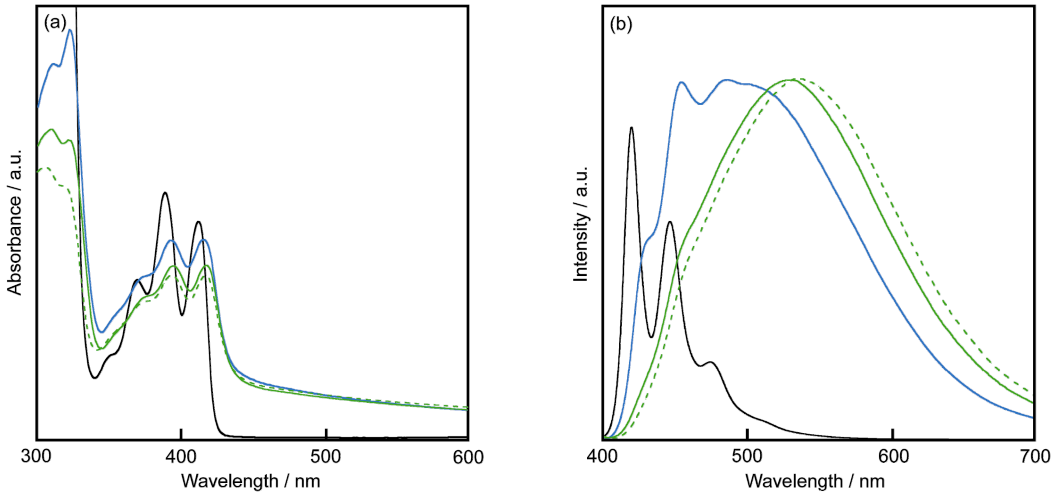


Fig. S4 Absorption spectra (a) and emission spectra (b) of **1** in the Sm2 phase at 88 °C (green dotted line), in the Sm3 phase at 98 °C (green solid line), in the SmA phase at 120 °C (blue line), and a chloroform solution (1.0×10^{-5} M) (black line).

Molecular modeling of 1

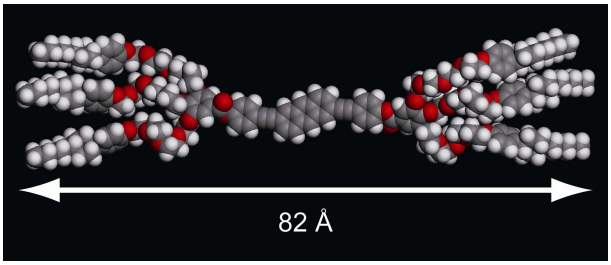


Fig. S5 Molecular model of **1** in the extended form.

Thermoanalysis for 2

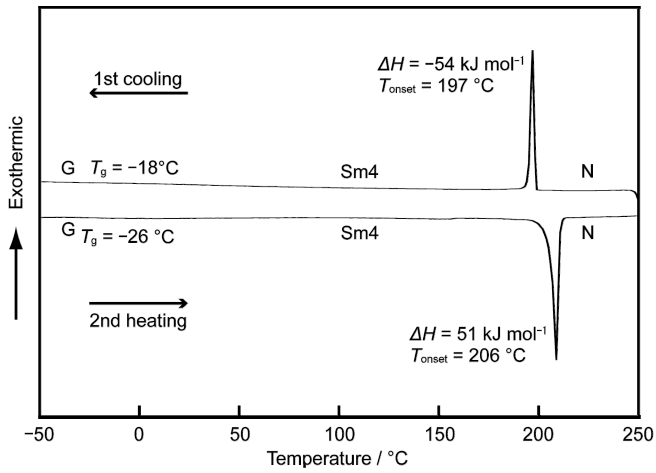


Fig. S6 DSC thermograms of **2** at a scanning rate of 5 °C min^{-1}.

POM observation for 2

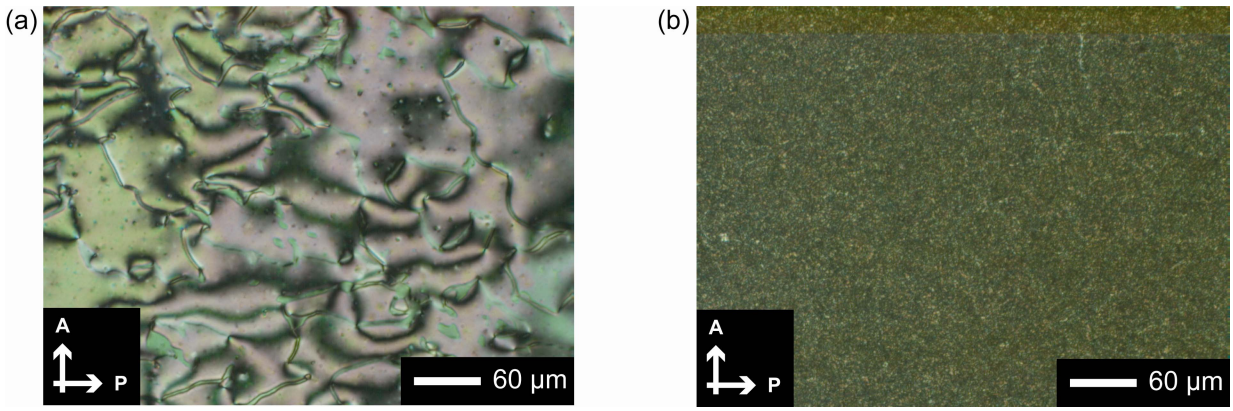


Fig. S7 Polarized optical photomicrographs of **2** in the N phase at 230 °C on heating (a) and Sm4 phase at 180 °C on cooling from 230 °C (b).

Reference

1 Y. Iinuma, K. Kishimoto, Y. Sagara, M. Yoshio, T. Mukai, I. Kobayashi, H. Ohno and T. Kato, *Macromolecules*, 2007, **40**, 4874–4878.

2 Y. Sagara, S. Yamane, T. Mutai, K. Araki and T. Kato, *Adv. Funct. Mater.*, in press.