

Supporting Information

**Linearly polarized electroluminescence device in which the polarized plane can be rotated electrically using a chiral liquid crystalline semiconductor**

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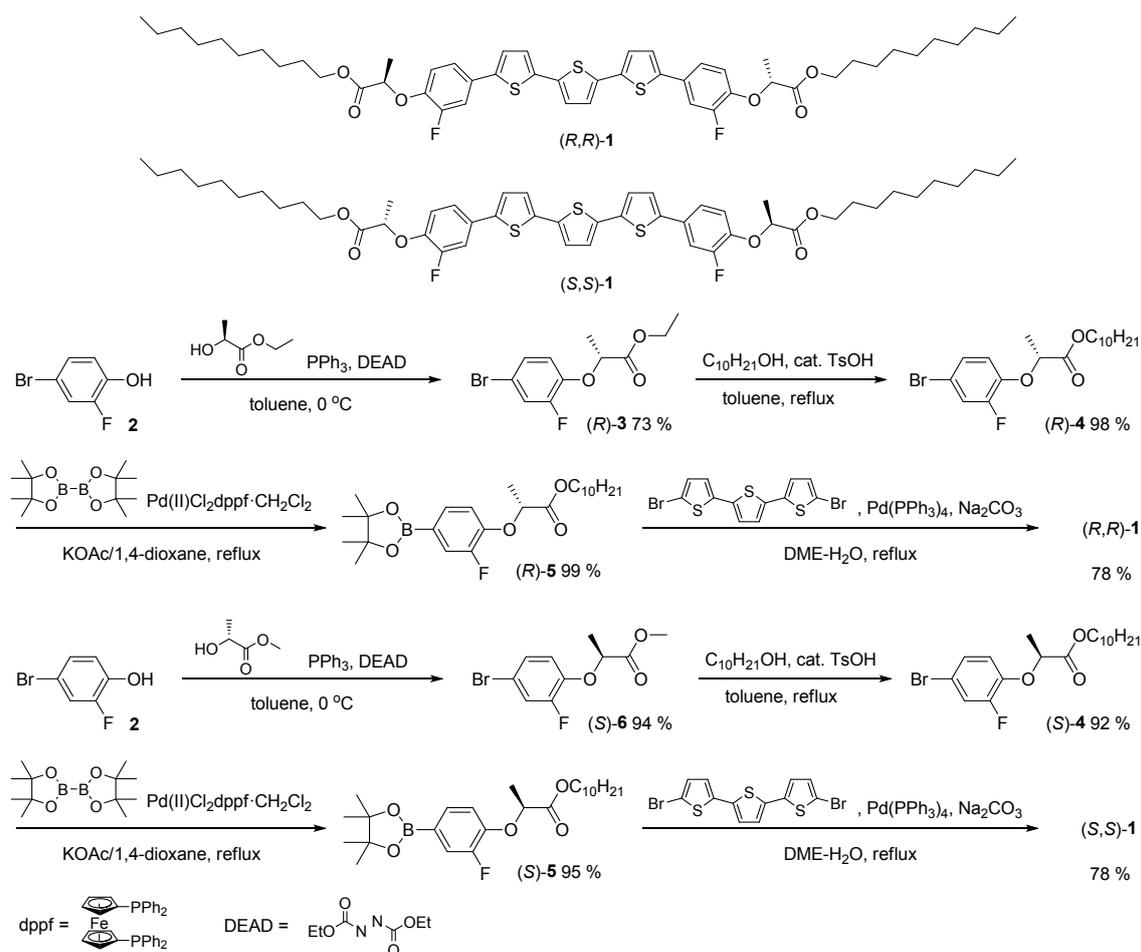
2217-20 Hayashi-cho, Takamatsu, Kagawa 761-0396, Japan

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## Synthesis of Materials

All  $^1\text{H}$  and  $^{13}\text{C}$ NMR spectra were recorded on a Varian UNITY INOVA400NB spectrometer. FT-IR measurements were conducted on a JASCO FT/IR-660 Plus spectrometer. MALDI-TOF Mass spectra were measured by Bruker Ultraflex III without matrix. Perylene tetracarboxylic acid anhydride and the Karstedt catalyst were purchased from Tokyo Chemical Industry and Gelest Inc., respectively. Zinc acetate, quinoline, and toluene (commercially available from Wako Pure Chemical Industries) were used without purification. Silica gel was purchased from Kanto Chemicals.



Scheme S1 Molecular structures of LC materials and their synthetic route

The compounds *(R,R)*-**1** and *(S,S)*-**1** were synthesized, as shown in Scheme S1. Lactate esters *(R)*-**3** and *(S)*-**6** were synthesized from 2-fluoro-4-bromophenol and ethyl lactate via the Mitsunobu reaction. The lactate esters *(R)*-**4** and *(S)*-**4** were converted to chiral 2-fluorophenylborate esters *(R)*-**5** and *(S)*-**5** using a coupling reaction between the aryl bromide and bis(pinacolato diboron) catalyzed by a Pd complex. The borate ester was coupled with dibromoterthiophene via the Suzuki coupling reaction in the presence of tetrakis triphenylphosphine palladium, affording compounds

(*R,R*)-**1** and (*S,S*)-**1**.

#### **4-Bromo-2-fluorophenoxy-(*R*)-lactic acid ethyl ester ((*R*)-**3**)**

4-Bromo-2-fluorophenol (**2**) (5.37 g, 28 mmol), (*S*)-ethyl lactate (4.04 g, 34 mmol), and triphenylphosphine (8.22 g, 31 mmol) were dissolved in toluene (100 ml) and the solution was stirred at 0 °C. A toluene solution of diethyl azodicarboxylate (2.2 M, 14 ml, 31 mmol) was added to the reaction mixture in 15 min. After stirring for 3 hours, the solvent was evaporated in vacuo. The residual mixture was filtered off and the precipitates were washed with a mixed solvent of *n*-hexane and ethyl acetate (3:1). The filtrate was purified by a silicagel column chromatography (*n*-hexane/ethyl acetate 10:1). Pale yellow oil (5.92 g, 20 mmol) was obtained in the yield of 73 %.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.24 (1H, dd, J = 10.4, 2.4 Hz), 7.14 (1H, dt, J = 8.8, 2.0 Hz), 6.80 (1H, t, J 8.8 Hz), 4.71 (1H, quart, J = 6.8 Hz), 4.21 (2H, dquart, J = 7.2, 1.6 Hz), 1.64 (3H, d, J = 6.8 Hz), 1.25 (3H, t, J = 7.2 Hz) ppm; <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>): δ = 166.5, 149.5, 146.9, 140.1, 122.5, 122.4, 115.4, 115.2, 113.8, 113.7, 108.9, 85.2, 69.9, 56.7, 13.7, 9.3 ppm; IR (ATR): ν = 2986, 1748, 1583, 1495, 1410, 1377, 1301, 1266, 1195, 1198, 1138, 1096, 1049, 1017, 866, 802, 638, 575, 452 cm<sup>-1</sup>; exact mass: 290.00; molecular weight: 291.11; elemental analysis (%) calculated for C<sub>11</sub>H<sub>12</sub>BrFO<sub>3</sub>: C, 45.38; H, 4.15; Br, 27.45; F, 6.53; O, 16.49; found: C, 45.5; H, 4.18.

#### **4-Bromo-2-fluorophenoxy-(*R*)-lactic acid decyl ester ((*R*)-**4**)**

4-Bromo-2-fluorophenoxy-(*R*)-lactic acid ethyl ester (**3**) (3.73 g, 12.8 mmol), *n*-decanol (3.62 g, 23 mmol) and toluenesulfonic acid monohydrate (70.9 mg, 0.37 mmol) were dissolved in toluene 50 ml and the solution was refluxed in an opened flask for 24 hours. After cooling the solution, an aqueous solution of sodium bicarbonate was added and the organic phase was separated. The solvent was evaporated. The crude product was purified by a silicagel column chromatography (*n*-hexane/ethyl acetate 10:1). Pale yellow oil (4.80 g, 11.9 mmol) was obtained in the yield of 93 %.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.24 (1H, dd, J = 10.8, 2.4 Hz), 7.14 (1H, ddd, J = 8.8, 2.4, 1.6 Hz), 6.79 (1H, t, J 8.8 Hz), 4.73 (1H, quart, J 6.8 Hz), 4.15 (1H, dt, J = 10.4, 6.8 Hz), 4.11 (1H, dt, J = 10.4, 6.8 Hz), 1.64 (3H, d, J = 6.8 Hz), 1.62-1.57 (2H, m), 1.32-1.20 (14H, m), 0.88 (3H, t, J = 6.8 Hz) ppm; <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>): δ = 171.3, 127.2, 127.1, 120.2, 119.9, 118.3, 117.7, 113.6, 74.6, 74.5, 65.5, 31.8, 29.5, 29.4, 29.3, 29.1, 28.5, 25.7, 22.6, 18.5, 14.1 ppm; IR (ATR): ν = 2924, 2854, 1737, 1498, 1467, 1302, 1272, 1195, 1138, 1097, 1048, 971, 870, 801, 638, 575 cm<sup>-1</sup>; exact mass: 402.12; molecular weight: 403.33; elemental analysis (%) calculated for C<sub>19</sub>H<sub>28</sub>BrFO<sub>3</sub>: C, 56.58; H, 7.00; Br, 19.81; F, 4.71; O, 11.90; found: C, 56.51; H, 7.18.

#### **4-(pinacolato)boryl-2-fluorophenoxy-(*R*)-lactic acid decyl ester ((*R*)-**5**)**

(*R*)-Lactic ester derivative ((*R*)-**4**) (5.11 g, 13 mmol), bis(pinacolato)diboron (4.11 g, 16.2 mmol) and 1,1'-Bis(diphenylphosphino)ferrocene palladium (II) dichloride dichloromethane complex (53.0

mg, 0.065 mmol) were dissolved in 1,4-dioxane (70 ml). To the solution, potassium acetate (1.55 g, 15.8 mmol) was added and the reaction mixture was refluxed for 3 hours. After cooling the mixture to room temperature, insoluble precipitates were filtered off and washed with methanol. The filtrate was concentrated and purified by a silicagel column chromatography (*n*-hexane/ethyl acetate 4:1). Colorless oil (5.80 g, 7.6 mmol) was obtained in the yield of 99 %.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.50 (1H, dd, J = 11.6, 1.2 Hz), 7.46 (1H, dd, J = 8.0, 0.8 Hz), 6.86 (1H, t, J = 8.0 Hz), 4.81 (1H, quartet, J = 6.4 Hz), 4.12 (2H, ddt, J = 14.8, 10.8, 6.8 Hz), 1.65 (3H, d, J = 6.4 Hz), 1.52-1.64 (3H, m), 1.32 (12H, s), 1.22-1.28 (13H, m), 0.88 (3H, t, J = 6.8 Hz) ppm; <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>):  $\delta$  = 171.5, 165.7, 148.2, 147.2, 131.2, 131.1, 122.4, 122.2, 115.6, 83.9, 83.4, 73.9, 65.5, 31.8, 29.5, 29.4, 29.2, 29.1, 28.4, 25.7, 25.0, 24.8, 24.7, 22.6, 18.5, 14.1 ppm; IR (ATR):  $\nu$  = 2925, 2855, 1756, 1737, 1614, 1421, 1355, 1268, 1193, 1136, 966, 854, 681 cm<sup>-1</sup>; exact mass: 450.30; molecular weight: 450.39; elemental analysis (%) calculated for C<sub>25</sub>H<sub>40</sub>BFO<sub>5</sub>: C, 66.67; H, 8.95; B, 2.40; F, 4.22; O, 17.76; found: C, 66.13; H, 7.34.

#### **4-Bromo-2-fluorophenoxy-(S)-lactic acid methyl ester ((S)-6)**

4-Bromo-2-fluorophenol (**2**) (5.16 g, 27 mmol), (*R*)-ethyl lactate (3.11 g, 30 mmol), and triphenylphosphine (7.27 g, 28 mmol) were dissolved in toluene (100 ml) and the solution was stirred at 0 °C. A toluene solution of diethyl azodicarboxylate (2.2 M, 13 ml, 29 mmol) was added to the reaction mixture in 15 min. After stirring for 3 hours, the solvent was evaporated in vacuo. The residual mixture was filtered off and the precipitates were washed with a mixed solvent of *n*-hexane and ethyl acetate (3:1). The filtrate was purified by a silicagel column chromatography (*n*-hexane/ethyl acetate 10:1). Pale yellow oil (7.02 g, 25 mmol) was obtained in the yield of 94 %.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.24 (1H, dd, J = 10.4, 2.4 Hz), 7.15 (1H, dt, J = 8.8, 2.0 Hz), 6.80 (1H, t, J = 8.8 Hz), 4.74 (1H, quartet, J = 6.8 Hz), 3.75 (3H, s), 1.64 (3H, d, J = 6.8 Hz) ppm; IR (ATR):  $\nu$  = 2954, 1755, 1583, 1490, 1448, 1409, 1377, 1301, 1266, 1201, 1138, 1097, 1050, 978, 874, 803, 638, 572 cm<sup>-1</sup>; exact mass: 275.98; molecular weight: 277.09; elemental analysis (%) calculated for C<sub>10</sub>H<sub>10</sub>BrFO<sub>3</sub>: C, 43.35; H, 3.64; Br, 28.84; F, 6.86; O, 17.32; found: C, 43.15; H, 3.94.

#### **4-Bromo-2-fluorophenoxy-(S)-lactic acid decyl ester ((S)-4)**

4-Bromo-2-fluorophenoxy-(*S*)-lactic acid methyl ester ((*S*)-**6**) (3.06 g, 11.0 mmol), *n*-decanol (2.06 g, 13.0 mmol) and toluenesulfonic acid monohydrate (150.3 mg, 0.79 mmol) were dissolved in toluene 50 ml and the solution was refluxed in an opened flask for 24 hours. After cooling the solution, an aqueous solution of sodium bicarbonate was added and the organic phase was separated. The solvent was evaporated. The crude product was purified by a silicagel column chromatography (*n*-hexane/ethyl acetate 10:1). Pale yellow oil (4.09 g, 10 mmol) was obtained in the yield of 92 %.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.24 (1H, dd,  $J$  = 10.8, 2.4 Hz), 7.14 (1H, ddd,  $J$  = 8.8, 2.4, 1.6 Hz), 6.79 (1H, t,  $J$  8.8 Hz), 4.73 (1H, quart,  $J$  6.8 Hz), 4.15 (1H, dt,  $J$  = 10.4, 6.8 Hz), 4.11 (1H, dt,  $J$  = 10.4, 6.8 Hz), 1.64 (3H, d,  $J$  = 6.8 Hz), 1.62-1.57 (2H, m), 1.32-1.20 (14H, m), 0.88 (3H, t,  $J$  = 6.8 Hz) ppm;  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta$  = 171.3, 127.2, 127.1, 120.2, 119.9, 118.3, 117.7, 113.6, 74.6, 74.5, 65.5, 31.8, 29.5, 29.4, 29.3, 29.1, 28.5, 25.7, 22.6, 18.5, 14.1 ppm; IR (ATR):  $\nu$  = 2924, 2854, 1737, 1498, 1467, 1302, 1272, 1195, 1138, 1097, 1048, 971, 870, 801, 638, 575  $\text{cm}^{-1}$ ; exact mass: 402.12; molecular weight: 403.33; elemental analysis (%) calculated for  $\text{C}_{19}\text{H}_{28}\text{BrFO}_3$ : C, 56.58; H, 7.00; Br, 19.81; F, 4.71; O, 11.90; found: C, 56.18; H, 7.18.

#### **4-(pinacolato)boryl-2-fluorophenoxy-(*S*)-lactic acid decyl ester ((*S*)-5)**

(*S*)-Lactic acid decyl ester ((*S*)-4) (3.24 g, 8.04 mmol), bis(pinacolato)diboron (2.15 g, 8.46 mmol) and 1,1'-Bis(diphenylphosphino)ferrocene palladium (II) dichloride dichloromethane complex (57.1 mg, 0.07 mmol) were dissolved in 1,4-dioxane (50 ml). To the solution, potassium acetate (1.13 g, 11.5 mmol) was added and the reaction mixture was refluxed for 3 hours. After cooling the mixture to room temperature, insoluble precipitates were filtered off and washed with methanol. The filtrate was concentrated and purified by a silicagel column chromatography (*n*-hexane/ethyl acetate 4:1). Colorless oil (3.43 g, 7.6 mmol) was obtained in the yield of 95 %.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.49 (1H, dd,  $J$  = 12.0, 1.6 Hz), 7.46 (1H, ddd,  $J$  = 8.4, 1.6, 0.4 Hz), 6.86 (1H, t,  $J$  = 8.4 Hz), 4.81 (1H, quart,  $J$  = 8.4 Hz), 4.13 (2H, ddt,  $J$  = 15.2, 10.8, 6.4 Hz), 1.65 (3H, d,  $J$  = 6.8 Hz), 1.52-1.64 (3H, m), 1.32 (12H, s), 1.22-1.28 (13H, m), 0.88 (3H, t,  $J$  = 6.8 Hz) ppm;  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta$  = 171.5, 148.2, 148.1, 131.2, 131.1, 129.8, 129.7, 122.4, 122.2, 115.6, 83.9, 73.9, 65.5, 31.8, 29.5, 29.4, 29.2, 29.1, 28.7, 28.4, 25.7, 25.0, 24.8, 25.7, 25.0, 24.8, 24.7, 22.6, 18.5, 14.1 ppm; IR (ATR):  $\nu$  = 2925, 2855, 1738, 1614, 1422, 1355, 1267, 1192, 1136, 966, 914, 855, 776, 681  $\text{cm}^{-1}$ ; exact mass: 450.30; molecular weight: 450.39; elemental analysis (%) calculated for  $\text{C}_{25}\text{H}_{40}\text{BFO}_5$ : C, 66.67; H, 8.95; B, 2.40; F, 4.22; O, 17.76; found: C, 66.45; H, 9.18.

#### **5,5''-Bis{4-((*R*)-decyl lactyloxy)-3-fluorophenyl}-2,2':5',2''-terthiophene ((*R,R*)-1)**

4-(Pinacolato)boryl-2-fluorophenoxy-(*R*)-lactic acid decyl ester (2.67 g, 5.9 mmol), 5,5''-dibromo-2,2':5',2''-terthiophene (0.97 g, 2.1 mmol), and tetrakis(triphenylphosphine)palladium(0) (30.2 mg, 0.026 mmol) were dissolved in dimethoxyethane (50 ml) and an aqueous solution of sodium carbonate (0.80 g, 7.6 mmol/ $\text{H}_2\text{O}$  20 ml) was added to the dimthoxyethane solution. The reaction mixture was refluxed for 1 hour. After cooling to room temperature, water (30 ml) was added to the reaction mixture to afford brown precipitates. The precipitates were filtered and washed by water and methanol. The crude precipitates were purified by a silicagel column chromatography (*n*-hexane/ethyl acetate 5:1). The obtained yellow solid was dissolved in dichloromethane and poured into methanol. Yellow waxy solids (1.46 g, 1.53 mmol) were obtained in the yield of 74 %.



## Characterization of liquid crystal phases

### Differential scanning calorimetry (DSC)

Differential scanning calorimetry experiments were conducted by a calorimeter (Netsch Maia 200F), using aluminum pans. Compounds (*R,R*)-**1** and (*S,S*)-**1** did not crystallize on the time scale of the DSC measurements. In contrast, (*rac*)-**1** gradually crystallized in several hours at room temperature. In the retention period at low temperature (-100 °C), the sample of (*rac*)-**1** should crystallize partially. The transition enthalpy from the M\* phase to the SmA\* phase in the heating process should be larger than that in the cooling process.

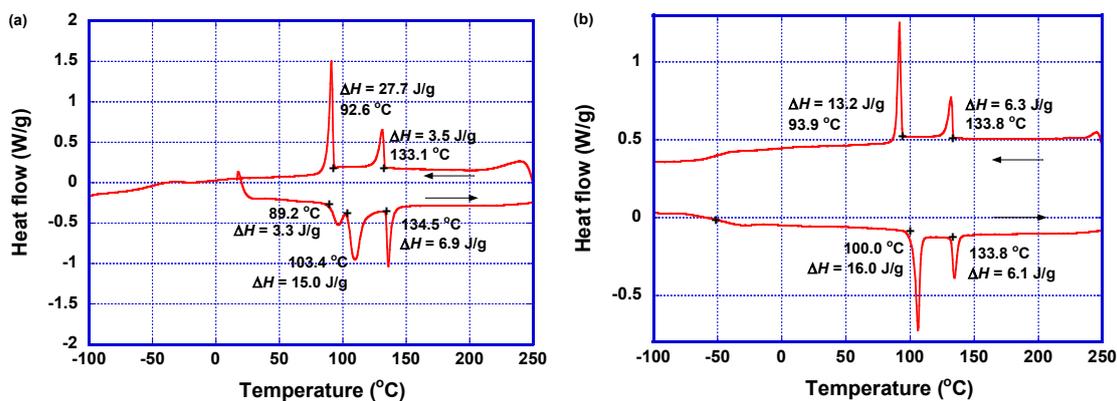


Figure S1 DSC thermograms of compound (*R,R*)-**1** in (a) the first and (b) the second cycle.

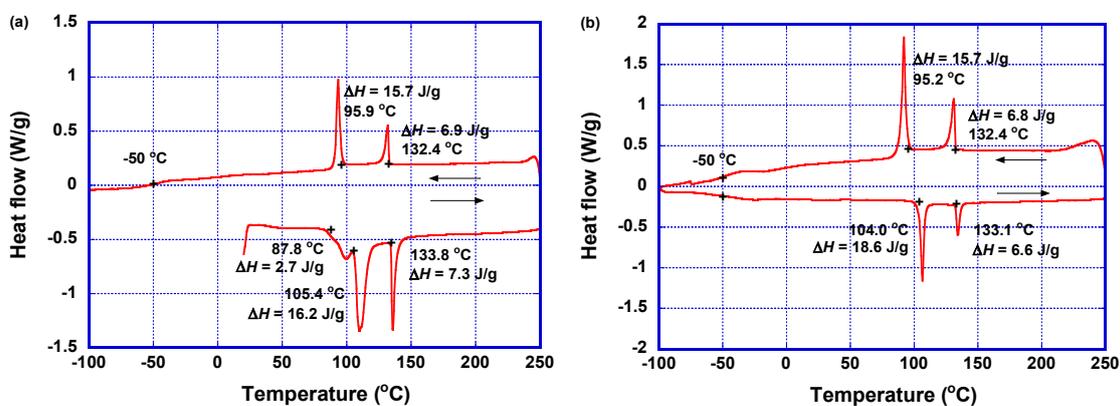


Figure S2 DSC thermograms of compound (*S,S*)-**1** in (a) the first and (b) the second cycle.

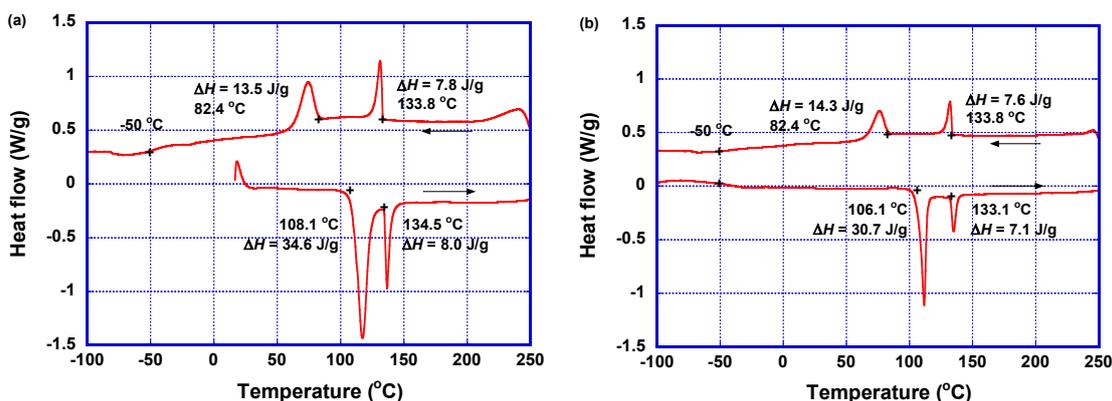


Figure S3 DSC thermograms of compound (*rac*)-1 in (a) the first and (b) the second cycle.

Table S1. Phase transition temperatures and enthalpies in the second cycle

( <i>R,R</i> )-1	Heating: M* 100.0 °C (16.0 J/g) SmA* 133.8 °C (6.1 J/g) Iso Cooling: Iso 133.8 °C (6.3 J/g) SmA* 93.9 °C (13.2 J/g) M*
( <i>S,S</i> )-1	Heating: M* 104.0 °C (18.6 J/g) SmA* 133.1 °C (6.6 J/g) Iso Cooling: Iso 132.4 °C (6.8 J/g) SmA* 95.2 °C (15.7 J/g) M*
( <i>rac</i> )-1	Heating: M* 106.1 °C (30.7 J/g) SmA* 133.1 °C (7.1 J/g) Iso Cooling: Iso 133.8 °C (7.1 J/g) SmA* 82.4 °C (14.3 J/g) M*

### X-ray diffraction

X-ray diffraction patterns were collected by an X-ray diffractometer (Rigaku Rapid II) equipped with a hand-made thermocontroller, using a capillary tube. The wavelength of the X-ray was 1.5418 Å (Cu K $\alpha$ ).

As shown in Figure S4(a), a weak and broad peak was observed at  $2\theta = 3.30$  deg. indicating  $d$  value of 26.79 Å in the high temperature phase. This peak is assigned to a (002) diffraction plane. Molecular length of compound **1** with full extension is comparable to the double of the  $d$  value. The peak derived from (001) diffraction plane could not be observed because of the limitation of the X-ray diffractometer. Other peaks were not obtained in the high angle region except for a halo around 18 deg, and the high-temperature phase was identified to be a SmA\* phase.

For the low temperature-phase, peaks originated from the (002), (003), (004), and (005) diffraction planes were observed in the low angle region. The peak derived from (001) diffraction plane could not also be observed. The peaks in high angle region were assigned as shown in Table S2, indicating a rectangular lattice with the lattice constants of 5.80 and 4.65 Å. The layer spacing determined from the diffraction plane is 38.3 Å, and this value indicates that the LC molecules tilt in 45 deg. to the layer normal in the high temperature phase. This result is consistent with the observation of optical textures as shown in Figure 3 in the main text. Therefore, the low-temperature phase was identified to be a crystal smectic H\* or K\* phase. This chiral crystal smectic phase is denoted by M\*.

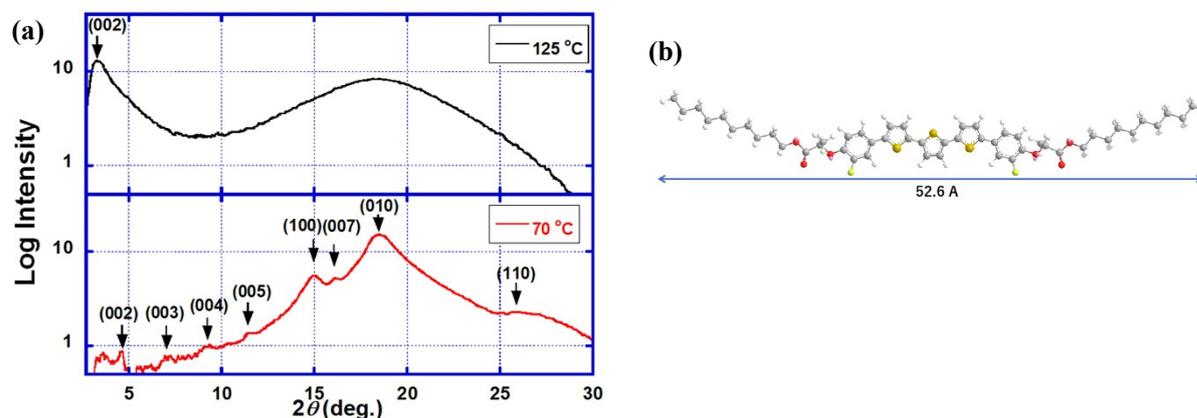


Figure S4 (a) X-ray diffraction patterns in the SmA\* phase (120 °C) and M\* phase (50 °C). (b) Molecular model of compound **1** optimized by MM2 calculation.

Table S2 Diffraction peaks in the X-ray diffraction pattern in the M\* phase of compound (*R,R*)-**1**

$2\theta$	d	index	Calc.
4.62	19.13	002	19.15
6.94	12.74	003	12.77
9.35	9.46	004	9.58
11.55	7.66	005	7.66
14.92	5.94	100	5.80
16.20	5.47	007	5.47
18.50	4.80	010	4.65
25.76	3.46	110	3.62

Lattice constants:  $a = 38.3 \text{ \AA}$ ,  $b = 5.80 \text{ \AA}$ ,  $c = 4.65 \text{ \AA}$

#### Polarizing micrographic textures in the SmA\* phase of (*R,R*)-**1**

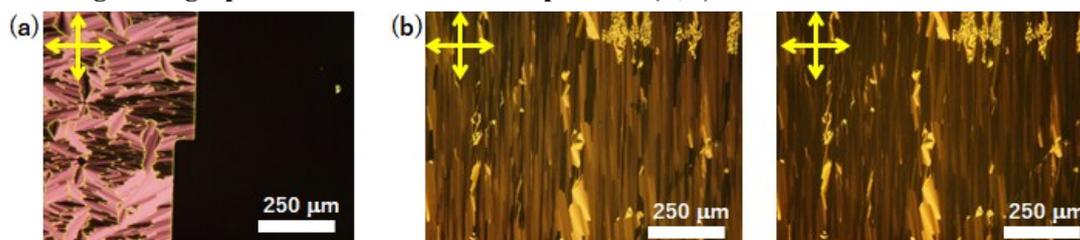


Figure S5. Polarizing optical micrograph in the SmA\* phase of compound (*R,R*)-**1** at 120 °C (a) on an ITO-coated glass substrate and (b) in a uniaxially aligned LC sample under the DC bias application of +20 V (left) and -20 V (right).

#### Absorption spectra

Absorption spectra of compound (*R,R*)-**1** in solution and thin film states were measured by a UV-VIS-NIR absorption spectrometer (Shimadzu UV-3000). For the measurement of solution state, a quartz cell with a thickness of 1 cm was used. For the measurement of a thin film state, the molten compound was capillary-filled between two quartz plates.

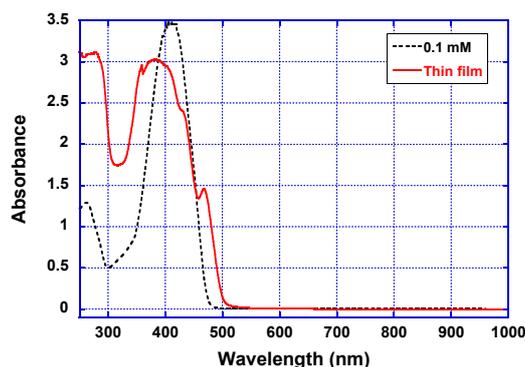


Figure S6 Absorption spectra of compound (*R,R*-1) in a solution state (0.1 mM in CHCl<sub>3</sub>) and a thin film state (thickness ~ 2.8 μm).

### TOF measurement in the non-polarized M\* phase

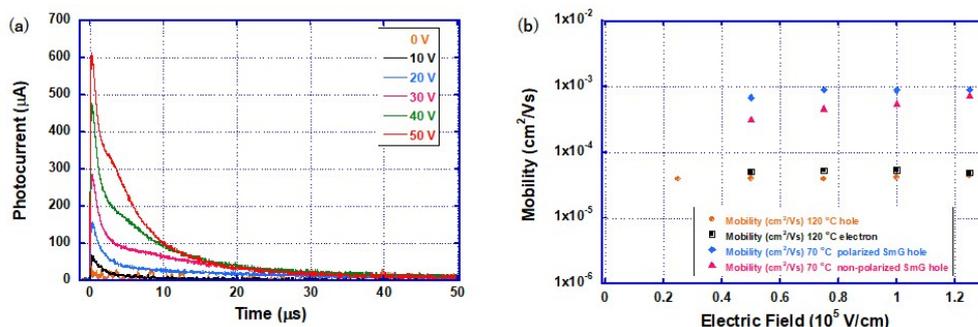


Figure S7. (a) Photoluminescence spectra in the SmA\* phase (120 °C) and polarized M\* phase (70 °C) and EL spectrum in the polarized M\* phase (70 °C) of (*R,R*)-1. (b) Polarized EL spectrum in the polarized M\* phase (70 °C) of (*R,R*)-1.

### PL and polarized EL spectra in the LC phases

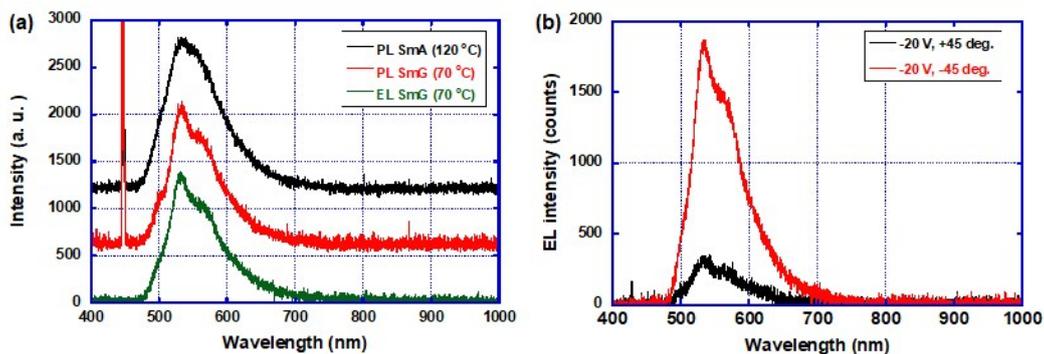


Figure S8. (a) Photoluminescence spectra in the SmA\* phase (120 °C) and polarized M\* phase (70 °C) and EL spectrum in the polarized M\* phase (70 °C) of (*R,R*)-1. (b) Polarized EL spectrum in the polarized M\* phase (70 °C) of (*R,R*)-1.

### Current-Voltage characteristics in the polarized and non-polarized M\* phase of (*R,R*)-1

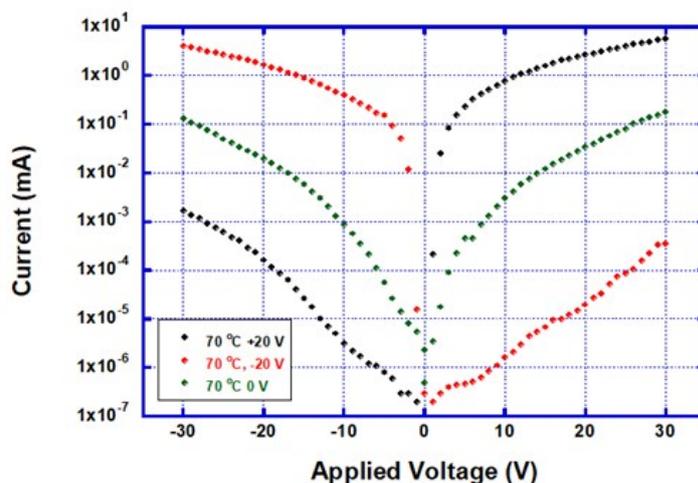


Figure S9 Current-Voltage characteristics in the polarized and non-polarized M\* phase of compound (*R,R*)-1 at 70 °C. In the cooling process, the electrode was biased at 70V, -70V, and 0 V.

### Current-voltage characteristic of (*rac*)-1

Current-Voltage characteristics in the M\* phase of a racemic mixture of compound **1** was measured by an electrometer (ADC 8252) using a LC cell consisting of two ITO coated glass plates with a thickness of 2  $\mu\text{m}$

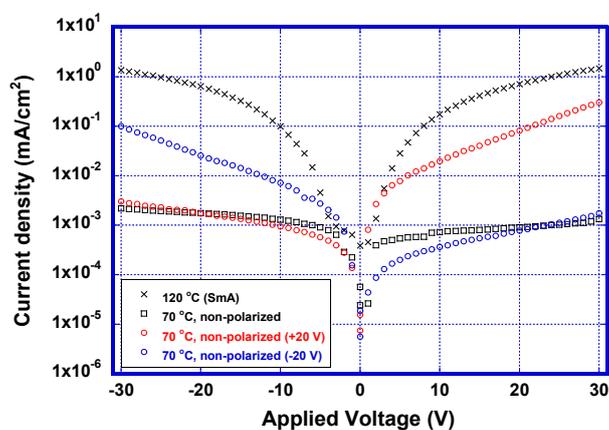


Figure S10 Current-voltage characteristics of a racemic mixture of compound **1**.

### Cyclic voltammetry

Cyclic voltammogram of compound (*R,R*-1) in a solution state was measured by a potentiostat (BAS ALS600B). Electrolyte was tetrabutyl ammonium perchlorate dissolved in acetonitrile (0.1 M). A working electrode, counter electrode, and standard electrode were a glassy carbon, a platinum wire, and an Ag/Ag<sup>+</sup> electrode, respectively.

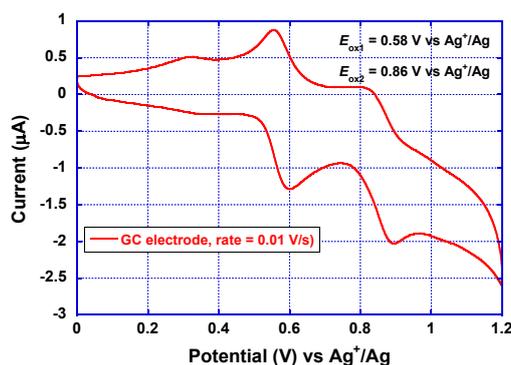


Figure S11 Cyclic voltammogram of compound (*R,R*)-**1** (1 mM) in a acetonitrile solution containing tetrabutyl ammonium perchlorate (0.1 M).

### Current-voltage characteristic of compound **7**

Current-Voltage characteristics in the SmG\* phase of compound **7** (Figure S13(a)) was measured by an electrometer (ADC 8252) using a LC cell consisting of two ITO coated glass plates with a thickness of 2  $\mu\text{m}$ .

For a single-layer EL device based on compound **7**, this internal electric fields formed in the SmC\* phase and the SmG\* phase have the potential for reducing the charge injection barriers at the anode and cathode. Compound **7** exhibits an SmC\* phase between 140  $^{\circ}\text{C}$  and 124  $^{\circ}\text{C}$  and the SmG\* phase below 124  $^{\circ}\text{C}$ . Figure S13(b) presents the current–voltage characteristics in the SmC\* and SmG\* phases. In the SmC\* phase, the curve is symmetrical and non-linear. In the SmC\* phase, the polarization was not immobilized, and the polarization was inverted between the forward and reverse biases. The current density was 1  $\text{mAcm}^{-2}$  at  $10^5 \text{ Vcm}^{-1}$ , which was 1 order of magnitude smaller than that in the SmG\* phase of compound **1**, and consequently, EL was not observed. A polarized SmG\* phase was also produced while cooling the device from the SmC\* phase to the SmG\* phase under the application of a DC bias as the formation of the polarized SmG\* phase of compound **1**. In the polarized SmG\* phase, EL was observed only between 124  $^{\circ}\text{C}$  and 110  $^{\circ}\text{C}$ . The current–voltage curve was asymmetric, thus indicating the reduction of the charge injection barrier, as shown in Figure S13(c). However, the current density was 4  $\text{mAcm}^{-2}$  at  $1 \times 10^5 \text{ Vcm}^{-1}$ , which was 1 order of magnitude smaller than that in the SmG\* phase of compound **1**, and brightness of the EL was lower than that of the EL device based on compound **1**. The current–voltage characteristics were of the Schottky type, which indicated an injection-limited mechanism. The EL disappeared at temperatures below 120  $^{\circ}\text{C}$ , which can be attributed to the reduction of the carrier mobility and electron trapping in the bulk of the LC layer.

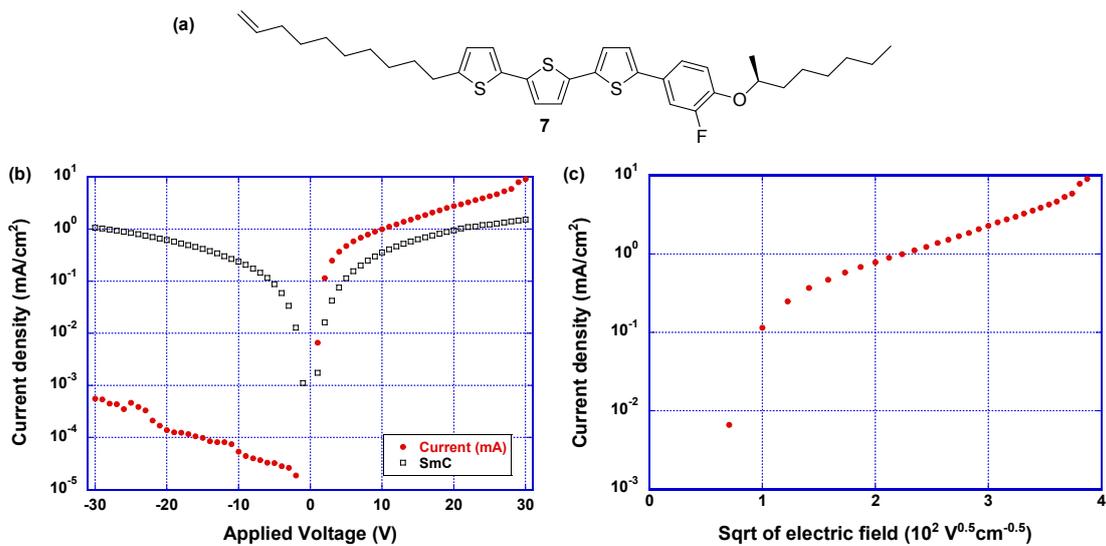


Figure S12. (a) An example of ferroelectric LC semiconductors exhibiting a photovoltaic effect in the ferroelectric phases. (b) Current–voltage characteristic in the polarized SmC\* phase (130 °C) and SmG\* phase (120 °C) of compound 7. (c) A Schottky plot under a forward bias in the polarized SmG\* phase of compound 7. The sample thickness was 2  $\mu\text{m}$ .