

Supporting information

**High open-circuit voltage in the bulk photovoltaic effect
for the chiral smectic crystal phase of a double chiral
ferroelectric liquid crystal doped with a fullerene
derivative**

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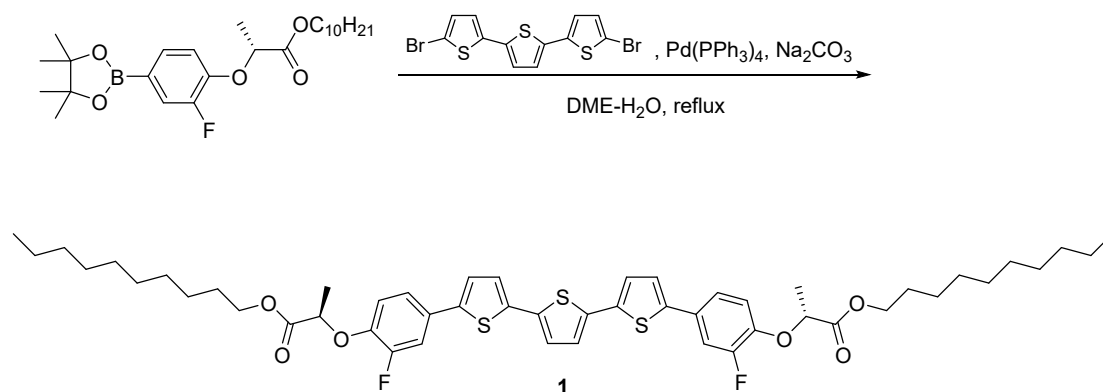
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Synthesis of Materials

^1H and ^{13}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. Dimethoxyethane (DME), tetrakis(triphenylphosphine)palladium, and sodium carbonate (Wako Pure Chemical Industries) were used without purification. Silica gel was purchased from Kanto Chemicals. Compound **1** was synthesized as shown in scheme

1.¹ Compound **2** was synthesized by the procedure reported previously.²



Scheme S1 Synthesis of compound **1**

5,5''-Bis{4-((*R*)-decyl lactyloxy)-3-fluorophenyl}-2,2':5',2''-terthiophene (**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/H₂O 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 %.

¹H NMR (400 MHz, CDCl₃): δ = 7.32 (2H, dd, J = 12.0, 2.4 Hz), 7.24 (2H, ddd, J = 8.4, 2.0, 1.2 Hz), 7.11 (2H, s), 7.11 (2H, d = 1.6 Hz), 7.08 (2H, d, J = 1.6 Hz), 6.91 (2H, t, J = 8.4 Hz), 4.80 (2H, quart, J = 6.8 Hz), 4.19 (2H, dt, J = 10.8, 6.8 Hz), 4.13 (2H, dt, J = 10.8, 6.8 Hz), 1.67 (6H, d, J = 6.8 Hz), 1.65-1.55 (4H, m), 1.30-1.20 (28H, m), 0.86 (6H, t, J = 6.8 Hz) ppm; ¹³C NMR (100 MHz CDCl₃): δ = 171.6, 154.2, 151.8, 145.1, 141.6, 136.3, 136.0, 128.9, 128.8, 124.5, 124.3, 123.7, 121.3, 121.3, 117.3, 113.9, 113.7, 74.5, 65.5, 31.8, 29.5, 29.3, 29.2, 28.5, 25.7, 22.7, 18.5, 14.0 ppm; IR (ATR): ν = 2956, 2920, 2852, 1742, 1527, 1497, 1454, 1426, 1299, 1287, 1271, 1194, 1136, 1117, 1097, 861, 836, 788, 626, 484 cm⁻¹; exact mass: 892.37; molecular weight: 893.22; elemental analysis (%) calculated for C₅₀H₆₂F₂O₆S₃: C, 67.23; H, 7.00; F, 4.25; O, 10.75; S, 10.77; found: C, 67.49; H, 6.84.

Table S1 Phase transition temperatures and enthalpies of compounds **1** and **3**.

compound	Phase transition temperature (enthalpy/ Jg ⁻¹)
1	Heating: M* 100.0 °C (16.0) SmA* 133.8 °C (6.1) Iso Cooling: Iso 133.8 °C (6.3) SmA* 93.9 °C (13.2) M* -48 C glassy M*
3	Heating: SmG* 124.3 °C (16.6) SmC* 139.9 °C (15.6) Iso Cooling: Iso 139.3 °C (15.6) SmC* 123.0 °C (15.6) SmG*

M*, SmA*, Iso, SmG*, and SmC* denote an unidentified chiral ordered smectic phase, a chiral smectic A phase, an isotropic phase, a chiral smectic G phase, and a chiral smectic G phase, respectively.

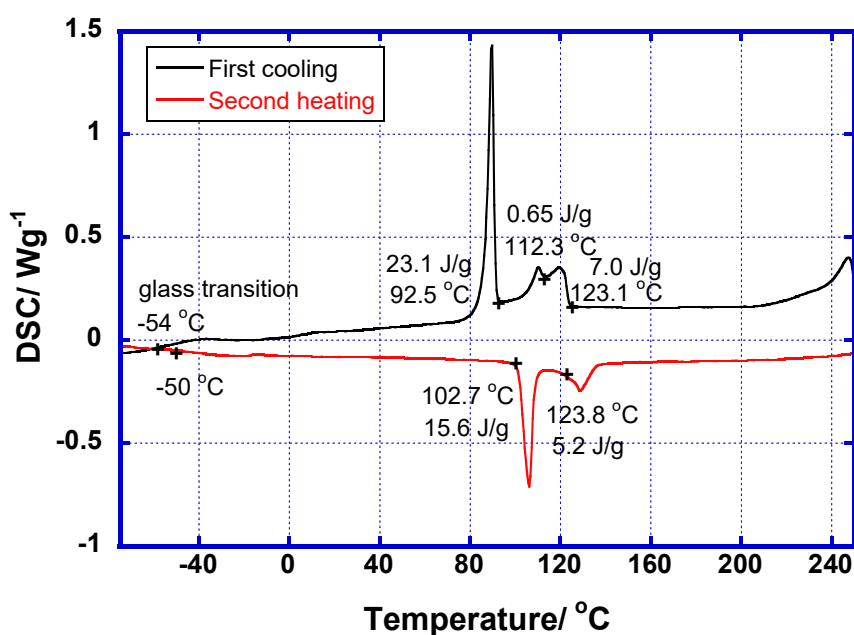


Figure S1 DSC thermograms of compound **1** doped with compound **2** (8 mol %) at heating and cooling rate of 10 Kmin⁻¹

Table S2 Phase transition temperatures and enthalpies of compound **1** doped with compound **2** (8 mol%).

compound	Phase transition temperature (enthalpy/ Jg ⁻¹)
1 doped with 2	Heating: glassy M* -50 °C M* 102.7 °C (15.6) SmA* 123.8 °C (5.2) Iso Cooling: Iso 123.1 °C (7.0) SmA* [112.3 °C (crystallization of compound 2)] 92.5 °C (23.1) M* -54 C glassy M*

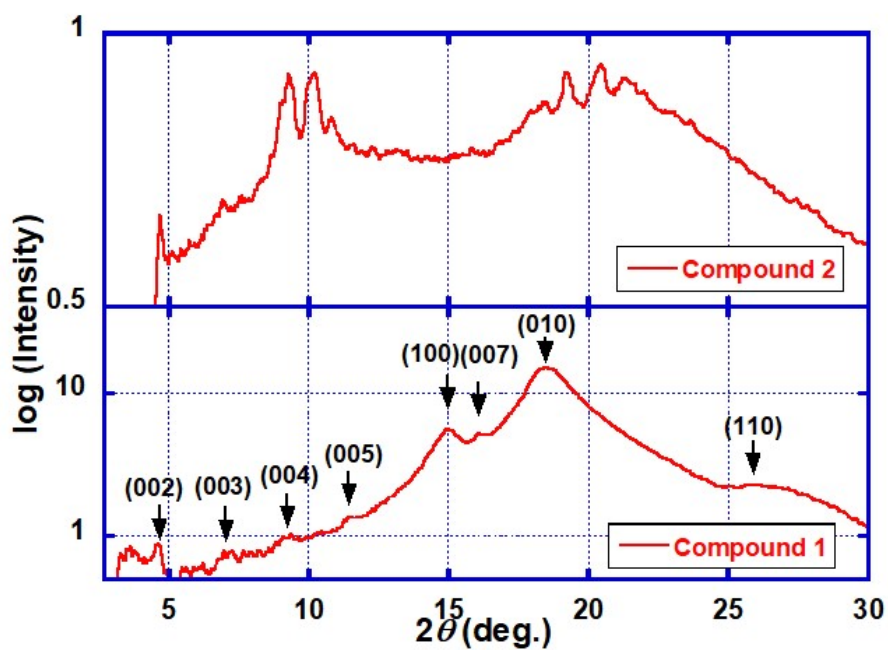


Figure S2 X-ray diffraction patterns of compound 1 (M* phase, 70 °C) and compound 2 (crystal phase, 30 °C).

Table S3 Diffraction peaks in the X-ray diffraction pattern in the M* phase of non-doped compound 1

$2\theta/\text{deg.}$	$d/\text{\AA}$	index	Calc./ \AA
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

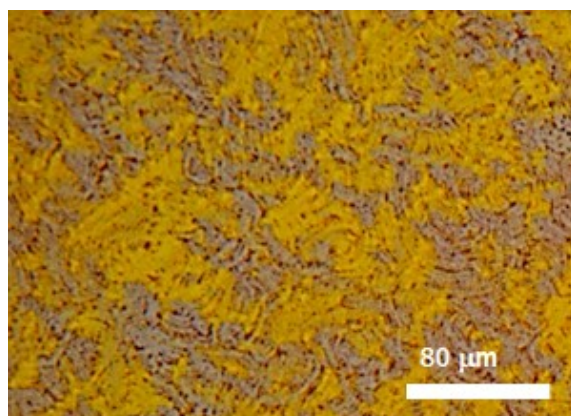


Figure S3 Polarizing optical micrographs for polarized M* phase of compound **1** doped with fullerene derivative **2** (8 mol %) at room temperature with one polarizer.

Photoluminescence of compound 1 doped with fullerene derivative 2

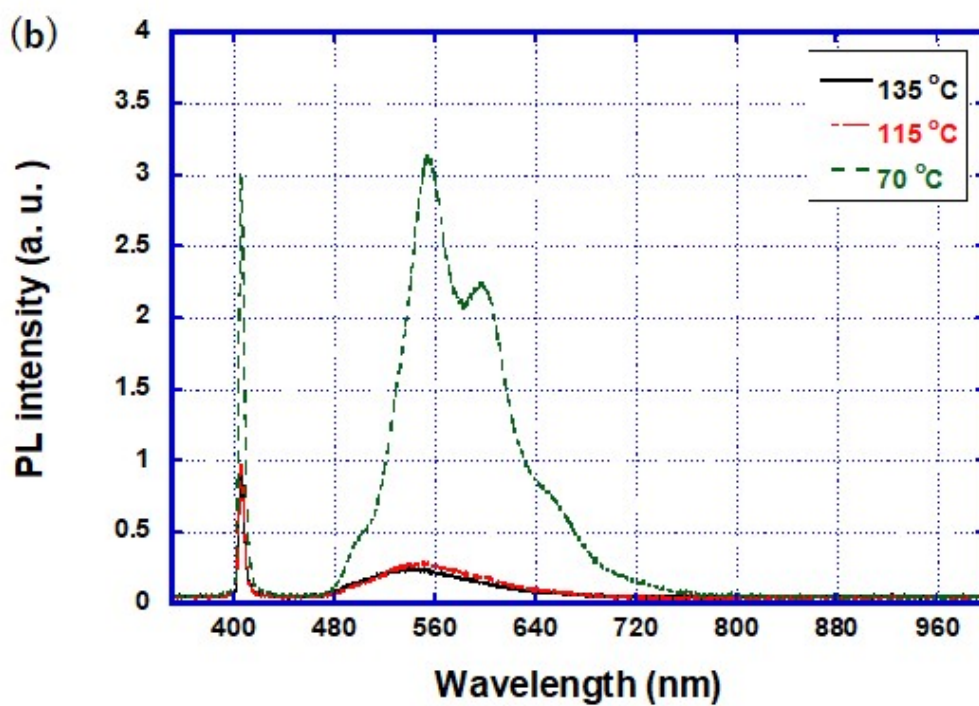
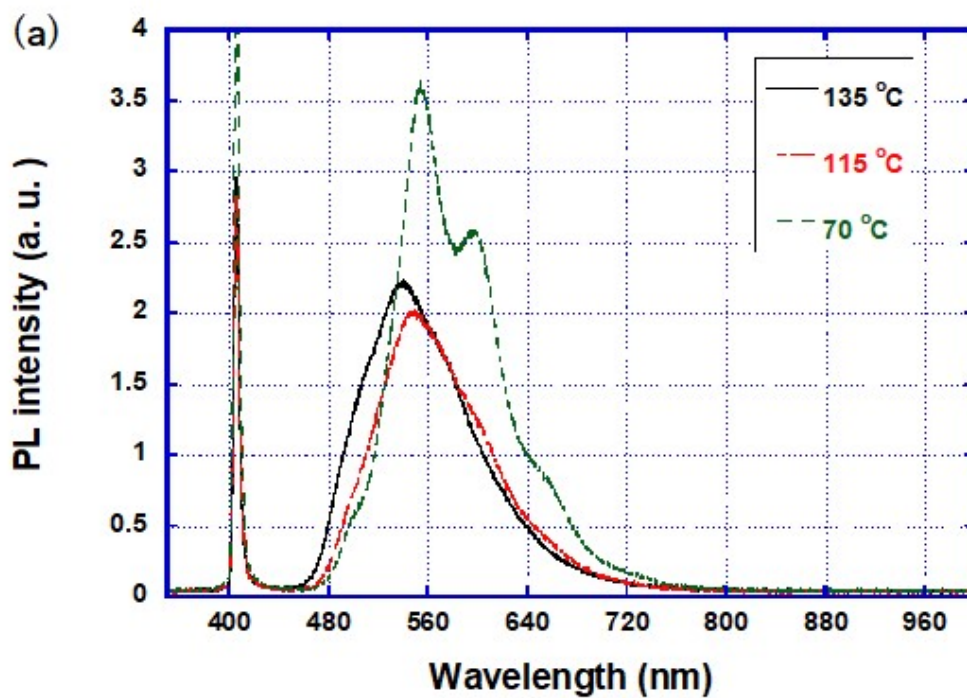


Figure S4. PL spectra of (a) pure compound **1** and (b) compound **1** doped with fullerene derivative **2** (8 mol %). The excitation light was a semiconductor laser with the wavelength of 410 nm.

Dielectric constants of compounds **1** and **3**

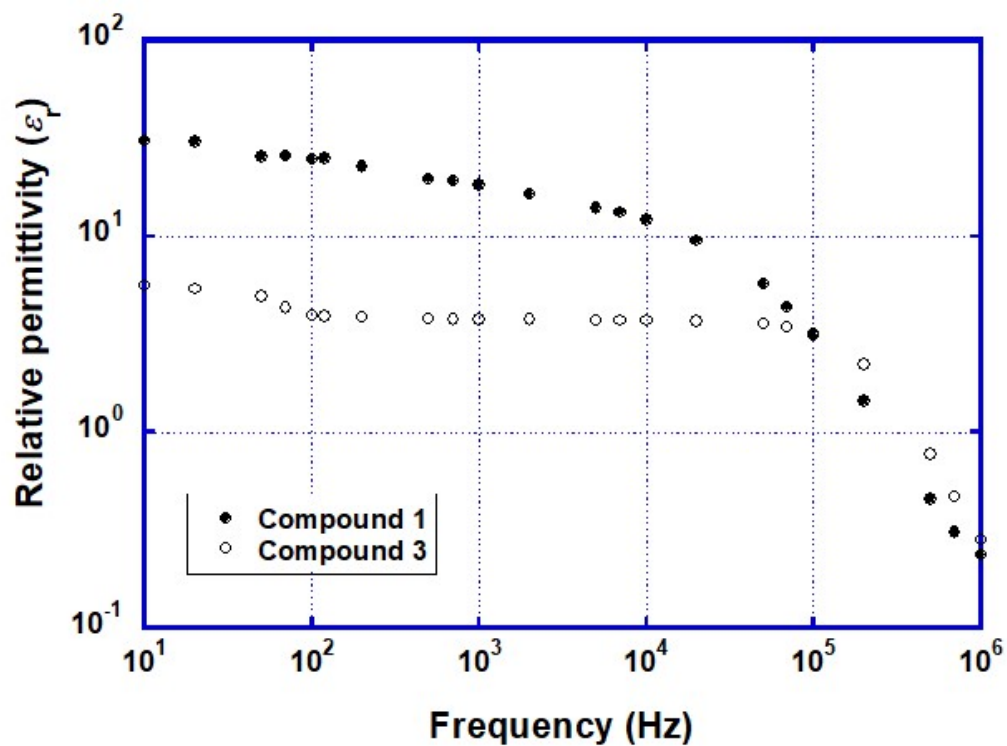


Figure S5. Relative permittivity as a function of frequency in the M* phase of compound **1** (70 °C) and in the smectic G* phase (90 °C) of compound **3**.

Current-Voltage characteristics of a cell consisting of an Al and an ITO electrodes

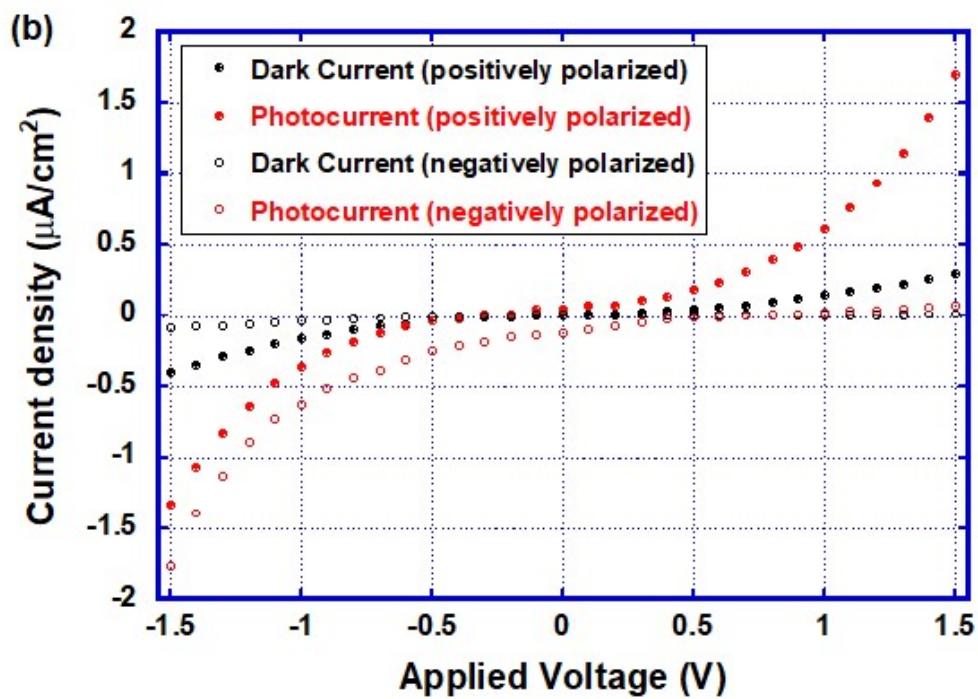
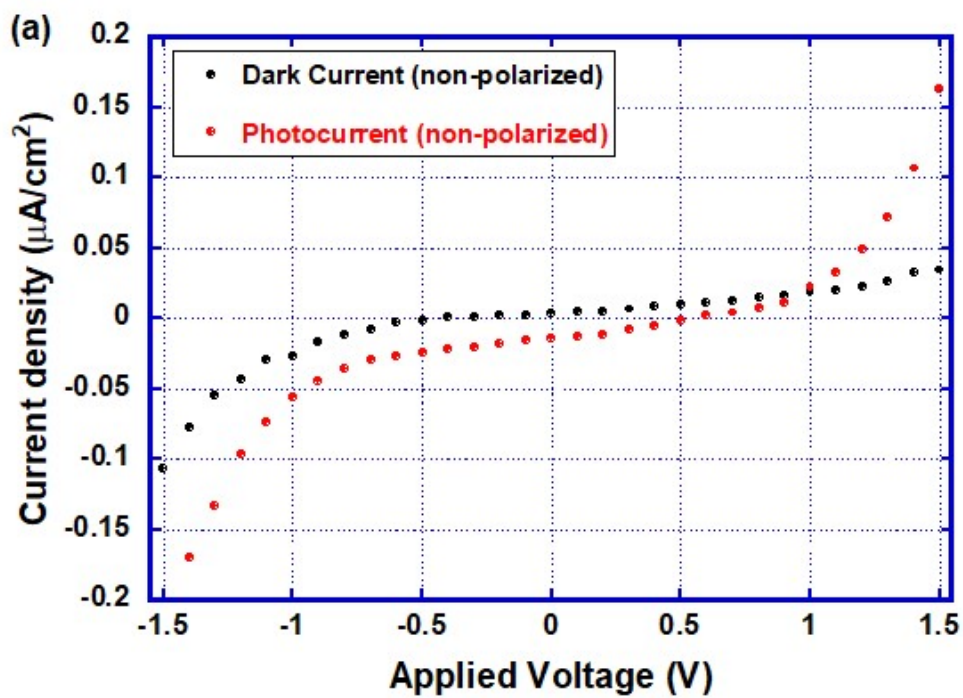


Figure S6. Current-voltage characteristics of pure compound **1** doped with fullerene derivative **2** in the M* phase (a) with polarization treatment and (b) without polarization. The sample cell consisted of an Al cathode and ITO anode and the thickness was 2 μm . A white LED (50 mWcm^{-2}) was illuminated.

Reference

1. M. Funahashi and Y. Mori, Linearly polarized electroluminescence device in which the polarized plane can be rotated electrically using a chiral liquid crystalline semiconductor, *Mater. Chem. Front.*, 2020, **4**, 2137-2148.
2. L. Zheng, Q. Zhou, X. Deng, W. Fei, N. Bin, Z.-X. Guo, G. Yu, and Y. Cao, The effect of side chains on the performance of solar cells fabricated from poly[2-methoxy-5-(2'-ethylhexoxy)-1,4-phenylene vinylene]and C60 dicarboxylate, *Thin Solid Films*, 2005, **489**, 251-256.