Supporting information

Room-temperature bulk photovoltaic effect in a terthiophene-based ferroelectric liquid crystal bearing dilactate side chains

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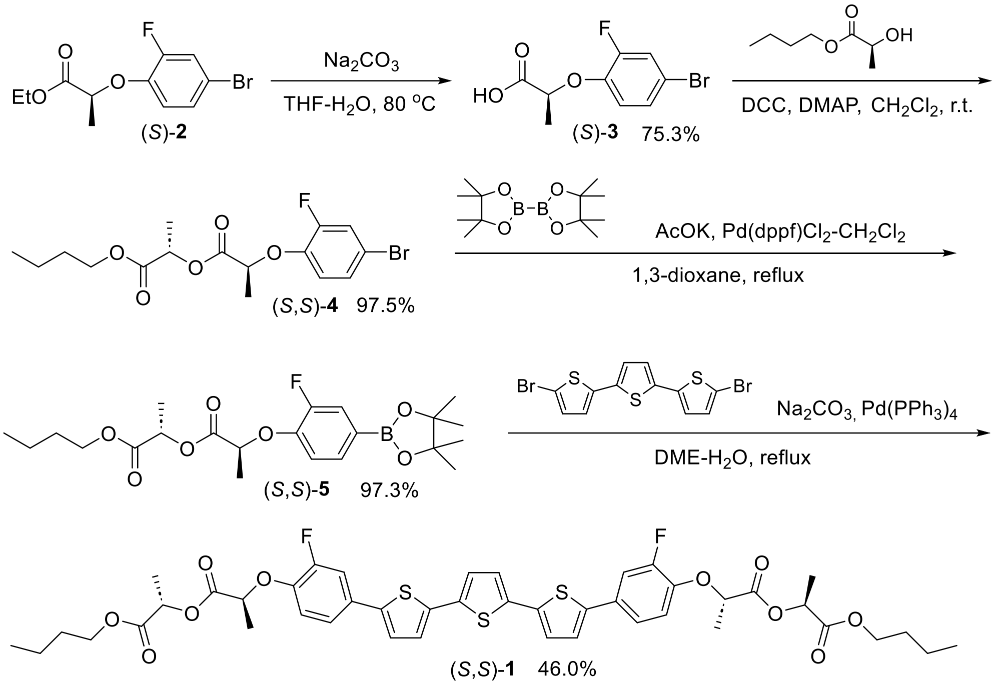
Synthesis of Materials

General

All reactions were performed under nitrogen atmosphere in a well-dried three-necked flask equipped with a magnetic stirring bar. Organic solvents and other chemicals were commercially available from Sigma-Aldrich, Tokyo Chemical Industry, Kanto Chemicals, and Fujifilm Wako Chemicals. Silica gel was purchased from Kanto Chemicals. All purchased materials were used as received. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Varian UNITY INOVA 400NB spectrometer. Infrared absorption spectra were determined using Perkin-Elmer Spectrum 3 FTIR.

Synthetic procedures and spectral data



Scheme S1 Synthetic route of compounds (*S*,*S*)-**1**

(*S*)-2-(4-bromo-2-fluorophenoxy)propanoic acid ((*S*)-3)

Ethyl (*S*)-2-(4-bromo-2-fluorophenoxy)propanoate ((*S*)-**2**) (23.81 g, 0.081 mol) was dissolved in ethanol (100 ml). An aqueous solution of sodium carbonate (10.80 g, 0.102 mol/ water 50 ml) was added to the solution and it was stirred at 80 °C for 3 hours. After cooling the reaction mixture to room temperature, and it was neutralized by dilute hydrochloric acid. The resultant solution was extracted by ethyl acetate. The extract was dried over sodium sulfate and the solvent was evaporated. The residual solids were recrystallized from *n*-hexane. White needles (17.81 g) were obtained in the yield of 75.3 %.

^{1}H-NMR (400 MHz, $CDCl_3$) : δ = 7.27 (1H, dt, J = 10.4, 2.4 Hz), 7.18 (1H, ddd, J = 9.2, 4.0, 2.4 Hz), 6.85 (1H, dt, J = 9.2, 2.4 Hz), 4.78 (1H, quartet, J 6.8 Hz), 1.68 (3H, d, J = 6.8 Hz) ppm.

FT-IR (ATR): ν = 2990.0, 2939.0, 1709.5, 1677.9, 1606.0, 1583.3, 1493.5, 1451.7, 1440.8, 1411.5, 1397.8, 1372.2, 1327.8, 1304.2, 1280.1, 1264.2, 1251.6, 1231.2, 1200.4, 1136.5, 1103.8, 1072.5, 1044.8, 950.0, 900.6, 864.3, 832.5, 794.3, 786.2, 636.1, 603.9, 575.9, 517.1, 499.3, 449.9 cm^{-1}.

Chemical Formula: $C_{11}H_{12}BrFO_3$, Exact Mass: 290.00, Molecular Weight: 291.12

m/z: 290.00 (100.0%), 291.99 (97.3%), 291.00 (12.1%), 293.00 (11.9%), 292.00 (1.3%), 294.00 (1.3%) Elemental Analysis: C, 45.38; H, 4.16; Br, 27.45; F, 6.53; O, 16.49. Found: C, 41.17; H, 3.13.

(*S*)-1-butoxy-1-oxopropan-2-yl (*S*)-2-(4-bromo-2-fluorophenoxy)propanoate ((*S*,*S*)-4)

Compound (*S*)-**3** (10.01 g, 38 mmol) and (*S*)-butyl lactate (6.08 g, 41 mmol) were dissolved in dichloromethane (120 ml). *N*,*N*'-dicyclohexylcarbodiimide (8.22 g, 40 mmol) was dissolved in dichloromethane (30 ml) and it was added dropwise to the solution of compound (*S*)-**3** and (*S*)-butyl lactate at 0 °C. After stirring the reaction mixture at room temperature for 1 hour, the crystals of dicylohexyl urea were filtered off and the filtrate was concentrated. The residual oil was purified by a silicagel column chromatography (elutant: dichloromethane). Colorless oil (14.40 g, 37 mol) was obtained in the yield of 97 %.

^{1}H-NMR (400 MHz, $CDCl_3$) : δ = 7.25 (1H, dd, J = 10.4, 2.4 Hz), 7.16 (1H, ddd, J = 8.4, 2.4, 1.6 Hz), 6.88 (1H, t, J = 8.4 Hz), 5.14 (1H, quartet, J = 7.2 Hz), 4.79 (1H, quartet, J = 6.4 Hz), 4.13 (2H, t, J = 6.4 Hz), 1.71 (3H, d, J 6.4 Hz), 1.46-1.66 (3H, m), 1.51 (3H, d, J = 7.2 Hz), 1.35 (2H, sextet, J = 6.8 Hz), 0.93 (3H, t, J = 6.8 Hz) ppm.

FT-IR (ATR): ν = 2961.3, 2875.0, 1744.3, 1583.5, 1497.2, 1455.7, 1409.7, 1378.4, 1347.6, 1302.0, 1266.0, 1184.9, 1134.0, 1092.0, 1046.5, 951.8, 864.9, 800.9, 784.6, 756.8, 637.8, 574.5, 503.2, 449.7, 385.3 cm^{-1}.

Chemical Formula: $C_{16}H_{20}BrFO_5$, Exact Mass: 390.05, Molecular Weight: 391.23

m/z: 390.05 (100.0%), 392.05 (99.7%), 391.05 (17.7%), 393.05 (17.2%), 394.05 (2.4%)

Elemental Analysis: C, 49.12; H, 5.15; Br, 20.42; F, 4.86; O, 20.45. Found: C, 48.66; H, 5.01.

(*S*)-1-butoxy-1-oxopropan-2-yl (*S*)-2-(2-fluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenoxy)propanoate ((*S*,*S*)-5)

Compound (*S*,*S*)-**4** (10.04 g, 25.7 mmol), potassium acetate (4.51 g, 55 mmol) and bis(pinacolato)diboron (11.00 g, 43 mmol) were dissolved in 1,3-dioxane (200 ml). To the suspension, [1,1'-bis(diphenylphosphino)ferrocene]palladium(II) Dichloride Dichloromethane Adduct (53.9 mg, 0.066 mmol) was added and the reaction mixture was refluxed for 5 hours. After cooling the mixture to room temperature, the insoluble precipitates were filtered off. The filtrate was dissolved in ethyl acetate and washed with water and brine. The extract was dried over sodium sulfate and concentrated. The residual oil was purified by a silcagel column chromatography (elutant: dichloromethane).

Colorless oil (10.95 g, 25.0 mmol) was obtained in the yield of 97.3 %.

^{1}H-NMR (400 MHz, $CDCl_3$) : δ = 7.51 (1H, d, J = 8.4 Hz), 7.48 (1H, d, J = 6.8 Hz), 6.93 (1H, t, J = 8.4 Hz), 5.15 (1H, quartet, J = 7.2 Hz), 4.89 (1H, quartet, J = 7.2 Hz), 4.12 (2H, t, J = 6.8 Hz), 1.72 (3H, d, J = 6.8 Hz), 1.59 (2H, quintet, J = 6.8 Hz), 1.51 (3H, d, J = 6.8 Hz), 1.38-1.32 (2H, m), 1.32 (12H, s), 0.92 (3H, t, J = 7.2 Hz) ppm.

FT-IR (ATR): ν = 2977.8, 1749.1, 1604.5, 1571.8, 1487.8, 1456.7, 1396.9, 1360.4, 1319.0, 1275.2, 1239.8, 1211.6, 1181.6, 1123.6, 1087.0, 1050.8, 1013.4, 961.7, 859.6, 848.9, 830.7, 735.2, 670.2, 654.5, 623.3, 578.2, 505.2, 448.1, 414.3, 397.9 cm^{-1}.

Chemical Formula: $C_{22}H_{32}BFO_7$, Exact Mass: 438.22, Molecular Weight: 438.30

m/z: 438.22 (100.0%), 439.23 (25.5%), 437.23 (24.8%), 438.23 (6.1%), 440.23 (4.4%)

Elemental Analysis: C, 60.29; H, 7.36; B, 2.47; F, 4.33; O, 25.55. Found: C, 57.83; H, 7.48.

Bis((*S*)-1-butoxy-1-oxopropan-2-yl) 2,2'-(([2,2':5',2''-terthiophene]-5,5''-diylbis(2-fluoro-4,1-phenylene))bis(oxy))(2*S*,2'*S*)-dipropionate ((*S*,*S*)-1)

Compound (*S*,*S*)-**5** (2.73 g, 6.2 mmol), 5,5”-dibromo-2,2’:5’,2”-terthiophene (0.98 g, 2.4 mmol), and tetrakis(triphenylphosphine) palladium (0) (17.2 mg, 0.015 mmol) were dissolved in dimethoxyethane (50 ml). An aqueous solution (20 ml) of sodium carbonate (0.67 g, 6.3 mmol) was added to the reaction mixture. It was refluxed for 30 minutes and cooled to room temperature. Water was added to the reaction mixture and resultant precipitates were filtered off. The precipitates were washed with water and methanol. The residual solids were purified by a silicagel column chromatography (elutant: dichloromethane). The crude product was dissolved in dichloromethane and the solution was poured into methanol. The yellow precipitates were filtered and recrystallized from a mixed solvent of ethyl acetate and *n*-hexane. Pale yellow needles (0.94 g, 1.1 mmol) were obtained in the yield of 46 %.

^{1}H-NMR (400 MHz, $CDCl_3$) : δ = 7.33 (2H, dd, J = 12.4, 2.4 Hz), 7.26 (2H, ddd, J = 8.4, 2.4, 1.2 Hz), 7.12 (4H, s), 7.10 (2H, s), 7.00 (2H, t, J 8.4 Hz), 5.17 (2H, quartet, J = 7.2 Hz), 4.87 (2H, quartet, J = 7.2 Hz), 4.14 (4H, t, J = 7.2 Hz), 1.74 (6H, d, J = 7.2 Hz), 1.61 (4H, quintet, J = 7.2 Hz), 1.53 (6H, d, J = 7.2 Hz), 1.36 (4H, sextet, J = 7.2 Hz), 0.92 (6H, t, J = 7.2 Hz) ppm.

FT-IR (ATR): ν = 2956.4, 1749.0, 1578.8, 1526.7, 1493.7, 1452.9, 1429.6, 1348.0, 1300.0, 1285.5, 1268.8, 1202.7, 1128.9, 1097.3, 1042.9, 954.7, 865.2, 837.2, 821.9, 789.9, 624.4, 484.8, 442.9, 397.8 cm^{-1}.

Chemical Formula: $C_{44}H_{46}F_2O_{10}S_3$, Exact Mass: 868.22, Molecular Weight: 869.02

m/z: 868.22 (100.0%), 869.23 (48.5%), 870.22 (14.6%), 870.23 (13.6%), 871.22 (6.7%), 871.23 (3.0%), 869.22 (2.4%), 872.22 (1.9%)

Elemental Analysis: C, 60.81; H, 5.34; F, 4.37; O, 18.41; S, 11.07. Found: C, 60.65; H, 5.36.

Structure of a substrate with planar electrodes

On a substrate with planar electrodes (Figure S1), a small amount of compound (*S*,*S*)-**1** was put and the substrate was heated to 120°C. A cover glass slide was put on the melt compound and the sample was cooled to room temperature.

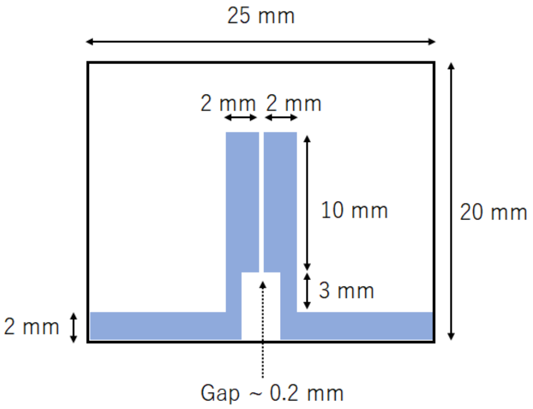


Figure S1 Schematic for a patterned ITO substrate with planar electrodes.

X-ray diffraction data of compound (*S*,*S*)-1

X-ray diffraction data of compound (*S*,*S*)-1 are summarized in Table S1. The FLC molecules are self-organized into a layer structure in which the layer spacing is 32.0 Å. The FLC molecules tilt in 45 deg. from the layer normal. Within the layers, the FLC molecules are arranged in a rectangular symmetry with the lattice constants of 11.8 Å and 4.7 Å.

Table S1 Diffraction peaks, assigned diffraction plane indices and d-spacings of compound (*S*,*S*)-**1**.

2θ/deg.	d_{exp} /Å	*h*	*k*	*l*	d_{calc} /Å
2.76	32.01	0	0	1	32.00
5.50	16.07	0	0	2	16.00
8.40	10.53	0	0	3	10.67
11.20	7.90	0	0	4	8.00
15.22	5.82	2	0	0	5.90
19.16	4.63	0	1	0	4.70
20.11	4.42	1	1	0	4.37
22.11	4.02	3	0	0	3.93
24.17	3.68	2	1	0	3.68

Photoconductivity in the non-polarized M* phase and thickness-dependence on bulk photovoltaic effect in the polarized M* phase

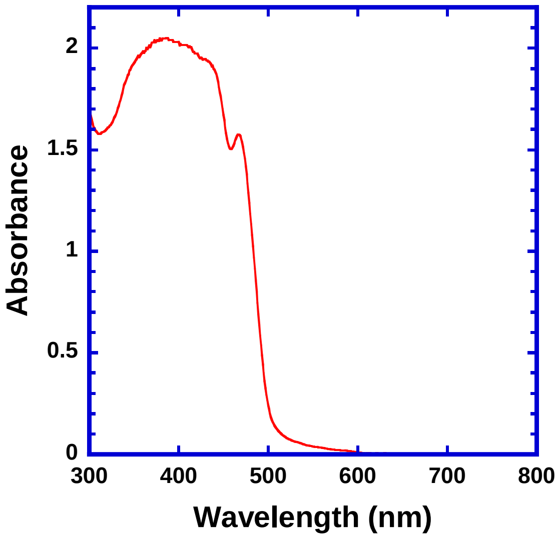


Figure S2 UV-VIS absorption spectrum of compound (*S*,*S*)-**1** in a thin film state (thickness ~ 1 µm)

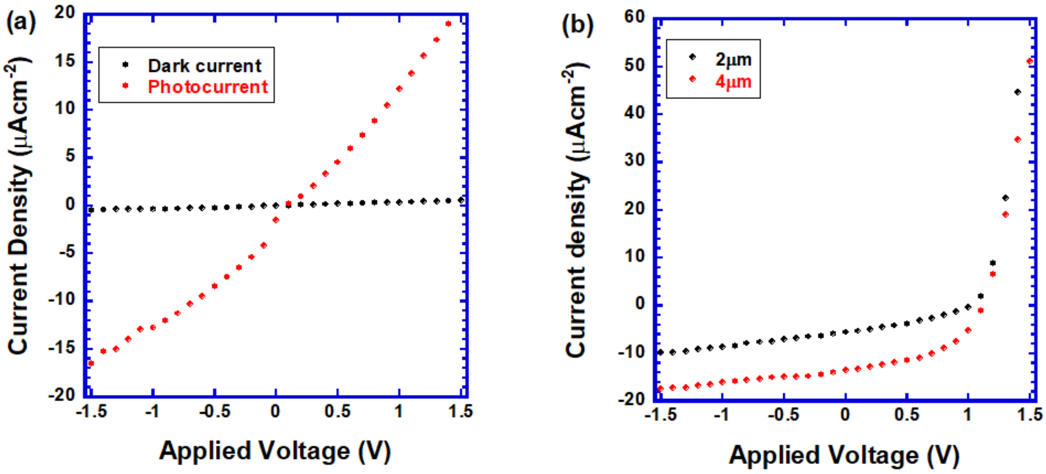


Figure S3 (a) Current-voltage characteristic in the non-polarized M* phase for white light (LED, 20 mW·cm^{-2}) illumination at room temperature. (b) Current-voltage characteristic in the polarized M* phase for white light (LED, 20 mW·cm^{-2}) illumination at room temperature for samples with different thicknesses.

Carrier transport in the M* phase of compounds (*S*,*S*)-1 and 6

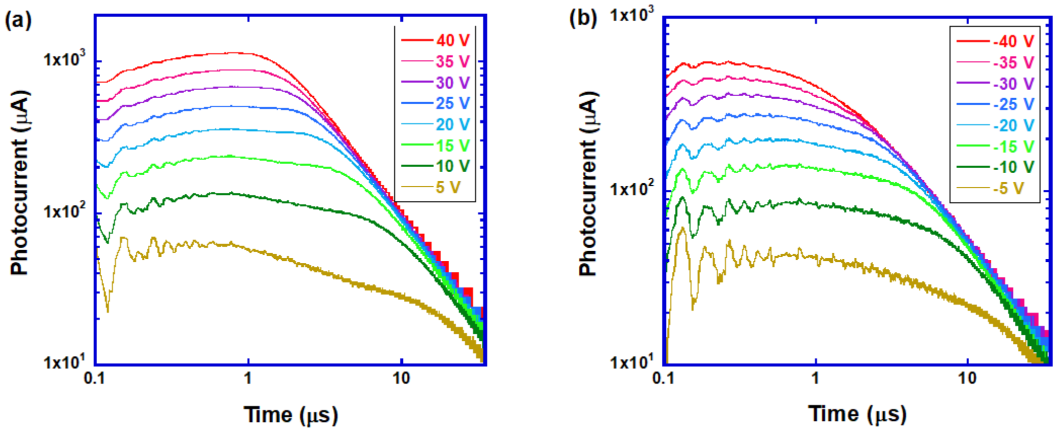


Figure S4 Transient photocurrent curves for (a) holes and (b) electrons in the M* phase of compound (*S*,*S*)-**1** at 70°C. The excitation light was THG of a Nd:YAG laser (wavelength = 356 nm) and the sample thickness was 4 μm.

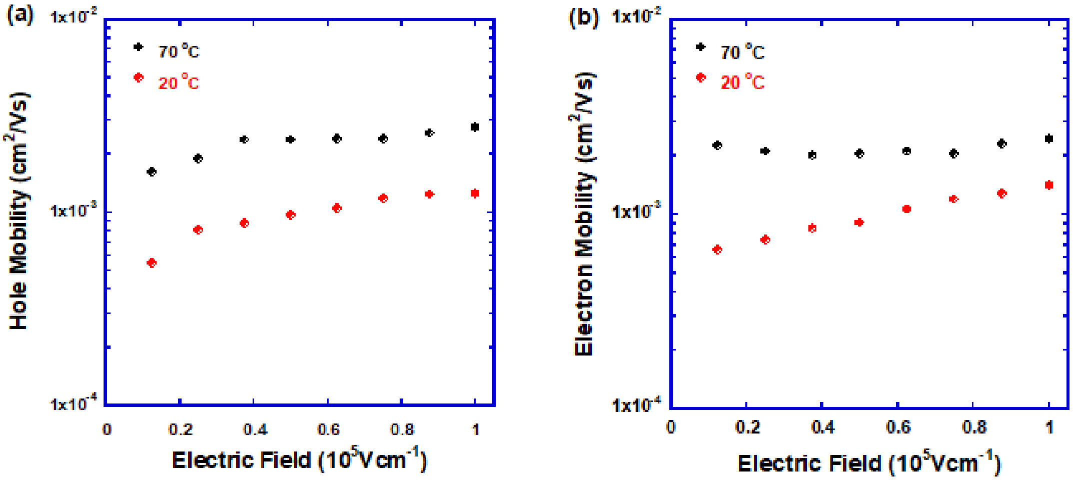


Figure S5 Carrier mobilities as a function of the electric field for (a) holes and (b) electrons in the polarized M* phase of compound (*S*,*S*)-**1** at 70°C and 20°C.

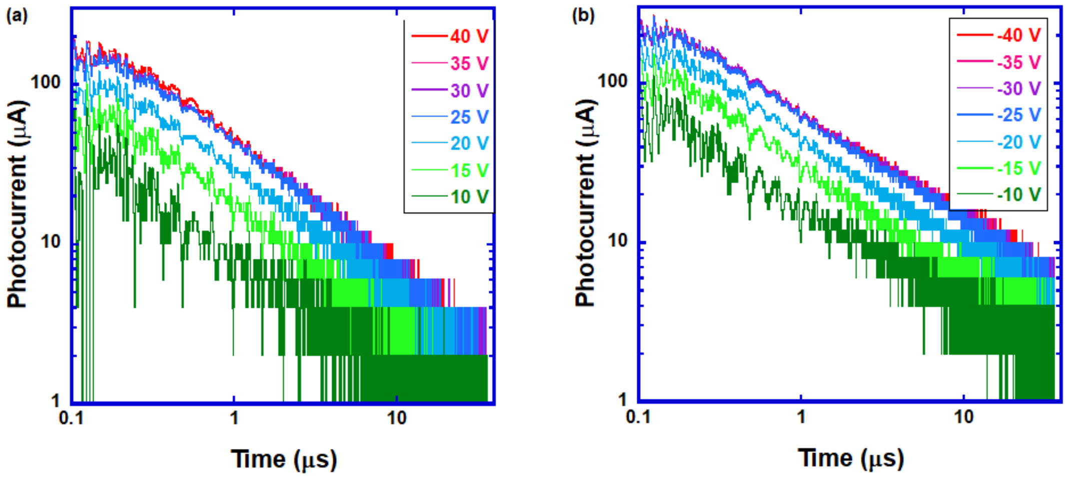


Figure S6 Transient photocurrent curves for (a) holes and (b) electrons in the polarized smectic phase of compound **6** at room temperature. The excitation light was THG of a Nd:YAG laser (wavelength = 356 nm) and the sample thickness was 4 μm.

Dielectric relaxation spectra of compound 6

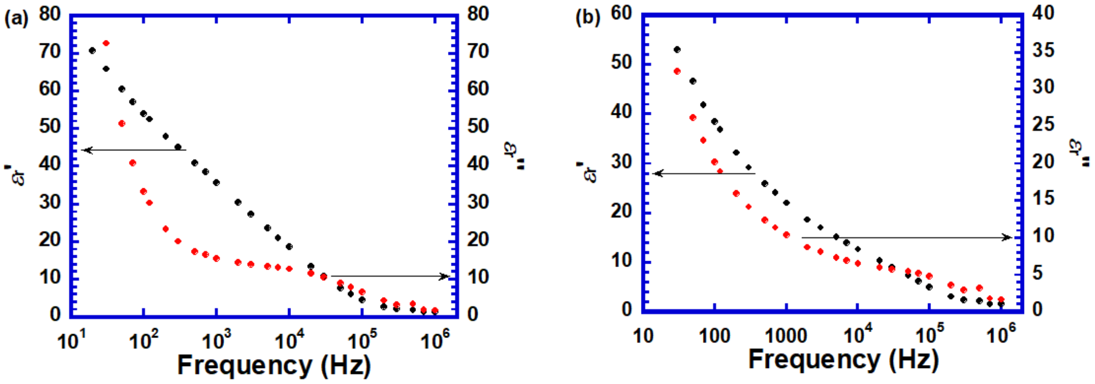


Figure S7 Dielectric relaxation spectra (a) in the non-polarized M* phase and (b) polarized M* phase of compound **6** at room temperature.

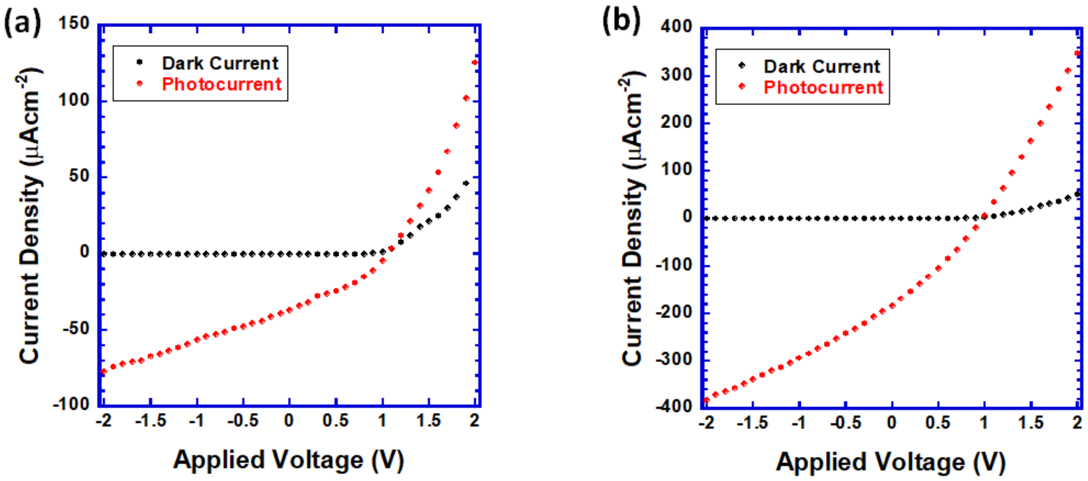


Figure S8 Current-voltage characteristics in the positively polarized M* phase of (a) pure (*S*,*S*)-**1** and (b) (*S*,*S*)-**1** doped with PCBM (8wt%) when AM1.5 (100 mW·cm^{-2}) was illuminated at room temperature. The sample thickness was 4 μm.

Table S2 Photovoltaic parameters of pure and PCBM-doped (8 wt%) compound (*S*,*S*)-**1** for AM1.5 illumination (100 mW·cm^{-2}).

	Open-circuit Voltage/ V	Short-circuit current density/ μAcm^{-2}	Fill factor	Power conversion efficiency/ %
Pure (*S*,*S*)-**1**	1.07	37.0	0.33	0.013
PCBM-doped (*S*,*S*)-**1**	0.98	183	0.29	0.05