Supporting Information for

Air-Stable Solution-Processed Ambipolar Organic Field-Effect Transistors Based on Dicyanomethylene-Substituted Terthienoquinoid Derivative

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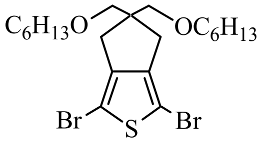
Contents

1. Synthesis

General: All chemicals and solvents are of reagent grade unless otherwise indicated. Toluene and THF were purified by standard distillation procedures prior to use. 1,3-Dibromo-5,5-bis(hexyloxymethyl)cyclopenta[*c*]thiophene[S1] was synthesized according to the reported procedures. Melting points were uncorrected. Nuclear magnetic resonance spectra were obtained in deuterated chloroform with a JEOL Lambda 400 spectrometer operating at 400 MHz for ^{1}H with TMS as internal reference; chemical shifts (δ) are reported in parts per million. NOESY spectra were obtained in deuterated dichloromethane with a Varian Mercury-300 spectrometer operating at 300 MHz. EI-MS spectra were obtained on a Shimadzu QP-5050A spectrometer using an electron impact ionization procedure (70 eV). The molecular ion peaks of the sulfur- and/or bromine- containing compounds showed a typical isotopic pattern, and all the mass peaks are reported on ^{32}S, ^{79}Se and ^{79}Br.

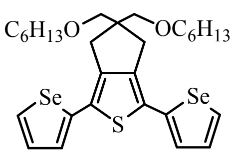
1,3-Dibromo 5,5-bis(hexyloxymethyl)cyclopenta[*c*]thiophene (3)



A solution of 5,5-bis(hexyloxymethyl)cyclopenta[*c*]thiophene[S1] (1.00 g, 2.84 mmol) in DMF (50 mL) was added *N*-bromosuccinimide (1.11 g, 6.23 mmol), and the resulting mixture was stirred at rt for 5 h. The reaction was quenched by an addition of saturated aqueous sodium carbonate solution (10 mL), and the mixture was extracted with hexane (100 mL × 3). The combined extract was washed with brine (100 mL), dried ($MgSO_4$), and concentrated in vacuo. The crude product was purified by column chromatography on silica gel eluted with hexane-dichloromethane (1:1, v/v) ($R_f = 0.6$) to give a yellow oil of **3** (1.36 g, 94%).

^1H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, *J* = 6.84 Hz, 6H), 1.25–1.35 (m, 12H), 1.52 (quint, *J* = 8.08 Hz, 4H), 2.54 (s, 4H), 3.35 (s, 4H), 3.40 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.6, 25.8, 29.4, 31.6, 34.4, 54.5, 71.4, 73.5, 101.4, 147.3; MS (EI) *m/z* = 508 (M^+)

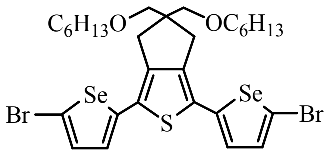
2,1';3',2''- Diselenyl-5',5'-bis(hexyloxymethyl)cyclopenta[*c*]thiophene (4)



Under nitrogen atmosphere, a solution of **3** (1.60 g, 3.14 mmol) and 2-tributylstannylselenophene[S2] (2.92 g, 6.93 mmol) in dry toluene (80 mL) was dearated by argon stream for 30 min. $Pd(PPh_3)_4$ (358 mg, 0.31 mmol) was added to the solution, and the resulting mixture was refluxed for 20 h in dark. After cooling, the mixture was filtered through a Celite pad, and the filtrate was concentrated *in vacuo* to give a yellow solid. The crude product was purified by column chromatography on silica gel eluted with hexane-dichloromethane (2:1, v/v) to give a yellow solid ($R_f = 0.5$). Analytical sample of **4** was obtained as pale yellow needles by recrystallization from ethanol-hexane (1.63 g, 85%).

mp 74–75 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.80 Hz, 6H), 1.26-1.29 (m, 12H), 1.52-1.56 (m, 4H), 2.71 (s, 4H), 3.41-3.44 (m, 8H), 7.24-7.27 (m, 4H), 7.92 (dd, *J* = 1.48, 5.36 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.6, 25.8, 29.4, 31.6, 34.4, 55.2, 71.4, 73.8, 125.1, 127.5, 129.6, 130.0, 141.8, 144.0; MS (EI) *m/z* = 612 (M^+); Anal. Calcd for $C_{29}H_{40}O_2SSe_2$: C, 57.04; H, 6.60; Found: C, 57.04; H, 6.63.

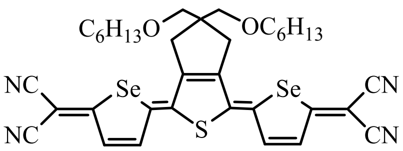
5,5''-Dibromo-2,1';3',2''-diselenyl-5',5'-bis(hexyloxymethyl)cyclopenta[*c*]thiophene (5)



To an ice-cooled solution of **4** (200 mg, 0.32 mmol) in chloroform (40 mL) was added *N*-bromosuccinimide (116 mg, 0.65 mmol), and the resulting mixture was stirred at rt for 5 h. The reaction was quenched by an addition of saturated aqueous sodium carbonate solution (10 mL), and the mixture was extracted with chloroform (50 mL × 3). The combined extract was washed with brine (100 mL), dried ($MgSO_4$), and concentrated in vacuo. The oily residue was chromatographed on silica gel eluted with hexane-dichloromethane (1:1, v/v) to give a yellow solid (R_f = 0.5). Recrystallization from ethanol-hexane gave analytical pure **5** as yellow needles (230 mg, 92%).

mp 64–65 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 6.84 Hz, 6H), 1.26-1.34 (m, 12H), 1.51-1.56 (m, 4H), 2.63 (s, 4H), 3.40-3.43 (m, 8H), 6.94 (d, *J* = 4.12, 2H), 7.16 (d, *J* = 4.12 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.6, 25.8, 29.4, 31.6, 34.1, 55.4, 71.5, 73.7, 114.6, 124.8, 127.0, 133.4, 143.4, 144.4; MS (EI) *m/z* = 768 (M^+); Anal. Calcd for $C_{29}H_{38}Br_2O_2SSe_2$: C, 45.33; H, 4.98; Found: C, 45.25; H, 5.05.

5,5''-Bis(dicyanomethylene)-5,5''-dihydro-$\Delta^{2,1';3',2''}$-diselenyl-5',5'-bis(hexyloxymethyl)cyclopenta[*c*]thiophene (2)



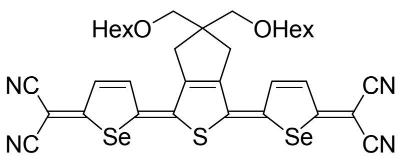
Under nitrogen atmosphere, Sodium hydride (60% in oil, 81 mg, 3.38 mmol) was added into a solution of malononitrile (112 mg, 1.70 mmol) in dry THF (20 mL), and the mixture was stirred at rt for 30 min. After tetrakis(triphenylphosphine)palladium (19 mg, 17.0 μmol) and dppf (19 mg, 35.2 μmol) were added, a solution of **5** (130 mg, 0.17 mmol) in dry THF (30 mL) was slowly added over a period of 20 min. The mixture was refluxed for 20 h, and then diluted hydrochloric acid (6 M, 30 mL) was added with ice-cooling.[S3,4] After stirred for 30 min under air, the mixture was extracted with chloroform (50 mL × 3), and the extracts were combined, washed with brine (100 mL), and dried ($MgSO_4$). After evaporation of the solvent, the residue was purified by column chromatography (silica gel, chloroform, R_f = 0.5) followed by recrystallization from dichloromethane-acetonitrile to give deep green crystals of **2** (79 mg, 63%).

mp 300 °C (melt with decomposition); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.40 Hz, 6H), 1.25-1.34 (m, 12H), 1.53-1.57 (m, 4H), 2.75-2.92 (m, 4H), 3.43-3.47 (m, 8H), 7.22-7.26 (m, 1H), 7.36-7.39 (m, 1H), 7.41-7.43 (m, 1H), 7.60-7.63 (m, 1H); MS (EI) *m/z* = 642 (M^+); IR (KBr) 2206.57 cm^{-1} (CN); Anal. Calcd for $C_{35}H_{38}N_4O_2S\,Se_2$: C, 57.06; H, 5.20; N, 7.61; Found: C, 57.06; H, 5.38; N, 7.69.

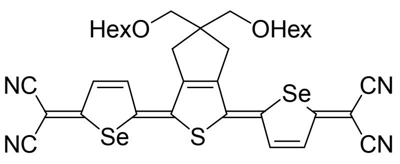
2. NMR spectra of 2

Compound **2** was isolated as an isomeric mixture, i.e. *cis-cis*, *cis-trans*, *trans-trans* in terms of the double bonds between three thiophene rings, which gave complicated ^{1}H NMR spectra (Figure

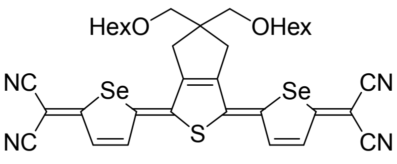
S1). In order to define each isomer on the spectra as well as the ratio of each isomer, NOESY measurements were carried out: clear correlated peaks between thiophene *β*-protons (δ 7.57–7.59, doublet) and methylene protons (δ 2.92 and 2.88, singlet) in the cyclopentane ring were observed (Figure S2). Therefore, all the signals for **2** were assigned as shown in Figure S1, and the ratio of isomers was determined to be *cis-cis* : *cis-trans*: *trans-trans* = 1 : 5 : 4. These isomers seem to exist as an equilibrium mixture in solution.



cis-cis



cis-trans



trans-trans

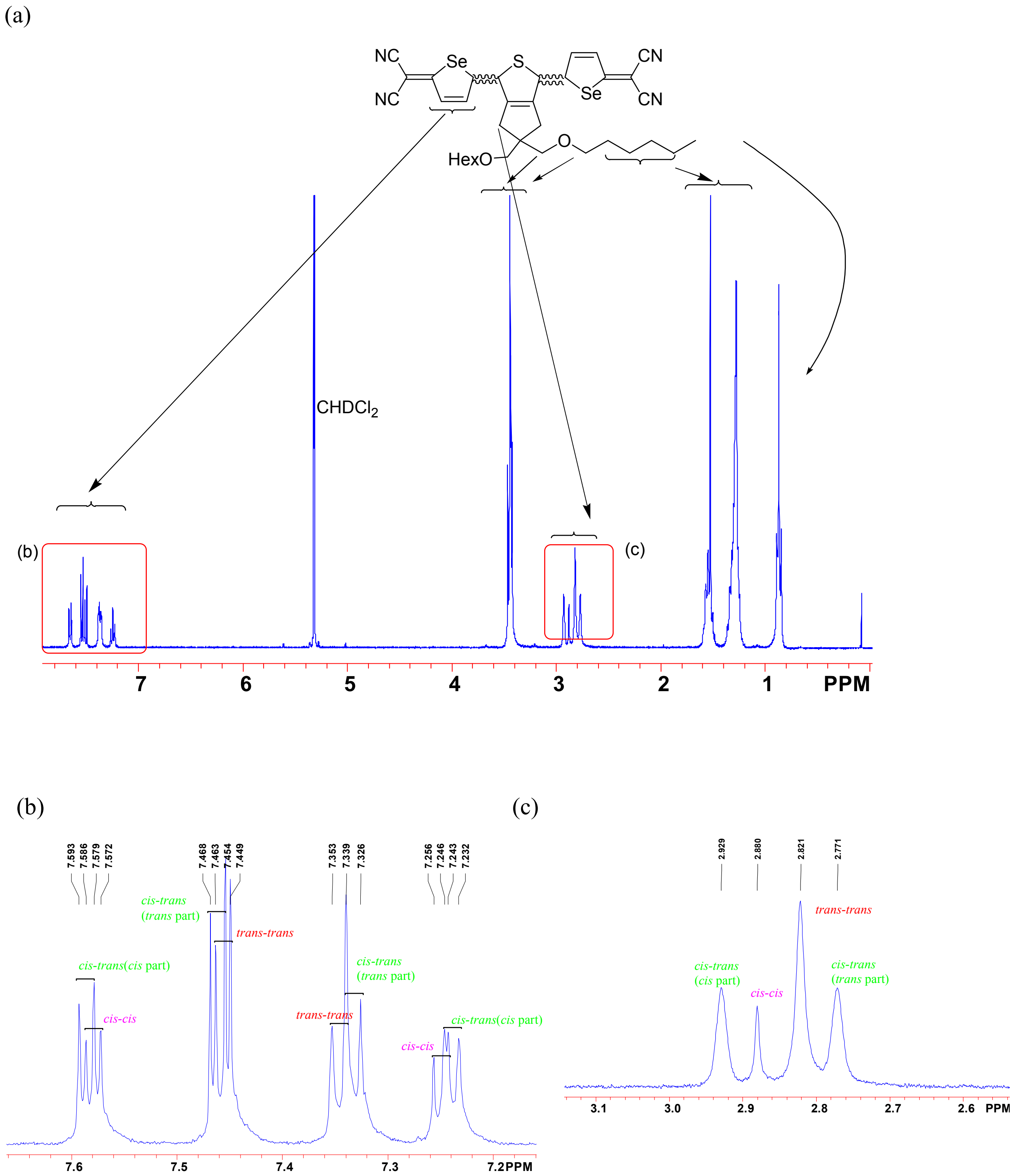


Fig. S1 ^{1}H NMR spectra of **2** in dichloromethane-d_2.

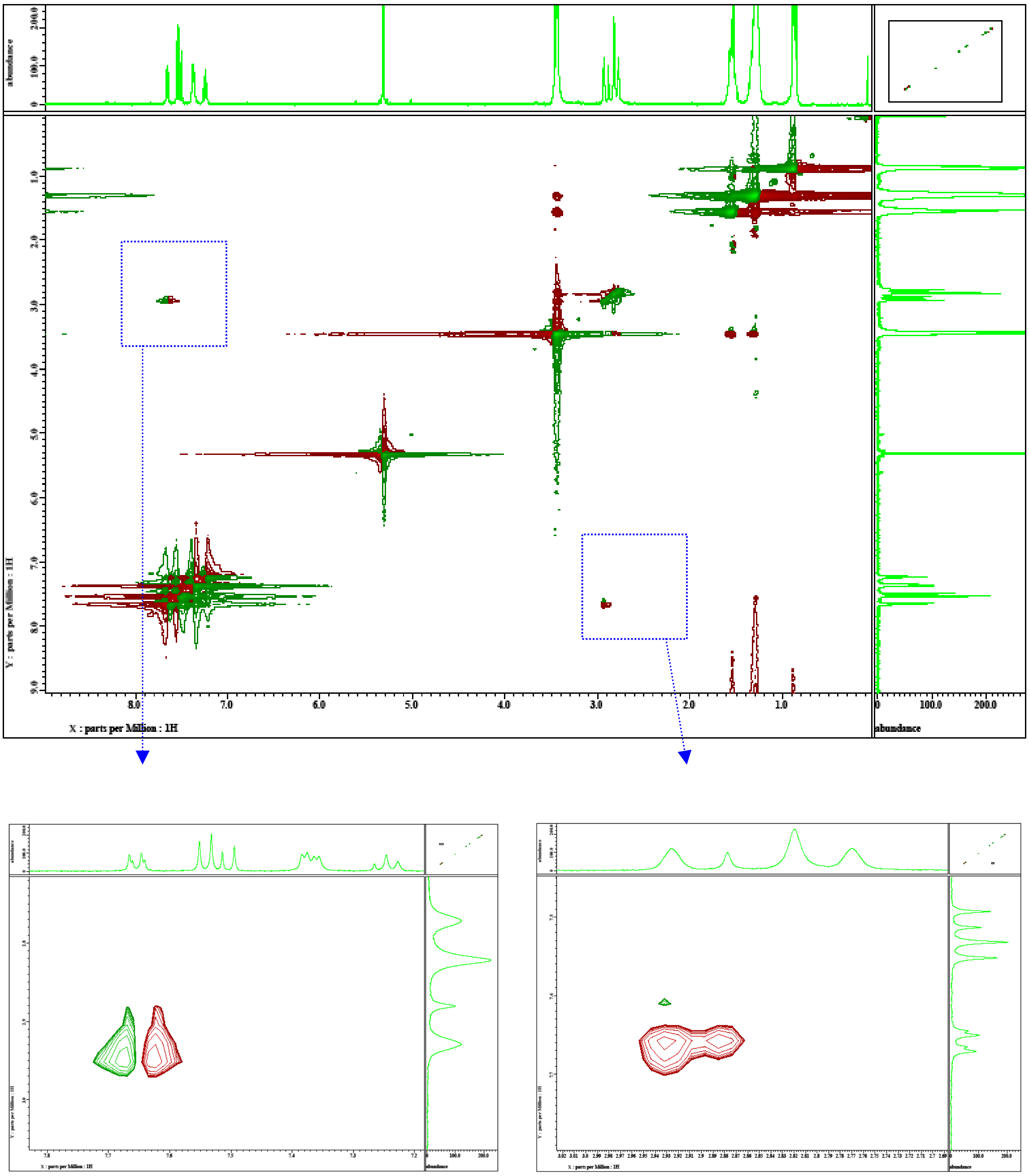


Fig. S2 NOESY spectra of **2** in dichloromethane-d_2.

3. Physicochemical properties (UV-vis, DSC, and CV)

Instruments. UV-vis spectra in chloroform solution was recorded on a Shimadzu UV-3100 spectrometer. Cyclic voltammograms (CVs) were recorded on a Hokuto Denko HA-301 potentiostat and a Hokuto Denko HB-104 function generator in benzonitrile containing tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, 0.1 M) as supporting electrolyte at a scan rate of 100 mV/s. Counter and working electrodes were made of Pt, and the reference electrode was Ag/AgCl. All the potentials were calibrated with the standard ferrocene/ferrocenium redox couple ($E^{1/2}$ = +0.46 V measured under identical conditions). Differential scanning calorimetry (DSC) was carried out on a Seiko Instruments EXSTAR6000 DSC6200.

Estimation of LUMO energy levels: From the onset of the reduction peak (ca. –0.1 V vs. Ag/AgCl, Figure S4), the LUMO energy level of **2** was estimated to be 4.16 eV below the vacuum level on the premise that the Fc/Fc^+ energy level is 4.8 eV below the vacuum level.[S5]

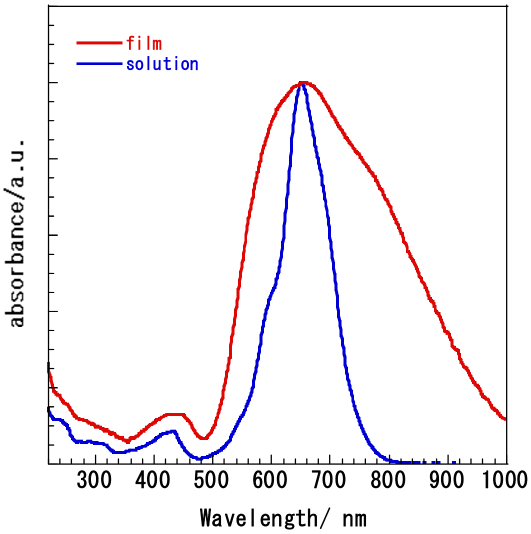


Fig. S3 UV-vis spectra of **2** in chloroform (blue line) and as-spun film of **2** (red line).

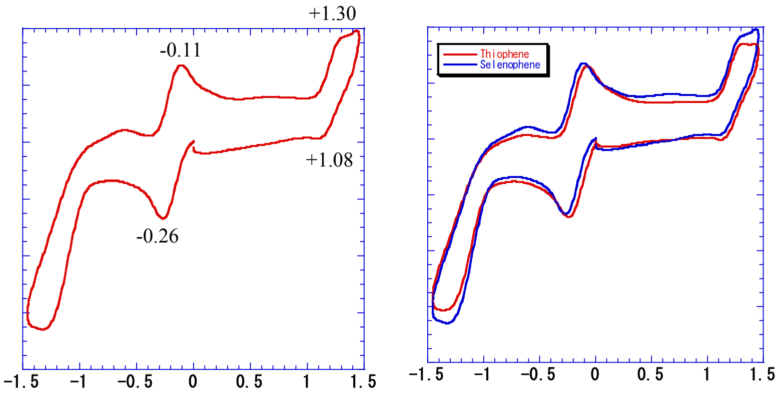


Fig. S4 Cyclic voltammogram of **2**. Redox potential of Fc/Fc$^+$ under identical conditions was +0.46 V.

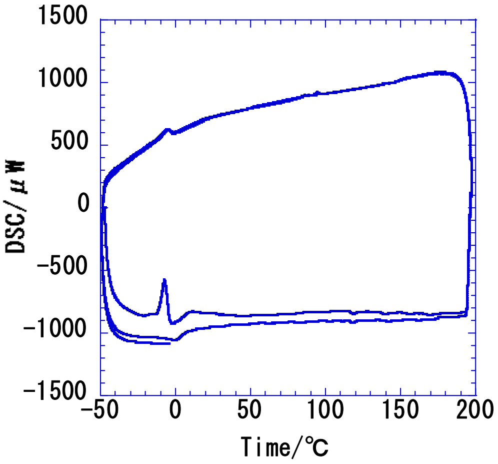


Fig. S5 DSC trace of **2**.

4. UV-vis spectra of thin films

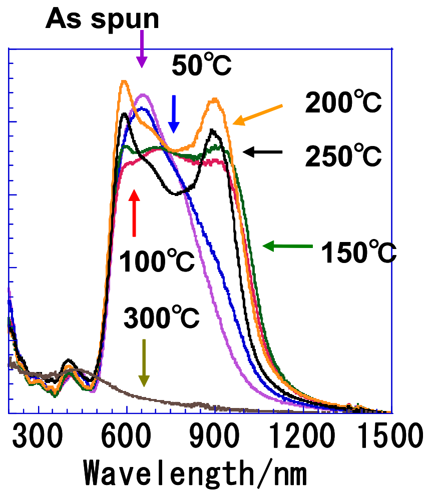


Fig. S6 UV-vis spectra of spin-coated thin film of **2**: annealing at 150~200 °C produced a characteristic shoulder at ca 1000 nm. However, higher annealing temperature than 200 °C weakened the peaks due to the thermal decomposition.

5. Device fabrications and evaluations

Fabrication of the OFETs was carried out at ambient conditions without taking any precautions to isolate from ambient oxygen, moisture or light. The devices were fabricated on a heavily doped n^+-Si (100) wafer with a 200 nm thermally grown SiO_2 (C_i = 17.3 nF cm^{-2}) as the gate dielectric. The SiO_2 surface was modified with an OTS (octyltrichlorosilane) SAM (self-assembled monolayer) by immersing the Si/SiO_2 substrate in 1 mM OTS in toluene at room temperature for 24 h. A semiconductor layer was first deposited on the OTS-modified SiO_2 substrate by spin-coating a 0.4 wt% solution of **3** in chloroform at 2000 rpm for 30 sec, and dried in air. Before deposition of source and drain electrode films were thermally annealed at 150 °C for 30 min under argon atmosphere.

On top of the organic thin film, gold films (ca. 80 nm) as drain and source electrodes were vacuum-deposited through a shadow mask (back pressure: ~1×10^{-4} Pa). The drain-source channel length (L) and width (W) are 50 μm and ca. 1.5 mm, respectively. Characteristics of the OFET devices were measured at room temperature in air with a Keithly 4200 semiconductor parameter analyzer. The field-effect mobility (μ_{FET}) was calculated in the saturation regime of the I_{ds} using the equation, $I_d = (WC_i/2L)\ \mu_{\mathrm{FET}}\ (V_g - V_{th})^2$, where C_i is the capacitance of the SiO_2 insulator, V_g and V_{th} are the gate and threshold voltages, respectively.

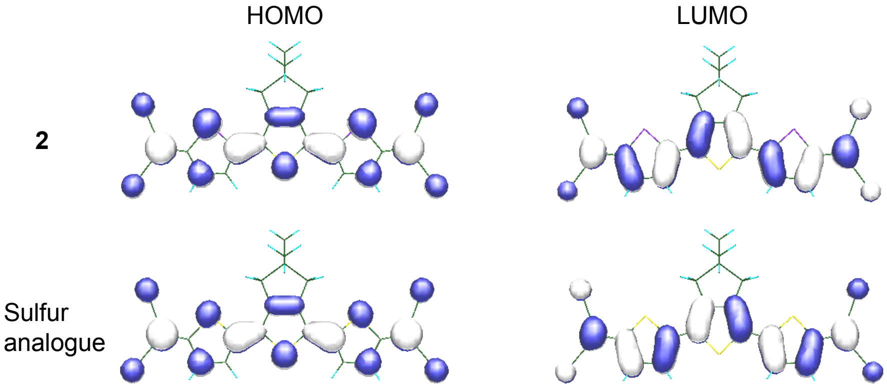
6. MO calculations

MO calculations were carried out by DFT methods at the B3LYP-6-31G(d) level using the Gaussian03 program.[S6]

The calculated HOMO and LUMO levels of **2** and its all sulfur analogue are listed in Table S1. Compound **2** has a slightly lower HOMO and LUMO energy levels, which are qualitatively consistent with the experimentally estimated data.

Table S1 Calculated frontier levels of **2** and the all sulfur analogue (**1**).

	HOMO / eV	LUMO / eV
2	–5.8489	–4.1953
1 (sulfur analogue)	–5.8725	–4.2463



7. References

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