

Electronic supplementary information

Vacuum processable donor material based on dithieno[3,2-b:2',3'-d]thiophene and pyrene for efficient organic solar cells

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Materials and instruments

All chemicals were purchased from commercial suppliers and used as received unless otherwise specified. 2,6-Dibromodithieno[3,2-b:2',3'-d]thiophene¹⁸ was prepared according to the literature procedure. **DDT** was purified by temperature gradient vacuum sublimation prior to use using a digital optic and vacuum (DOV) sublimation instrument. Mass spectra were obtained using a MALDI-TOF mass spectrometer from Bruker. Elemental analysis (EA) was performed with a Carlo-Erba model EA 1112 elemental analyzer. Thermogravimetric analysis (TGA) was carried out on a TGA Q-5000-IR (TA instrument) at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere. Differential scanning calorimetry (DSC) analysis was performed on a DSC-Q-1000 at 10 °C min⁻¹ under nitrogen flow. Absorption (UV) spectra were recorded on a Beckman DU 650 spectrophotometer. Emission (PL) spectra were recorded on a Jasco FP-7500 spectrophotometer. For solid-state measurements, materials were thermally vapor deposited onto quartz plates in a vacuum chamber to form 30 nm thick films. The cyclic voltammetric apparatus used was a CH Instruments model 700 C electrochemical workstation. Cyclic voltammograms were obtained at room temperature in a three-electrode cell with a working electrode (Au), a reference electrode (Ag/AgCl), and a counter electrode (Pt), in dichlorobenzene containing TBAPF₆ as a supporting electrolyte, at a scan rate of 0.1 Vs⁻¹. All potentials were calibrated with the standard ferrocene/ferrocenium (Fe/Fe⁺) redox couple. Molecular orbital (MO) calculations were carried out by density functional theory (DFT) methods at the B3LYP-6-31G (d, p) level using the Gaussian 03 program. Atomic force microscopy (AFM) experiments were performed using an Asylum MFP-3D instrument in AC mode with Si₃N₄ cantilevers. X-ray diffraction (XRD) analyses were carried out with a Rigaku (k= 1.5418 Å, 298 K) X-ray instrument.

Synthesis

2,6-di(pyren-1-yl)dithieno[3,2-b:2',3'-d]thiophene (DDT): A mixture of 2,6-dibromodithieno[3,2-b:2',3'-d]thiophene (1.43 g, 4.04 mmol), 1-pyreneboronic acid (2.50 g, 10.1 mmol), potassium carbonate (2 M, 20 mL), and palladium tetrakis(triphenylphosphine)

(233 mg, 0.202 mmol) in THF (100 mL)/H₂O (20 mL) was heated at 80 °C for 72 hr. After cooling to room temperature, the mixture was vacuum filtered using a Büchner funnel, and then dried at room temperature. The resulting product was sublimated using a vacuum sublimation apparatus (Yield: 1.07 g 44.3%). Mass: calcd. for C₄₀H₂₀S₃ [M]⁺ 596.0727, HR-Mass: 596.0740. EA: Anal. calcd. for C₄₀H₂₀S₃, C 80.50, H 3.38, S 16.12%, found: C 80.50, H 3.30, S 16.11%.

OSC fabrication

To investigate the organic solar cell device performances of **DDT**, two types of devices were fabricated. The first device had the configuration of ITO/MoO₃ (5 nm)/**DDT** (10, 20, 30 nm)/C₇₀ (40 nm)/BCP (8 nm)/Al (100 nm). The second device was made from ITO/MoO₃ (5 nm)/**DDT**:C₇₀ = 1:1, 1:4 (50 nm)/BCP (8 nm)/Al (100 nm). MoO₃ of 5-nm thickness was used as a hole injection layer. Active layers were fabricated using two different methods: i) thin films of **DDT** with thicknesses ranging from 10 nm to 30 nm were prepared by a vapor deposition process. A fullerene C₇₀ (40 nm) layer, used as an acceptor, was then vapor deposited. ii) thin films of **DDT**:C₇₀ = 1:1, 1:4 (50 nm) were prepared by a vapor co-evaporation process. Next, a BCP layer of 8-nm thickness (to be used as an exciton blocking layer) was vapor deposited, and finally, an aluminum layer of 100-nm thickness was vapor deposited onto the BCP layer. The hole only device of **DDT** was made from ITO/MoO₃ (3 nm)/**DDT** (60 nm)/MoO₃ (10 nm)/Al (100 nm). All the layers were successively evaporated onto substrate at a rate of 1 Ås⁻¹ without breaking the vacuum. The devices had active areas of 2×2 mm². A patterned insulator on the ITO and the top cathode deposited through a shadow mask defined the cell area. After fabrication, the devices were encapsulated using epoxy resin with glass cans in an N₂ environment. The current (*J*)–voltage (*V*) measurements of the devices were performed on a Keithley 237 instrument. The device performances were characterized under uniform illumination using a solar simulator. The light intensity at each wavelength was calibrated using the standard Si solar cell as a reference.

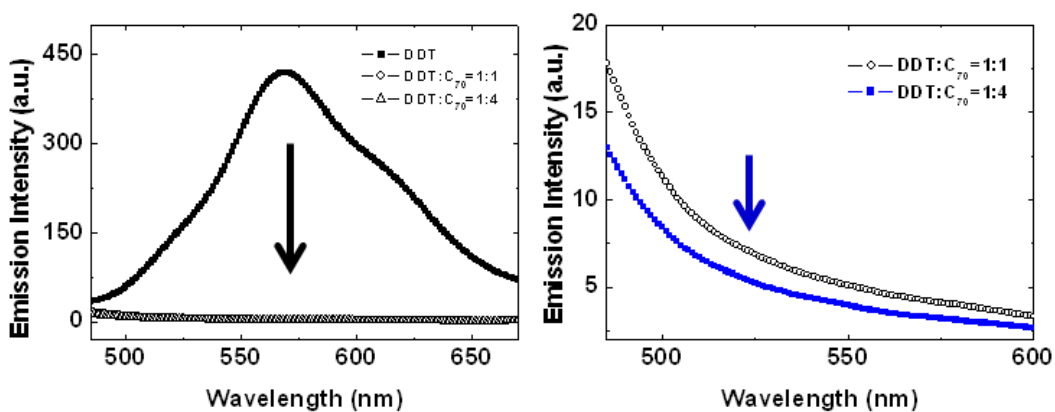


Fig. S1. PL spectra of **DDT**, **DDT:C₇₀=1:1**, and **DDT:C₇₀=1:4** at 450 nm excitation in the solid film state.

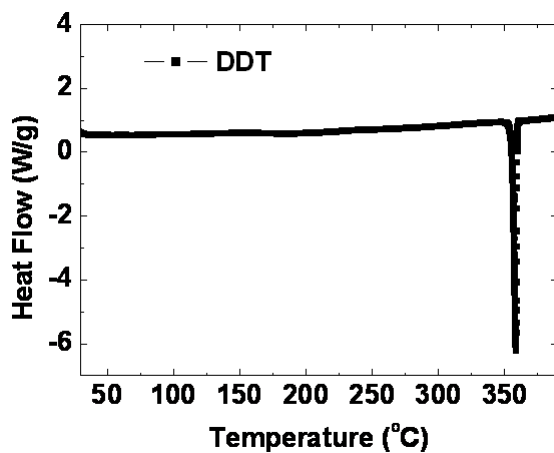


Fig. S2. DSC data of **DDT**.

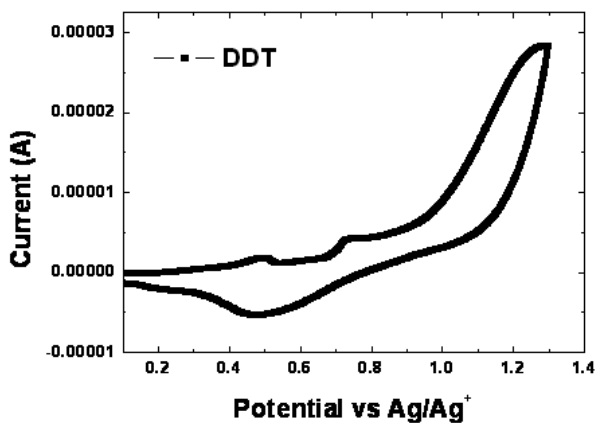


Fig. S3. Cyclic voltammogram of **DDT** in ODCB.

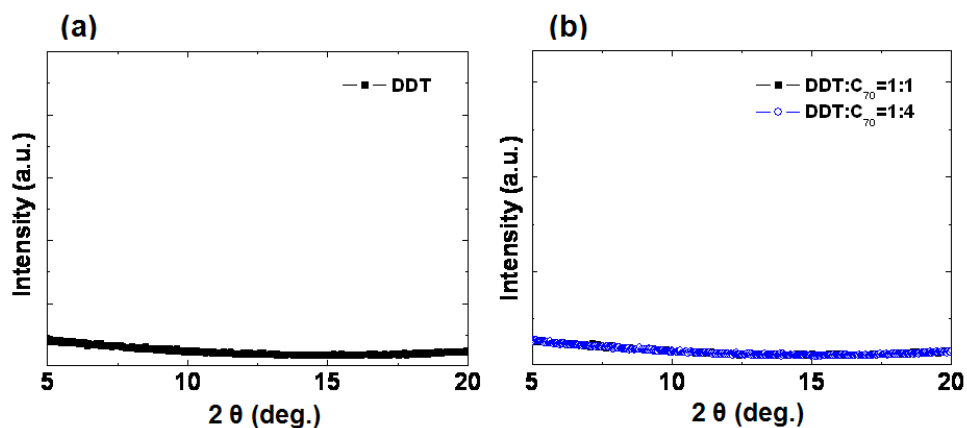


Fig. S4. XRD patterns of **DDT** (a), **DDT:C₇₀=1:1** (b), and **DDT:C₇₀=1:4** (b) deposited thin films.

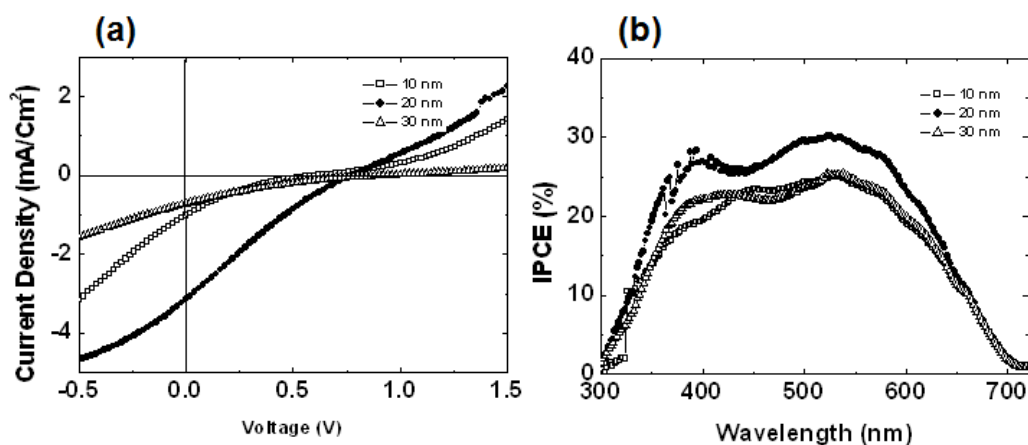


Fig. S5. (a) *J*-*V* characteristic curves and (b) IPCE spectra of the OSCs with the following structure: ITO/MoO₃ (10 nm)/**DDT** (10, 20, 30 nm)/C₇₀ (40 nm)/BCP (8 nm)/Al (100 nm). The *J*-*V* characteristics were measured under AM 1.5G 100 mW cm⁻² solar simulated light irradiation.

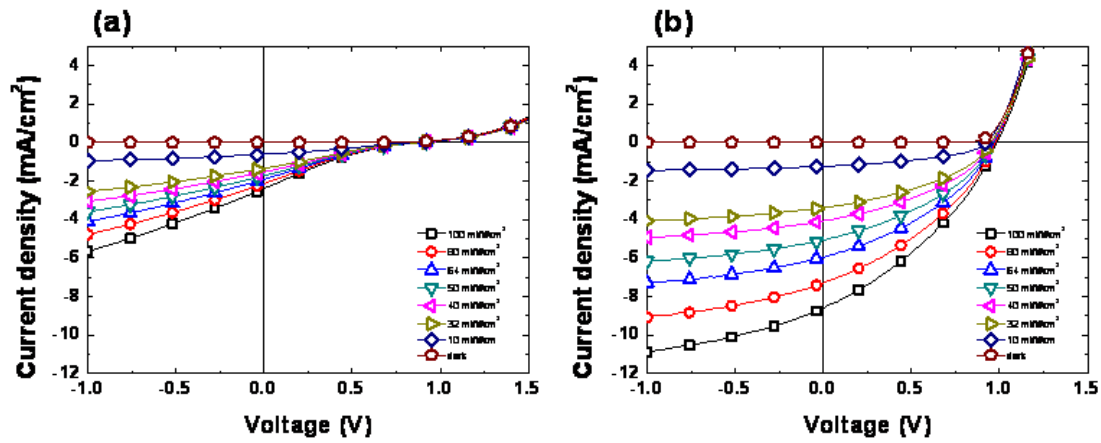


Fig. S6. J - V characteristic curves of the device with **DDT**: C_{70} =1:1 (a) and **DDT**: C_{70} =1:4 (b) are measured under various intensity of the solar simulated light. The light intensity was controlled from 10 mWcm^{-2} to 100 mWcm^{-2} by using the AM 1.5G solar simulated light source with the neutral density filter.

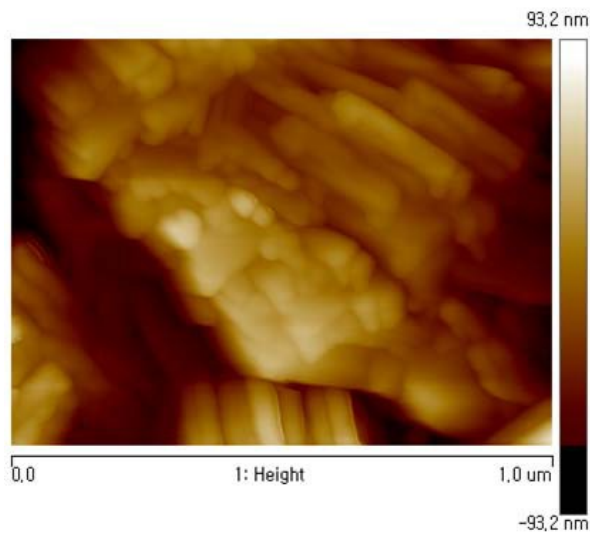


Fig. S7. $1 \times 1 \mu\text{m}$ AFM image of **DDT** deposited thin film.

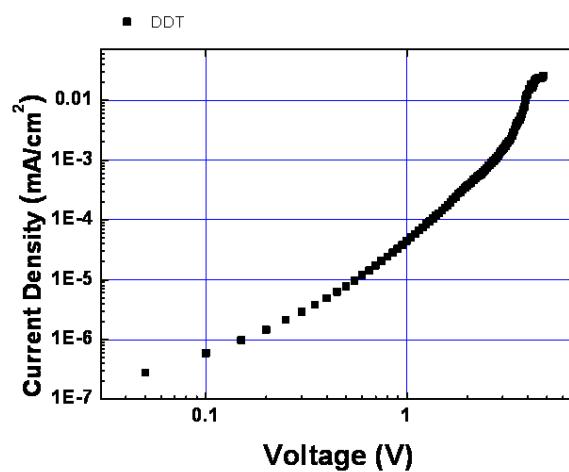


Fig. S8. J - V characteristic of the hole-only devices of ITO/MoO₃/DDT (60 nm)/MoO₃/Al.