

SUPPORTING INFORMATION

Dithienogermole-Based Solution-Processed Molecular Organic Solar Cells with Efficiency Over 9%

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1. Materials. 4,7-Dibromo-5-fluorobenzo[*c*][1,2,5]thiadiazole (FBT-Br₂) was purchased from 1-Material Organic Nano Electronic Corporation. Compound 1 was synthesized in our labs via standard procedures. Toluene was purified according to standard procedures and distilled under nitrogen before use.

2. Measurements.

2.1. General. Nuclear magnetic resonance (NMR) spectra were obtained on a Varian Unity Inova 500 MHz and an actively shielded Varian Unity Inova 600 MHz spectrometer. Microwave assisted reactions were performed in a Biotage Initiator TM microwave reactor. Differential scanning calorimetry (DSC) was determined by a TA Instruments DSC (Model Q-20) with about 5 mg polymers samples at a rate of 10 °C/min in the temperature range of -20 to 300 °C. UV-Vis absorption spectra were recorded on a Shimadzu UV-2401 PC dual beam spectrometer. Cyclic voltammetry (CV) measurements were conducted using a standard three-electrode configuration under an argon atmosphere. A three-electrode cell equipped with a glassy carbon working electrode, an Ag wire reference electrode, and a Pt wire counter electrode was employed. The measurements were performed in acetonitrile with tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte at a scan rate of 50-100 mV/s. DTG(FBT₂Th₂)₂ films for CV test were drop-casted onto the glassy carbon working electrode from a 2 mg/mL chloroform solution. The absolute energy level of ferrocene/ferrocenium (Fc/Fc⁺) redox couple used for these studies was 4.8 eV below vacuum.

2.2. Device fabrication. ITO-coated glass substrates (20 Ω/□) were cleaned by ultrasonic agitation in detergent, deionized water, acetone and isopropanol sequentially, followed by UV ozone treatment for 10 min. The hole transport material of PEDOT:PSS (Clevious PH) was

spin-coated at 5000 rpm for 60 s to obtain the film thickness of ~ 30 nm. The DTG(FBT₂Th₂)₂:PC₇₁BM (50/50) blend solution was prepared in chlorobenzene and 5 wt.% chloroform with 0.4 vol % of DIO processing additive from the weight of 35 mg/mL. The solution was stirred at 60°C overnight. Before spin casting, the prepared solution was heated at 90 °C for 15 min. The BHJ film was obtained from spin-casting the solution at 1500 rpm for 45 s. The coated BHJ films were annealed at 80 °C for 15 min to evaporate residual solvent. The thickness of the BHJ film is ~ 100 nm, determined by a surface profiler. Then, the Ca layer was thermally evaporated with the thickness 20 nm, and the Al cathode was continuously deposited to ~ 80 nm at the vacuum condition of 10^{-6} Torr. The fabricated solar cells were encapsulated with epoxy and cover glass.

2.3. Device characterization. The J-V characteristics of the solar cells were measured by a Keithley 2420 source meter unit. The light source was calibrated by using silicon reference cells with an AM 1.5G solar simulator with an intensity of 100 mW/cm². The *J-V* curves and PCE parameters of V_{OC} , J_{SC} , FF were obtained under exposure to AM 1.5 solar simulator with the intensity of 100 mW/cm². During the testing, an aperture with an area of 6 mm² was used to accurately measure the performance of solar cells.

2.4. Thin Film Characterization. The nanomorphology of pristine DTG(FBT₂Th₂)₂ film and p-DTG(FBT₂Th₂)₂:PC₇₁BM BHJ film were investigated by AFM (AFM Asylum MFP3D) to characterize the surface morphology. XRD measurements were carried out by a diffractometer (Rigaku Smartlab high-resolution diffractometer). The films were spin-cast on ITO/PEDOT:PSS and glass for AFM and XRD measurements, respectively. The absorption was measured by a UV-vis-NIR spectrophotometer system (PerkinElmer Lambda 950).

3. Synthesis. Br-FBT-DTG-FBT-Br (2). In a N₂ filled glove box, a 20 mL glass tube was charged with FBT-Br₂ (830 mg, 2.65 mmol), 5,5'-bis(trimethylstannyl)-3,3'-di-2-ethylhexylgermole-2,2'-bithiophene (843 mg, 1.07 mmol), Pd(PPh₃)₄ (75 mg, 0.06mmol) and toluene (15 mL), then sealed with a Teflon® cap. The reaction mixture was heated to 80 °C for 48 h. Upon cooling, the material was then loaded onto silica gel and purified by flash chromatography using *n*-hexane/dichloromethane gradient. After fraction collection and solvent removal, a red solid was obtained. Recovered yield: (677 mg, 72%). ¹H NMR (500 MHz, CDCl₃): δ = 8.20–8.18 (t, *J* = 4.29 Hz, 2H, DTS), 7.70–7.68 (d, *J* = 10.10 Hz, 2H, FBT), 1.60–1.54 (m, 4H, EH), 1.43–1.21 (m, 19H, EH), 0.85–0.79 (m, 12H, EH) ppm.

Synthesis of DTG(FBT₂Th₂)₂. In a N₂ filled glove box, a 5 mL glass tube was charged with 3 (100 mg, 0.17mmol), Br-FBT-DTG-FBT-Br (2) (81 mg, 0.08 mmol), Pd(PPh₃)₄ (12 mg, 0.01mmol) and toluene (3 mL), and sealed with a Teflon® cap. The reaction mixture was heated to 100 °C for 1 minute, 120 °C for 1 min, 140 °C for 10 min, 150 °C for 10 min, and 160 °C for 40 min using a Biotage microwave reactor. Upon cooling, the material was then loaded onto silica, washed with methanol and purified by flash chromatography using *n*-hexane/dichloromethane gradient *in duplicate*. After fraction collection and solvent removal, a purple solid was obtained. The solid was slurried in a 3:1 mixture of methanol and *n*-hexane, sonicated for 1 hour and stirred overnight. The suspension was filtered, washed with acetone and dried in vacuo. The product was recovered as a purple solid. Recovered yield: (135 mg, 49 %). ¹H NMR (600 MHz, 1,1,2,2-tetrachloroethane-d₂): δ = 8.16–8.05 (m, 6H, Ar), 7.80 (s, 2H, Ar), 7.52–7.50 (m, 4H, Ar), 6.73 (s, 2H, Ar), 2.77 (s, 4H, alkyl), 1.49–1.32 (m, 32H, alkyl), 0.97–0.88 (m, 24H, alkyl) ppm. FD-TOF MS: Calculated for C₇₆H₇₄F₄GeN₈S₁₀: 1568.2. Found: 1568.2 (M⁺), 784.1 (M²⁺).

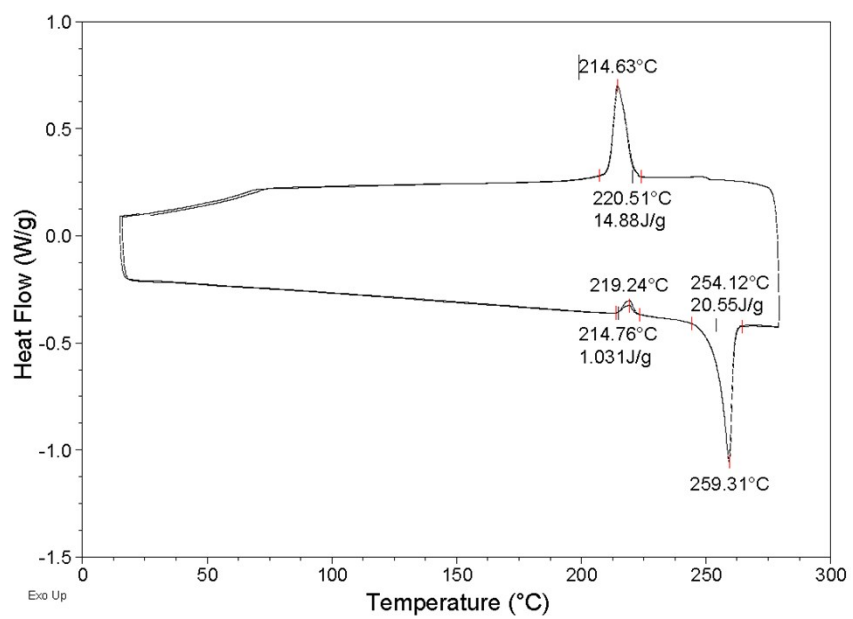


Figure S1. Differential scanning calorimetry (DSC) of DTG(FBT₂Th₂)₂ molecule.

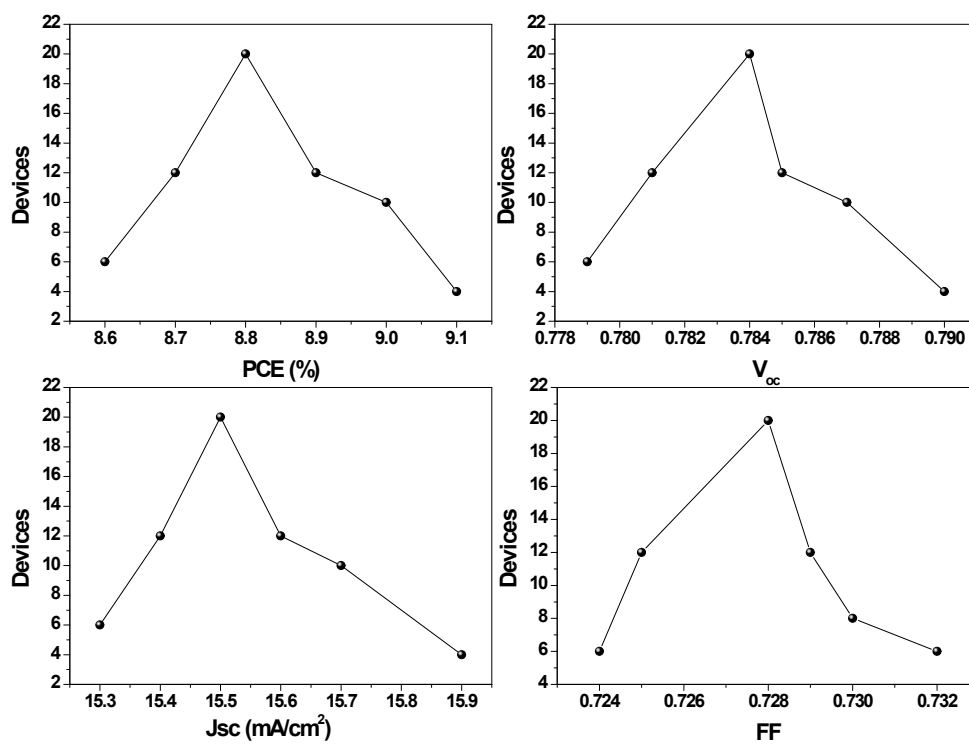


Figure S2. The average performance values of DTG(FBT₂Th₂)₂/PC₇₁BM devices.

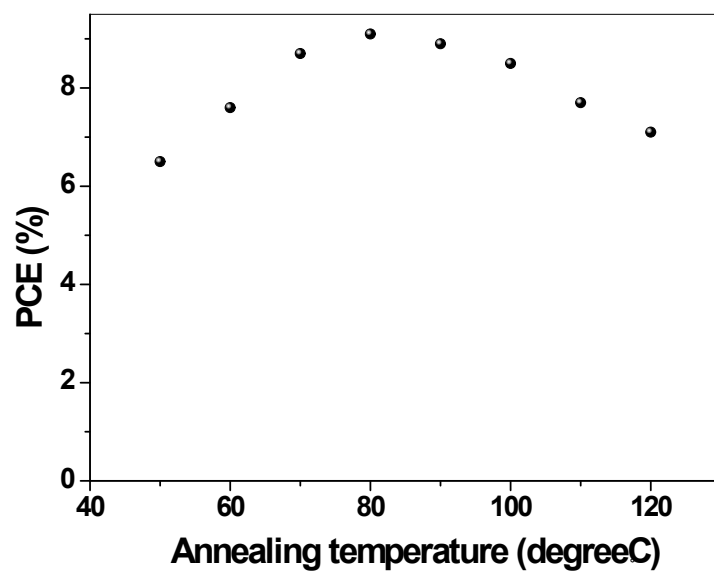


Figure S3. Temperature dependence of performance of DTG(FBT₂Th₂)₂/PC₇₁BM devices

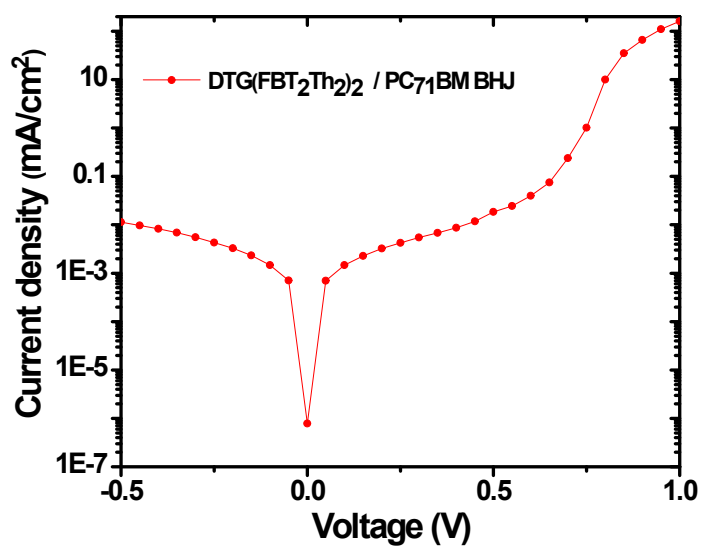


Figure S4. Dark J-V curve of DTG(FBT₂Th₂)₂/PC₇₁BM BHJ solar cell.

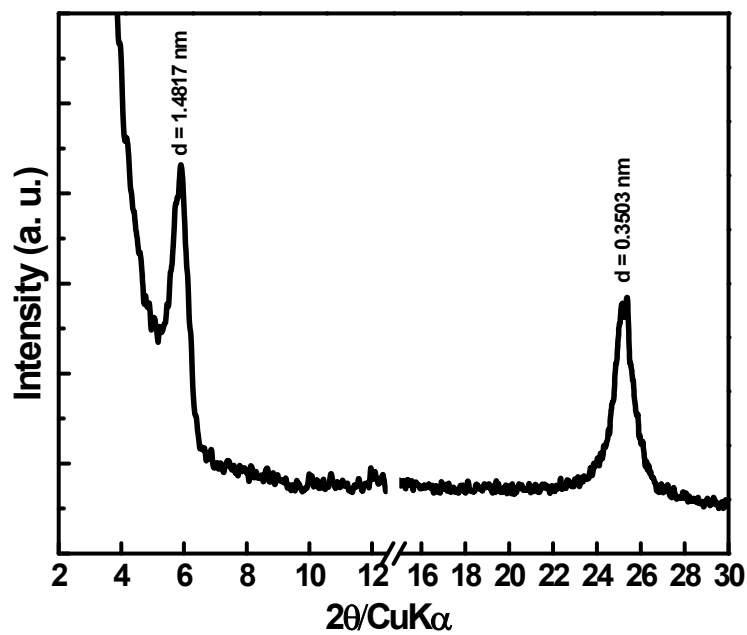


Figure S5. X-Ray diffraction (XRD) data of the DTG(FBT₂Th₂)₂ film.

The film preparation was identical to that of device fabrication. Out-of-plane X-ray scans reveal a sharp peak with high intensity at $2\theta \approx 5.96^\circ$ ($d \approx 1.48$ nm). This spacing is most reasonably assigned to the lattice spacing for the alkyl groups which is well study for p-DTS(FBTTh₂)₂ molecule^{1,2}. In-plane incidence X-ray scans reveal fundamental reflection at $2\theta \approx 25.4^\circ$ corresponding to a d-spacing of 0.35 nm which is lower than that of 0.36 nm, as reported p-DTS(FBTTh₂)₂^{1,2}, indicative of π - π stacking, with strong intermolecular interaction along the π - π stacking direction.

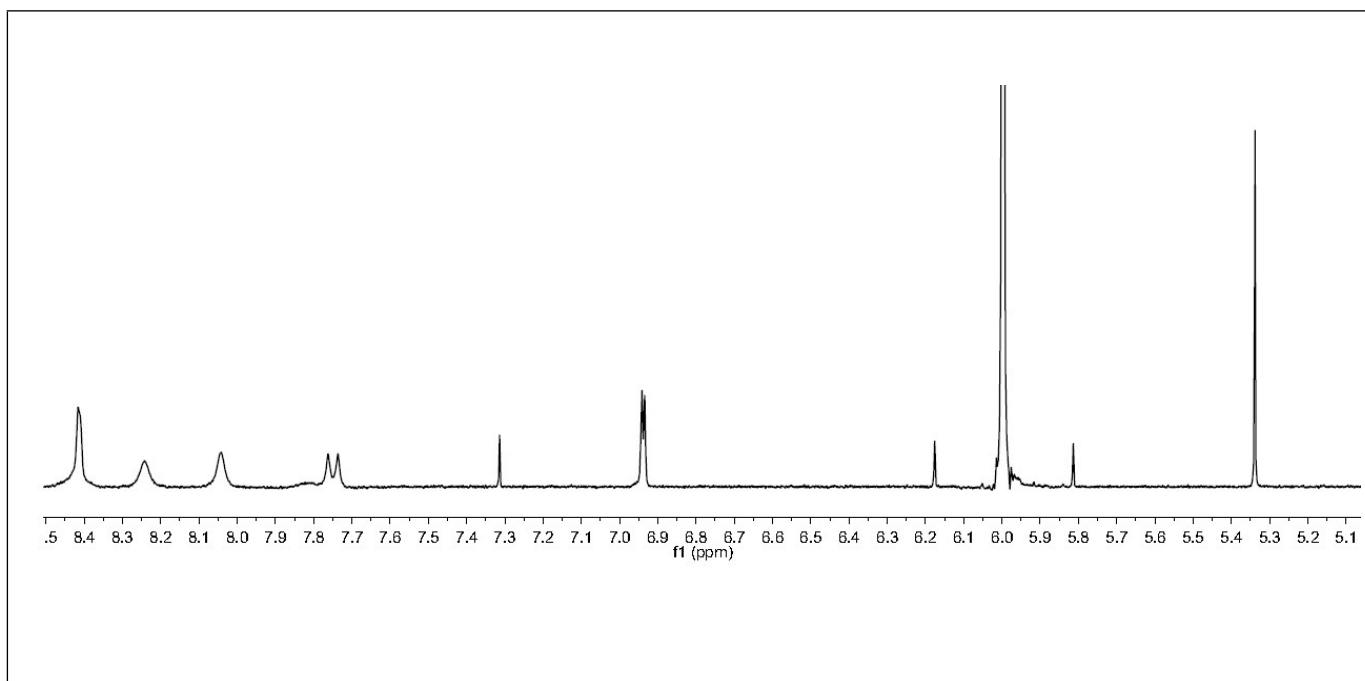


Figure S6. ¹H NMR spectrum of DTG(FBT₂Th₂)₂ in 1,1,2,2-tetrachloroethane-d₂ at 80 °C

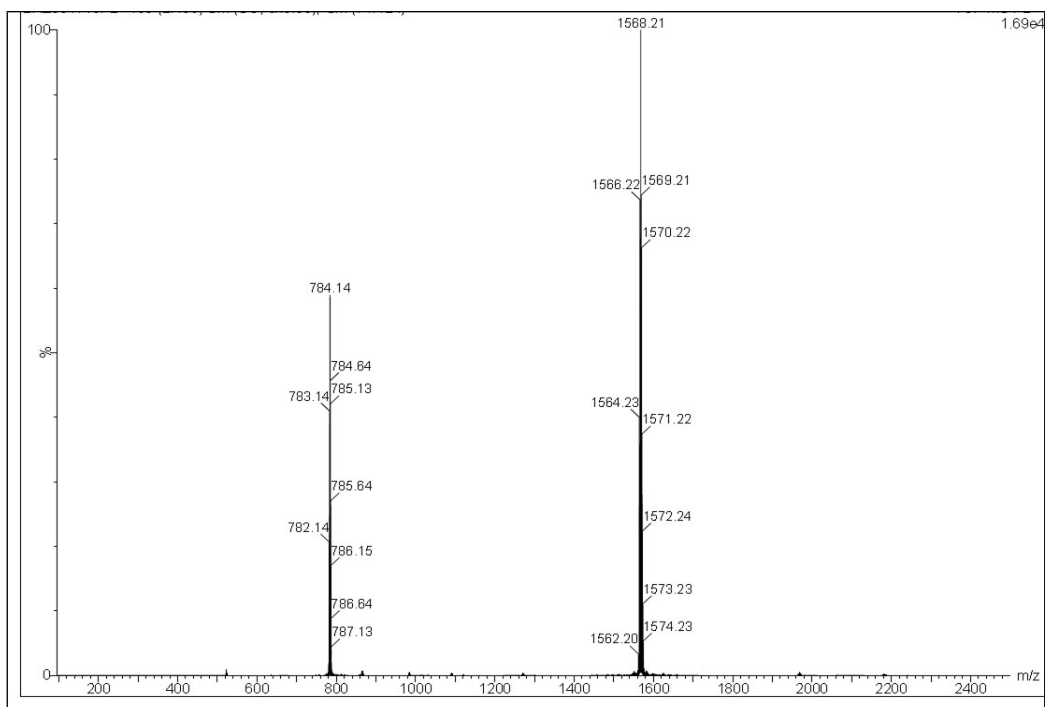


Figure S7. Mass spectrum of DTG(FBT₂Th₂)₂.

References

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2. Love, J. A.; Proctor, C. M.; Liu, J.; Takacs, C. J.; Sharenko, A.; van der Poll, T. S.; Heeger, A. J.; Bazan, G. C.; Nguyen, T.-Q. *Adv. Funct. Mater.* **2013**, *23*, 5019.