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Supplementary Information

A high mobility conjugated polymer based on dithienothiophene and diketopyrrolopyrrole for organic photovoltaics

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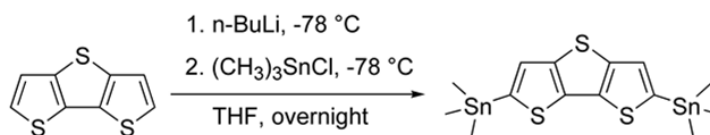
1. Characterization

^1H NMR spectra were obtained from a Bruker Avance DPX 300 or Bruker Avance 500 NMR spectrometer with deuterated chloroform as a solvent. TGA was performed on Perkin Elmer TGA7. Size exclusion chromatography was performed on Agilent 1200 GPC System (eluted with CHCl_3). The working temperature was room temperature, and the concentration of the samples was 1.0 mg mL^{-1} . Prior to the analysis, the solution was stirred at $50 \text{ }^\circ\text{C}$ for 24 h, and then at room temperature for 2 h and filtered with PTFE $0.45 \text{ }\mu\text{m}$ syringe filter. The molecular weights were calculated according to relative calibration with polystyrene standards and toluene as a flow marker. Elemental analysis was performed on Flash Elemental Analyzer 1112. TGA analysis was undertaken using a TA Instrument Q500 with a heating rate of $20 \text{ }^\circ\text{C}/\text{min}$. UV-Vis absorption spectra were measured with a Lambda 25 (Perkin Elmer) spectrometer. Cyclic voltammetry experiments were carried out on a potentiostat/galvanostat (VMP 3, Biologic) in an electrolyte solution of 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile. Platinum wire and gold electrode were used as a counter and a working electrode, respectively, and silver/silver ion (Ag in 0.1 M AgNO_3 solution) was used as a reference electrode. The architecture of the solar cell device is ITO/PEDOT:PSS/active layer/LiF/Al. The active layer solution was spin coated onto the PEDOT:PSS (Clevious AI 4083, 40 nm of thickness) coated ITO glass. For optimization, a mixture of chloroform (CF), *o*-dichlorobenzene (DCB), and diiodooctane (DIO) was used as a solvent. After drying completely, LiF (1 nm) and Al (100 nm) were thermally deposited as a cathode under 5×10^{-6} Torr. The photovoltaic performance was measured under nitrogen atmosphere inside a glove box. The current density-voltage (J-V) characteristics were measured with a Keithley 2400 source-meter under AM 1.5 G ($100 \text{ mW}\cdot\text{cm}^{-2}$) simulated by a Newport-Oriel solar simulator. The light intensity was calibrated using a NREL-certified photodiode and light source meter prior to each measurement. The active area was 0.06 cm^2 . The incident photon-to-current efficiency (IPCE) was measured using a lock-in amplifier with a current preamplifier under short circuit current state with illumination of monochromatic light. The thin film morphology was characterized by Atomic Force Microscopy (AFM) with a Dimension 3100 system (Digital Instruments/Veeco) operating in tapping mode and Transmission Electron Microscopy (TEM) with a JEOL 2000 FX MARK II operating in 200 kV of acceleration voltage. The AFM measurement was performed on the solar cell device where the cathode was not deposited. For TEM measurement, the solar cell device was immersed in deionized water and then the active layer was floated onto the Cu grid. Grazing incidence wide angle x-ray scattering spectra were obtained at the Advanced Light Source at the Lawrence Berkeley National Laboratory. The experimental set-up and sample cell were designed for the surface studies on thin films. The PDTPDPP solution in CF was spin coated on UV- O_3 treated Si wafer. An X-ray beam impinged onto the sample at a grazing angle above and below the critical angle of the polymer film ($\alpha_c=0.16$), but below the critical angle of the silicon substrate ($\alpha_c=0.22$). The wavelength of X-rays used was 1.240 \AA , and the scattered intensity was detected by using two-dimensional charge-coupled device camera with image sizes of 2304×2304 pixels.

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2. Preparation of monomers

2.1. 2,6-Bis-trimethylstannanyl-dithieno[3,2-*b*;2',3'-*d*]thiophene (DTT)



After dithieno[3,2-*b*;2',3'-*d*]thiophene (0.50 g, 2.55 mmol) was dissolved in 30 mL of anhydrous THF at -78 °C, 8 mL of *n*-butyllithium solution (8 mmol, 1.6 M in hexane) was then added dropwise. After stirring for 30 min, the solution was further stirred for 2 h at room temperature, and then cooled to -78 °C again. After stirring for 30 min, 10 mL of trimethylstannylchloride solution (10 mmol, 1 M in THF) was added to the solution by syringe in one portion. After further stirring for 6 h at room temperature, the reaction was quenched by addition of 30 mL of water. After extraction with diethyl ether three times, organic phases were washed with water and brine, and then dried over MgSO₄. After evaporation of the solvent, the crude product was purified by recrystallization from acetonitrile yielding the pure product as green needles (1.00 g, 75%).

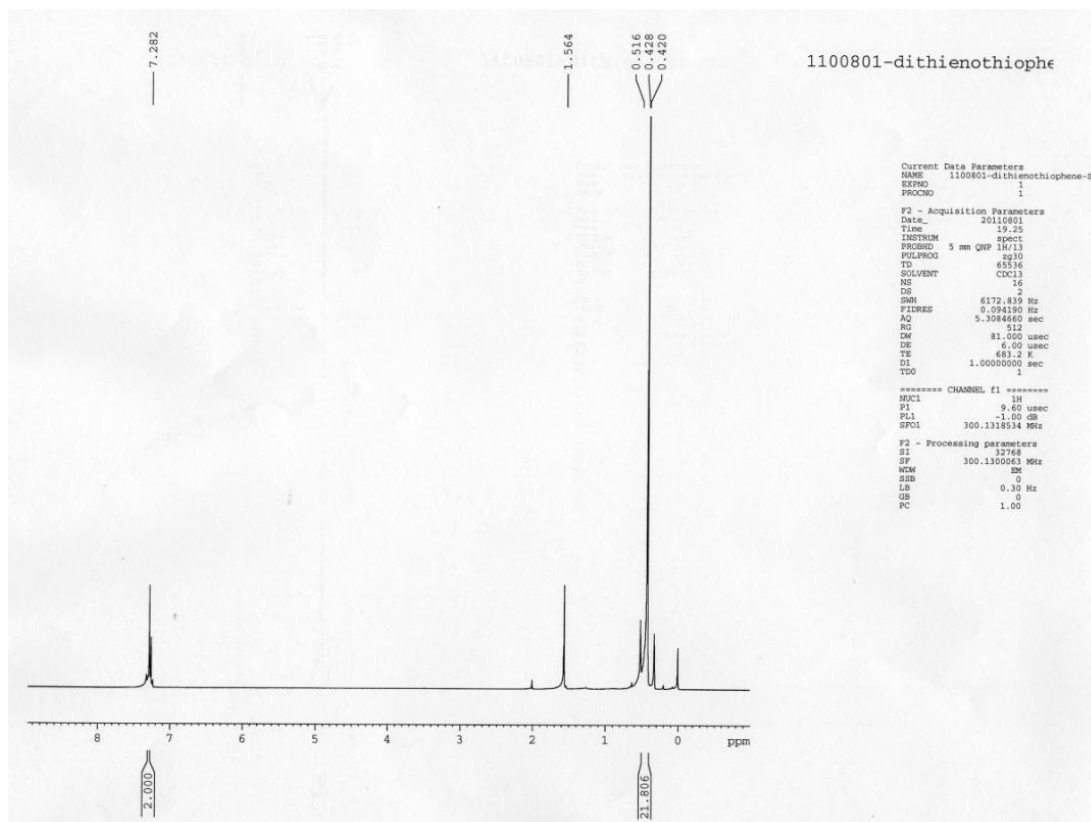


Figure S1. ¹H-NMR spectrum of DTT.

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2.2. 3,6-Bis-(5-bromo-thiophen-2-yl)-*N,N'*-bis(2-octyl-1-dodecyl)-1,4-dioxo-pyrrolo[3,4-*c*]pyrrole (DPP)

DPP was prepared according to the reported method.¹

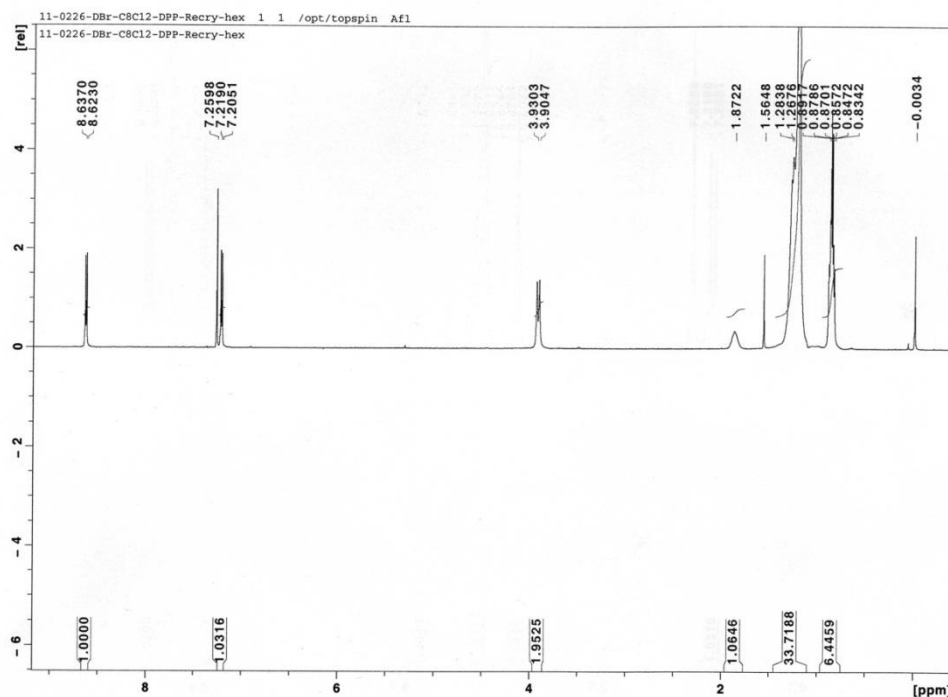
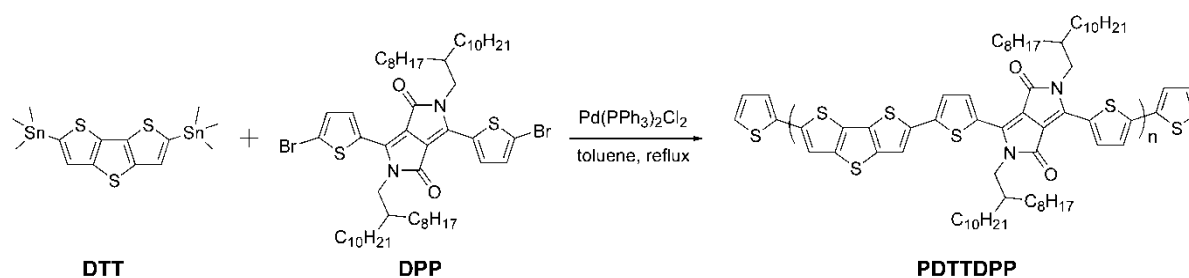


Figure S2. ¹H-NMR spectrum of DPP.

3. Synthesis of PDTTDP



After 87.2 mg of DTT (0.167 mmol) and 170 mg of DPP (0.167 mmol) was dissolved in 5 ml of anhydrous toluene in 25 ml round-bottom flask under nitrogen, the solution was degassed for 30 min, and then 3.5 mg of bis(triphenylphosphine)palladium(II)dichloride (5.3 μ mol) was added to the solution. The solution was refluxed for 48 h, followed by end-capping using 2-bromothiophene and 2-tributyltinthiophene successively. After cooling down to room temperature, the solution was precipitated in methanol, filtered, and then purified by Soxhlet extraction by methanol, acetone, hexane, and then chloroform. Finally the chloroform fraction was concentrated, and then precipitated again in methanol. The dark purple solid was obtained after filtering by PTFE filter and dried overnight. (102 mg, Yield: 85%)

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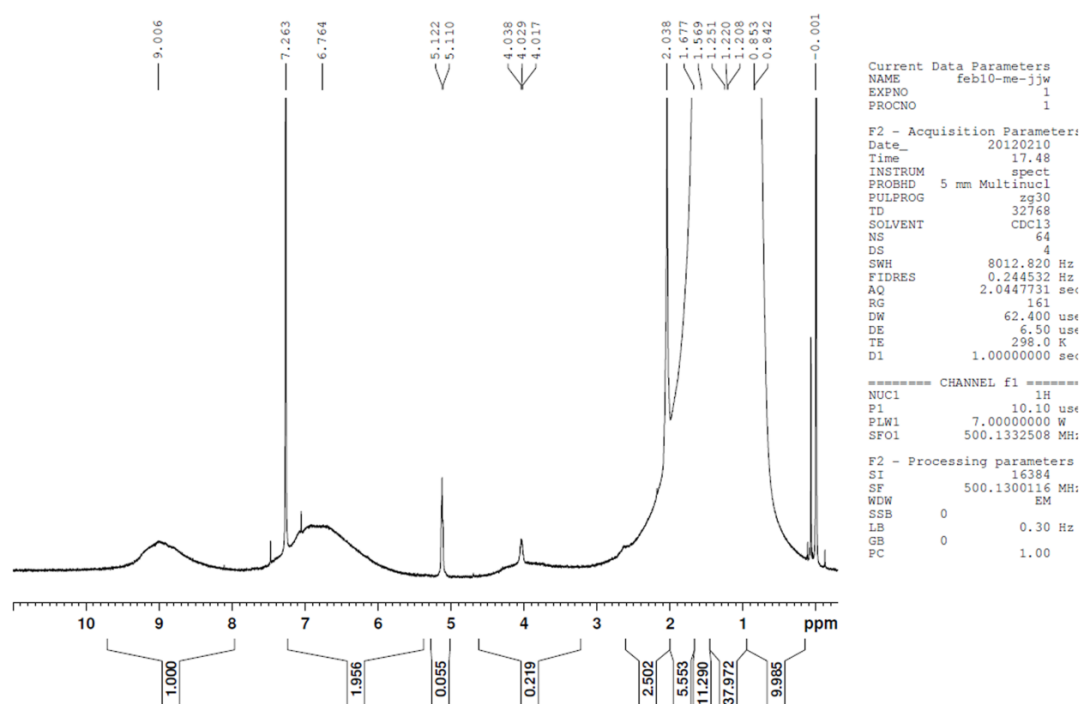


Figure S3. ^1H -NMR spectrum of PDTTDPP.

Elemental Analysis:

Calcd for PDTTDPP, $(\text{C}_{62}\text{H}_{88}\text{N}_2\text{O}_2\text{S}_5)_n$: C, 70.67; H, 8.42; N, 2.66; S, 15.22.
 Found: C, 70.38; H, 8.43; N, 2.67; S, 15.53.

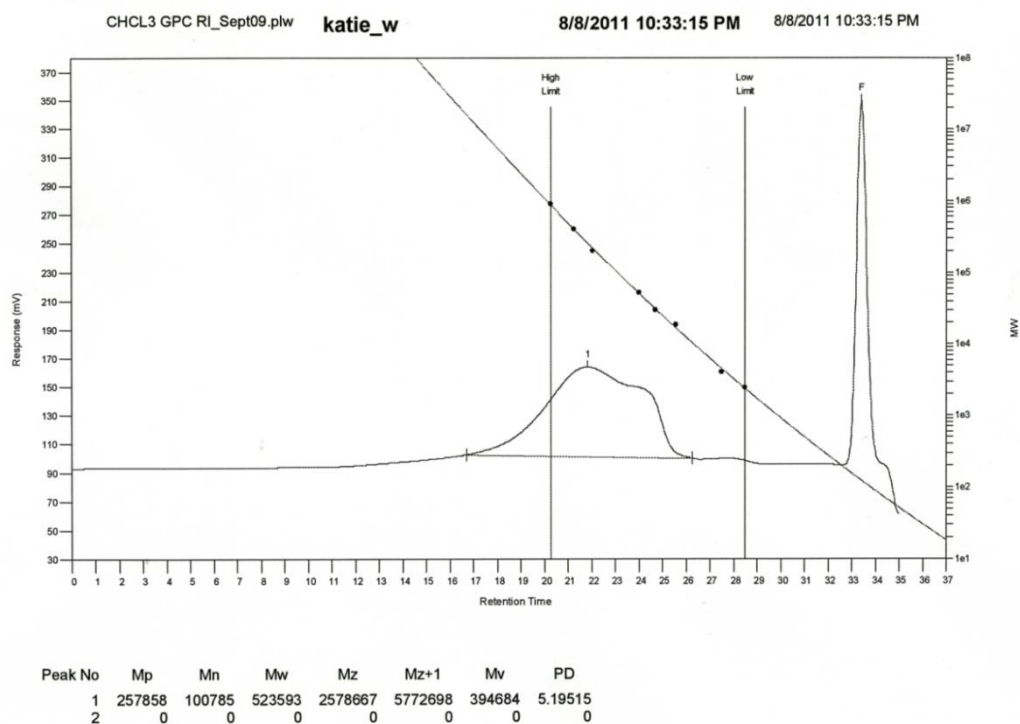


Figure S4. GPC trace of PDTTDPP eluted with CF (reference: polystyrene).

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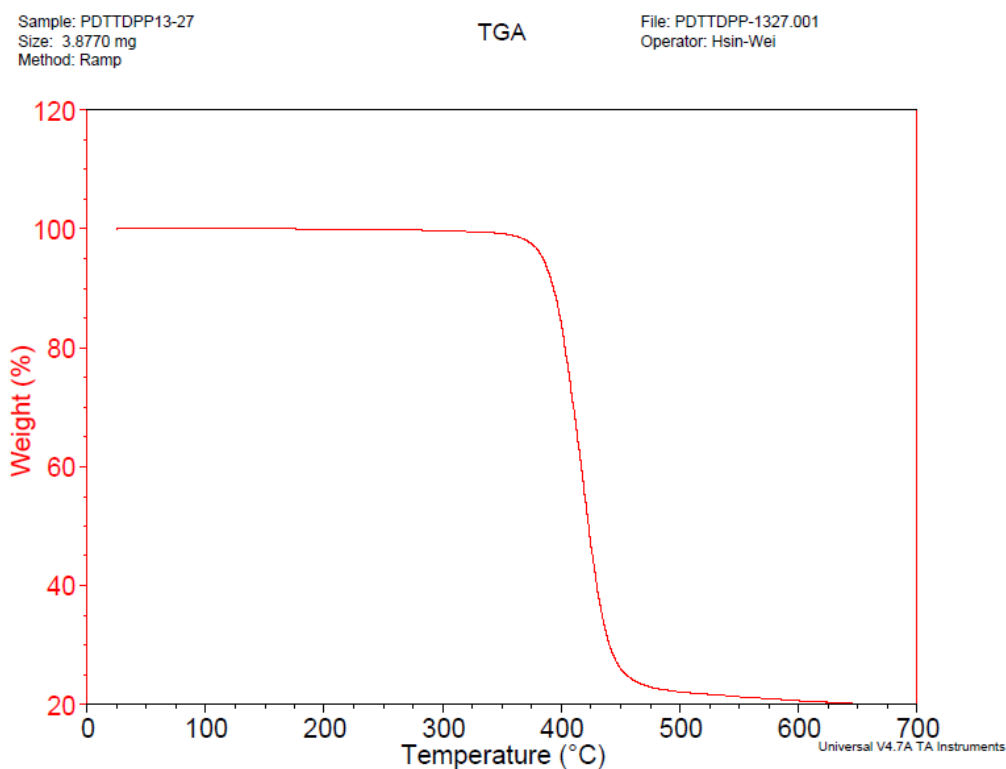


Figure S5. TGA thermogram of PDTTDPP.

4. OFETs of PDTTDPP

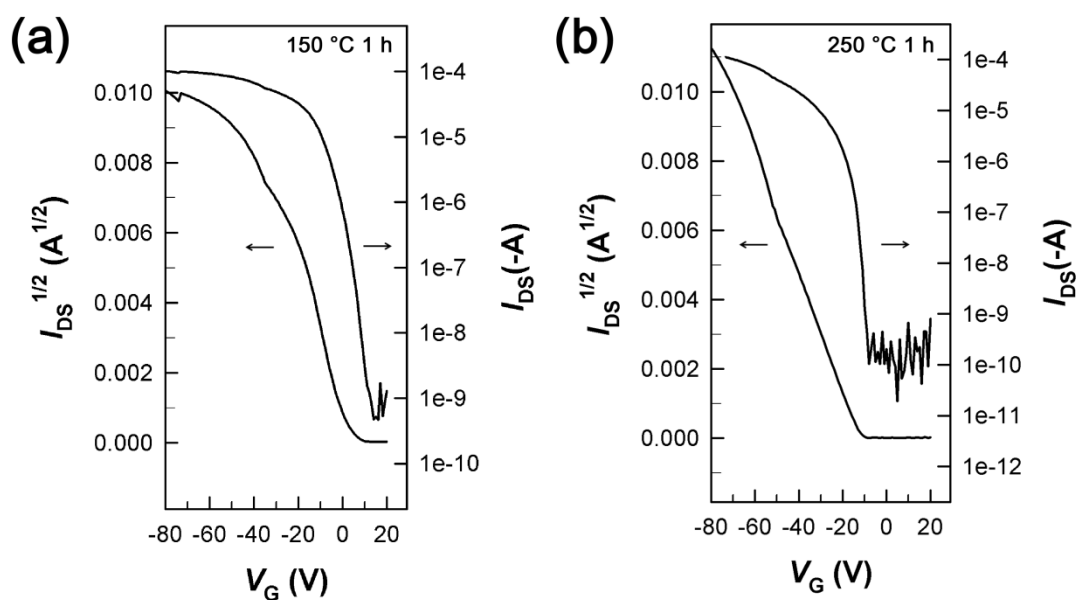


Figure S6. Transfer characteristics of OFETs based on PDTTDPP thin film after thermal annealing at (a) 150 °C ($\mu_{\text{hole}} = 0.70 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$) and (b) 250 °C ($\mu_{\text{hole}} = 0.75 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$).

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5. Photovoltaic properties

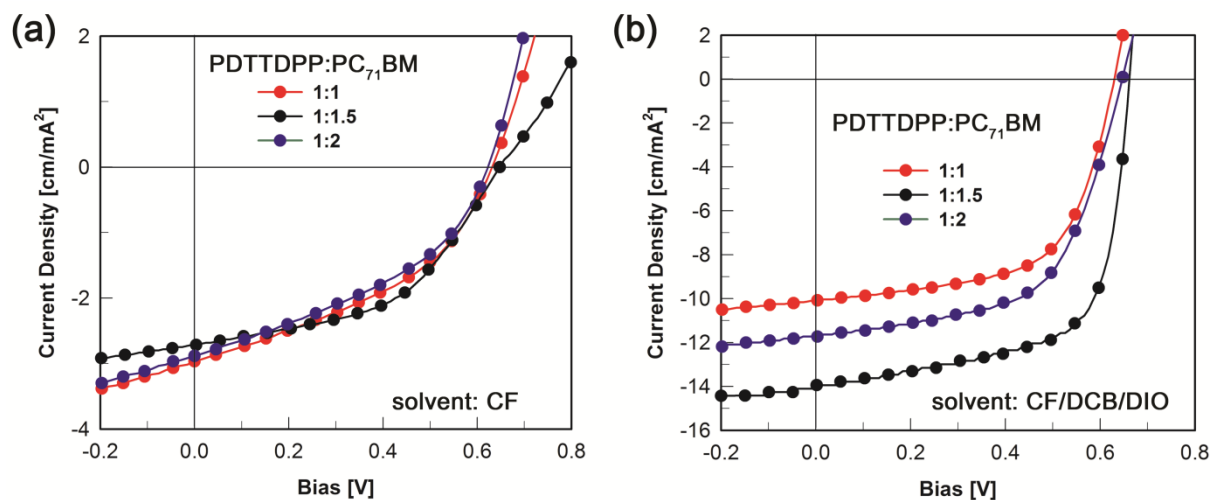


Figure S7. (a) *J-V* curves of OPVs based on PDTTDPP and PC₇₁BM from (a) CF and (b) CF/DCB (4/1 of volume ratio) with 2.5 vol% of DIO as an additive.

Table S1. Summary of photovoltaic properties of PDTTDPP:PC₇₁BM with different ratio from different solvent.

Solvent	PDTTDP:PC ₇₁ BM (weight ratio)	V _{OC} (V)	J _{SC} (mA/cm ²)	FF (%)	η (%)
CF	1:1	0.63 ± 0.02	2.8 ± 0.2	41.2 ± 3.5	0.75 ± 0.52
	1:1.5	0.65 ± 0.02	2.7 ± 0.4	47.5 ± 2.0	0.80 ± 0.44
	1:2	0.62 ± 0.01	2.7 ± 0.4	37.8 ± 3.1	0.74 ± 0.82
CF/DCB (V/V = 4/1)	1:1	0.61 ± 0.01	8.8 ± 0.5	41.4 ± 2.9	2.28 ± 0.33
	1:1.5	0.62 ± 0.03	13.4 ± 0.2	55.5 ± 2.4	4.42 ± 0.35
	1:2	0.61 ± 0.03	7.9 ± 0.5	62.1 ± 4.8	2.94 ± 0.48
CF/DCB (V/V = 4/1) with 2.5 vol% of DIO	1:1	0.63 ± 0.03	9.9 ± 0.3	61.3 ± 2.5	3.82 ± 0.27
	1:1.5	0.66 ± 0.02	13.7 ± 0.2	66.1 ± 3.0	6.05 ± 0.17
	1:2	0.65 ± 0.01	11.2 ± 0.6	55.4 ± 5.2	3.94 ± 0.70

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6. Space charge limited current (SCLC) hole mobilities

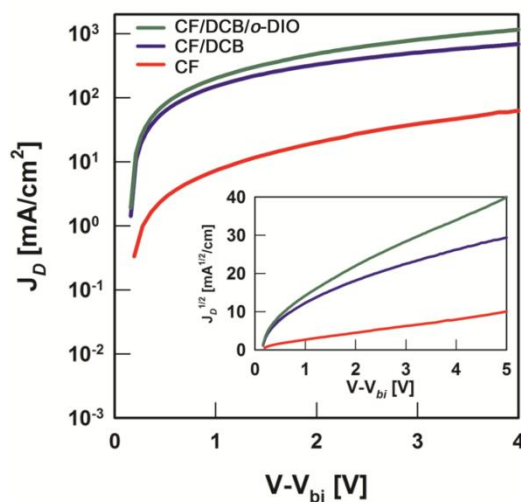


Figure S8. Dark current density-effective voltage characteristics of hole single carriers (SCLC mobilities) in PDTTDP:PC₇₁BM (1:1.5 of weight ratio) thin film cast from different solvent. Red: CF, Blue: CF/DCB (4/1 of volume ratio), Green: CF/DCB (4:1 of volume ratio) with 2.5 vol% of DIO

Table S2. Summary of SCLC hole mobilities of PDTTDP:PC₇₁BM (1:1.5 of weight ratio) thin film cast from different solvent.

solvent	hole mobility (cm ² /V·s)
CF	1.68×10^{-3}
CF/DCB	3.39×10^{-3}
CF/DCB/DIO	5.33×10^{-3}

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7. Thin film morphologies

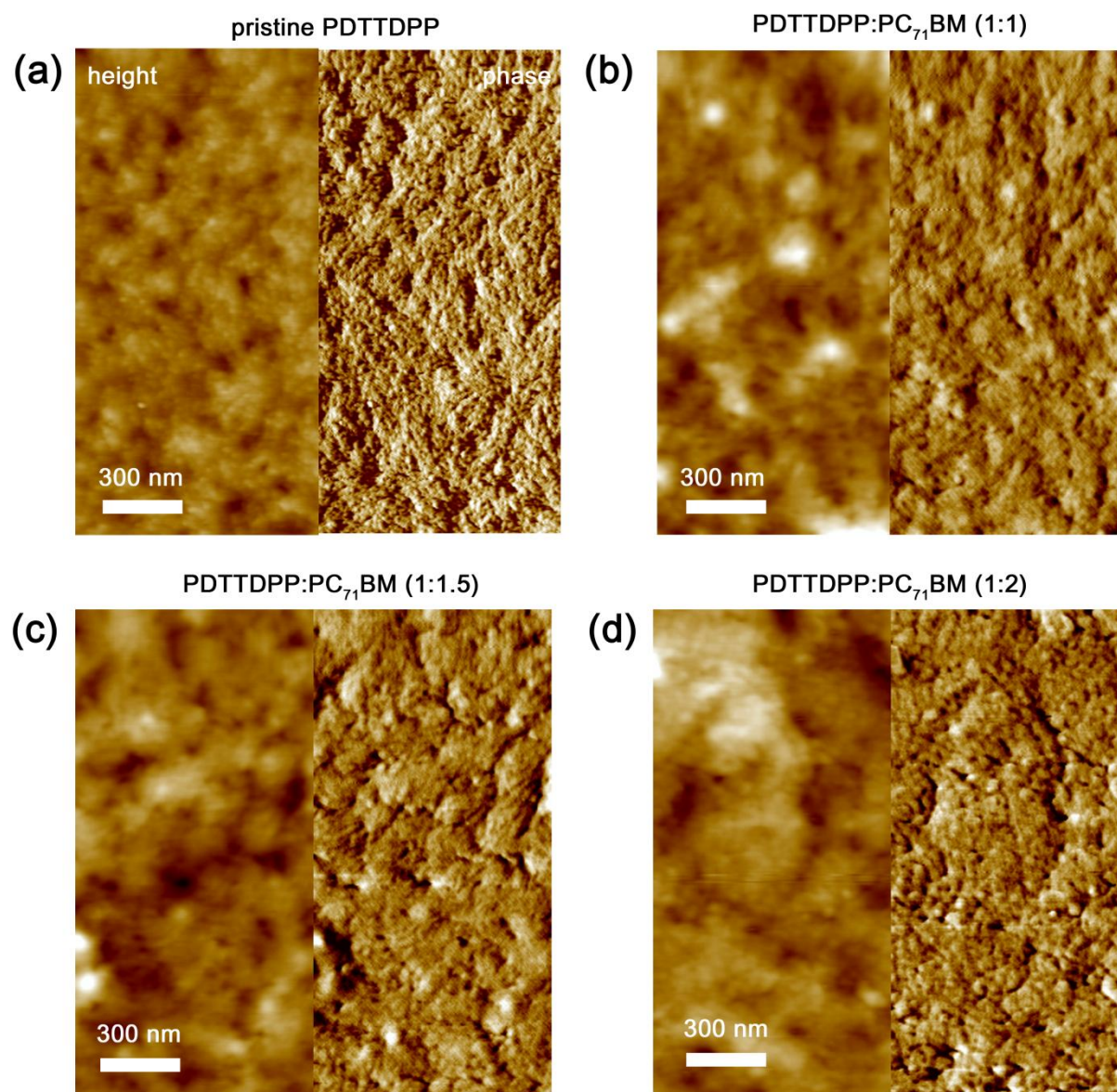


Figure S9. Morphological images observed by tapping mode AFM of (a) pristine PDDTDPP cast from CF, and (b) 1:1, (c) 1:1.5, and (d) 1:2 blend of PDDTDPP:PC₇₁BM thin film cast from CF/DCB/DIO. The volume ratio of CF to DCB is 4 to 1, and 2.5 vol% of DIO was added to the solution. Left side: height image, right side: phase image.

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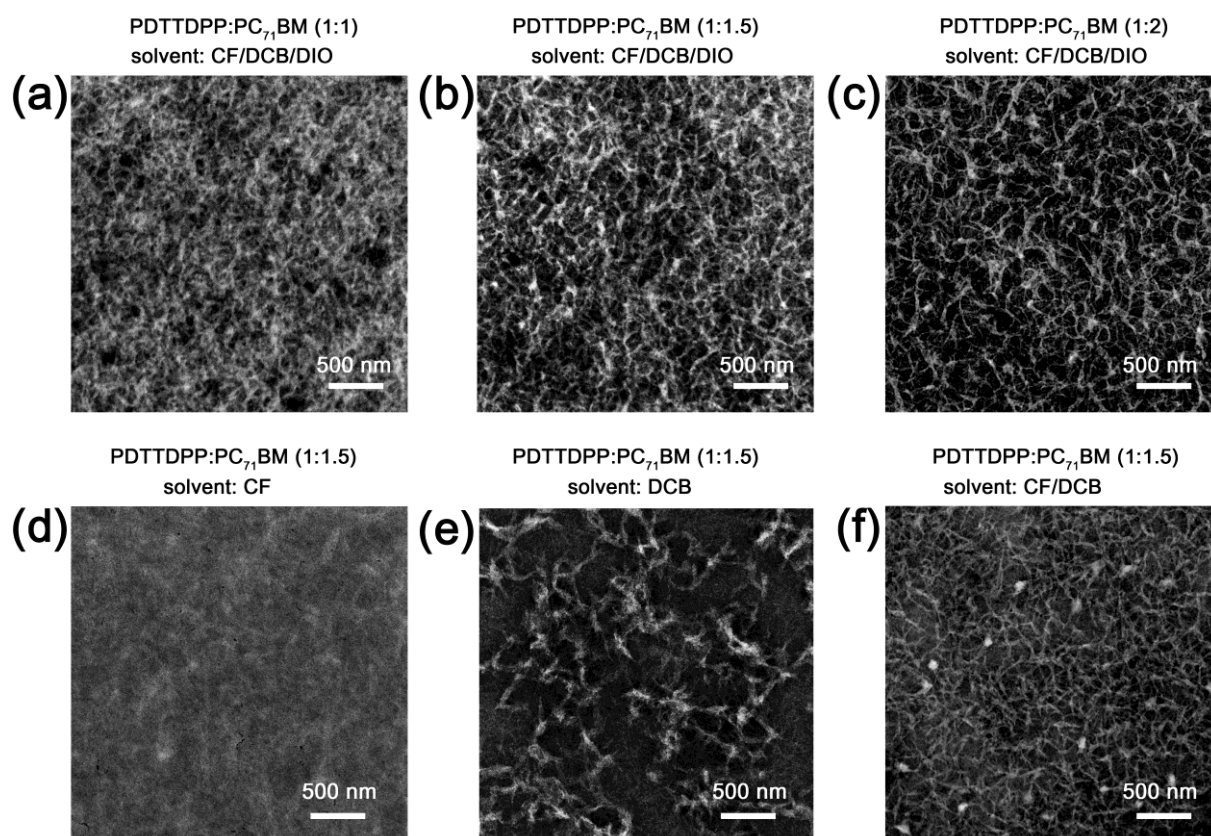


Figure S10. Morphological images observed by TEM of PDDTDPP:PC₇₁BM thin film with weight ratio of (a) 1:1, (b) 1:1.5, (c) 1:2 cast from CF/DCB/DIO, and 1:1.5 blend thin film cast from CF/DCB/DIO.

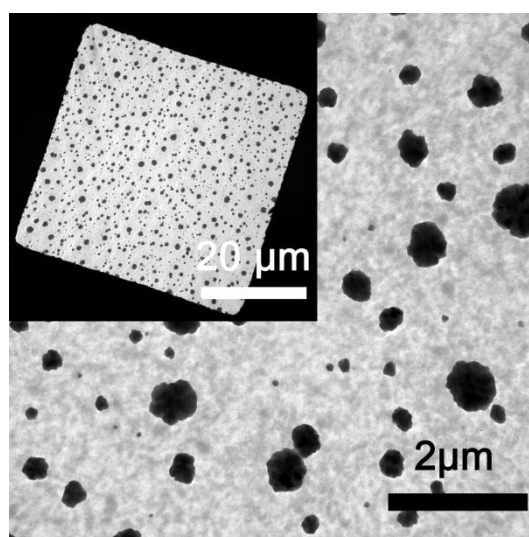


Figure S11. Morphological images observed by TEM of PDDTDPP:PC₇₁BM thin film with weight ratio of 1:1.5 cast from CF/DCB/DIO after thermal annealing at 150 °C for 15 min.

8. References

1. *Energy Environ. Sci.* **2011**, *4*, 2288.